

Developing New Methods of Quantum Spectroscopy with Nonlinear Integrated Photonics

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ABSTRACT

Photon pairs produced through spontaneous parametric down-conversion exhibit entanglement in their time-energy degrees of freedom, offering <100 fs entanglement times while simultaneously exhibiting a joint energy resolution dictated by that of the continuous-wave pump laser. While entangled photon pairs have found many applications in sensing and imaging, taking advantage of their ultrafast correlations has proven to be more difficult.

In this dissertation, we advance a number of practical aspects of spectroscopy with entangled pairs of photons. First, we show that the ultrafast correlations in photon pairs are useful for fluorescence lifetime measurements, enabling a CW laser to perform time-resolved measurements through a simple heralding scheme. Next, we develop bright, efficient, and single spatial mode sources of entangled photons using thin-film lithium niobate nanophotonics, bringing these devices to the visible and near-IR for the first time. In the process, we develop a source of UV light and investigate the performance of thin-film lithium niobate for evanescent sensing. Finally, we show promising results that two down-conversion processes in the same waveguide can be cascaded to generate entangled photon triplets with high efficiency, enabling pairs of photons to be heralded.

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NOMENCLATURE

C153. Coumarin-153.

CSPDC. Cascaded spontaneous parametric down-conversion.

CW. Continuous wave.

EMICCD. Electron multiplying intensified charge-coupled device.

FLIM. Fluorescence lifetime imaging microscopy.

GVD. Group velocity dispersion.

ICG. Indocyanine green.

IR. Infrared.

IRF. Instrument response function.

QPM. Quasi phase matching.

SHG. Second harmonic generation.

SNSPD. Superconducting nanowire single photon detector.

SPAD. Single photon avalanche detector.

SPDC. Spontaneous parametric down-conversion.

TCSPC. Time-correlated single-photon-counting.

TE. Quasi transverse-electric.

TFLN. Thin-film lithium niobate.

UV. Ultraviolet.

Chapter 1

INTRODUCTION

Spontaneous parametric down-conversion (SPDC), the process where one photon splits into two, has captured the minds of scientists and engineers since it was first observed in 1967 because it is one of the most reliable ways to generate high quality entanglement between two particles [1]. With just one laser (the source of photons that will be split) and a properly designed crystal (the material that will enable the photon splitting process), pairs of photons are produced that can be easily isolated, routed over long distances, and detected. These photons can exhibit strong correlations in various degrees of freedom such as wavelength [2], timing [3], polarization [4], emission angle [5], path [6], and more [7]. When these correlations are such that the quantum state of the pair cannot be decomposed into a product of two independent states, the degrees of freedom are entangled [8]. Entangled photons have been used for many of the fundamental tests quantum mechanical principles, and are very promising for quantum communication, quantum cryptography, and quantum computing, all of which require well controlled quantum states which can be eventually measured [9]. To a chemist or a biologist, these applications probably seem interesting but might not be immediately useful for the lab (it could be a very long time before a quantum computer can execute electronic structure calculations [10]). On the other hand, there is a growing field of research finding applications for photon pairs in imaging, microscopy, and spectroscopy, a subset of the broader field of quantum sensing [11]. Many of these experiments use the correlations present in the photon pairs without needing to fully characterize the entanglement (indeed, verifying time-energy and position-momentum entanglement and tomographically measuring the highly multidimensional state are very challenging, yet these are the main types of correlations used in spectroscopy and microscopy [5, 12, 13]). In other experiments, no forms of entanglement are present, and the simple fact that SPDC photons arrive in pairs is the useful attribute. This stands in sharp contrast to communication and computation, where the fidelity and purity of the quantum state are critical parameters that need to be determined and will govern the success of the measurement. As we will show, SPDC has a number of use cases for spectroscopy and microscopy where correlations enable improved performance

over classical light, while operating at ultralow fluxes which ensures that samples are only interacting with one or two photons at a time.

One drawback of SPDC is that the process is relatively weak, meaning that the conversion of pump photons into SPDC pairs occurs with low probability (typically in the $10^{-6} - 10^{-12}$ range). In many experiments this fact might seem unimportant, since only a few picowatts of SPDC are required to saturate most single photon detectors. However, there are certain types of spectroscopy experiments where far brighter sources of SPDC are needed to observe nonlinear light-matter interactions, or experiments where the detection is highly multiplexed (over many camera or spectrometer pixels, for example). In other cases, an inefficient SPDC source necessitates a bright pump beam, which generates unwanted photons through fluorescence or Raman transitions that cannot be easily filtered away and "contaminates" the SPDC [14]. In these cases, the efficiency of SPDC can become a limiting factor, and this has led to five decades of source improvements. Within the last few years thin-film lithium niobate (TFLN) has become commercially available, which is the precursor to nanoscale waveguides with the exceptional property that they can be tailored for many nonlinear optical processes with great efficiency [15]. With this platform, we hope to make more efficient sources of SPDC, new states of light useful for quantum optics, and begin integrating spectroscopy experiments with entangled photons onto a much smaller scale.

This thesis has been broadly split between SPDC source development and exploration of new spectroscopy techniques using entangled photons. Chapter 2 gives an overview on the theory of SPDC, some of its unique qualities, and a broad overview of spectroscopy experiments with entangled photon pairs. Chapter 3 gives a new spectroscopy technique using entangled photons to measure fluorescence lifetimes without requiring a pulsed laser. Chapter 4 gives our first foray into nanophotonics on the TFLN platform, where we investigate ultraviolet second harmonic generation in preparation for Chapter 5, where we generate SPDC in the visible and near-infrared with exceptional efficiency. Chapter 6 then explores how to interrogate samples with light in a waveguide for future on-chip spectrometers. Chapter 7 shows that by using two highly efficient TFLN SPDC sources, entangled photon triplets can be produced at record rates, which can enable the efficient heralding of entangled photon pairs.

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Chapter 2

BACKGROUND

2.1 Nonlinear optics primer

Before giving specific examples of how SPDC is useful for spectroscopy and imaging, some of the salient features of the process itself are described. A full derivation of the Hamiltonian that can quantitatively predict the rate of SPDC is out of the scope of this introduction [1], but a semiclassical explanation in comparison to other nonlinear optical interactions gives some of the qualitative features [2]. The easiest nonlinear optical process to explain is second harmonic generation (SHG), where a classical electromagnetic wave generates a new field with twice the frequency. In linear optical materials, the electric field of light generates a linearly proportional polarization due to the displacement of charges in the material. This polarization radiates its own field, which will have the same frequency of the driving light (i.e., no new wavelengths are generated). In nonlinear materials, due to anharmonicities in the potential energy wells that govern the forces the charges will experience, the polarization is no longer linearly proportional to the electric field, as shown in Figure 2.1. Taylor expanding the polarization gives a new term proportional to the square of the electric field (neglecting higher order terms), the magnitude of which is governed by $\chi^{(2)}$, which quantifies how strong this material response is:

$$\mathbf{P}(\mathbf{E}) = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \dots \quad (2.1)$$

When an electric field at one frequency ω is sent into this material, a new frequency is generated in the material's polarization:

$$\mathbf{E}_{\text{in}}(t) = A\sin(\omega t) \quad (2.2)$$

$$\begin{aligned} \mathbf{P}_{\text{out}}(t) &= A\chi^{(1)}\sin(\omega t) + A^2\chi^{(2)}[\sin(\omega t)]^2 \\ &= A\chi^{(1)}\sin(\omega t) + A^2\chi^{(2)}\frac{1 - \cos(2\omega t)}{2}. \end{aligned} \quad (2.3)$$

The component of the polarization at $\cos(2\omega t)$ will radiate a new field at twice the frequency. In this way, the nonlinear polarizability of the material has generated a new color of light.

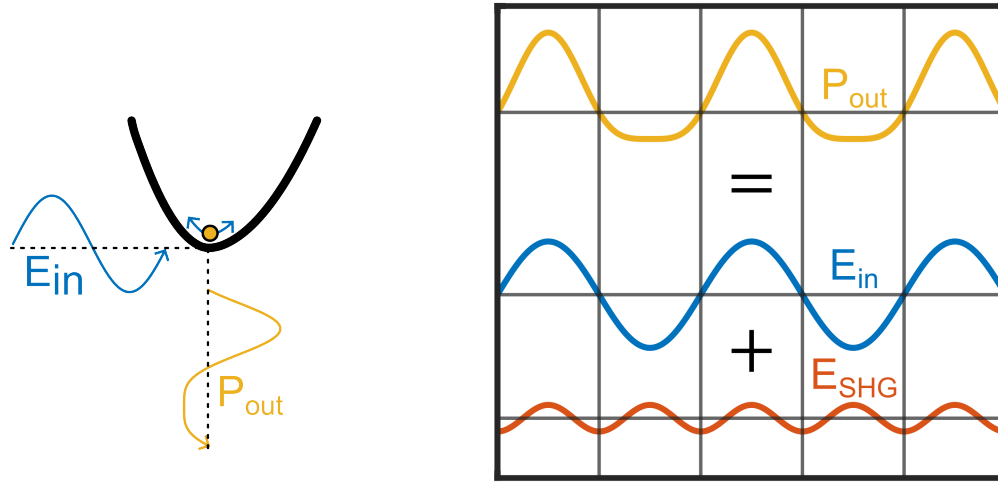


Figure 2.1: Qualitative picture of SHG, showing a particle driven in an anharmonic well. The particle is polarized more on the first half-cycle of the driving field than the second. The resulting polarization can be decomposed into two frequencies, one at the frequency of the driving field, the other at twice that frequency.

Similarly, two different frequencies can interact through $\chi^{(2)}$, generating a third wave at the sum or difference frequencies. When the frequencies subtract, the process is called difference frequency generation, and energy is transferred from one input field to another, generating the new difference frequency wave in the process. SPDC is similar in that one field is depleted, transferring energy to two other fields. However, classical nonlinear optics predicts that difference frequency generation will not occur if power is only initially present in one of the three waves. When Maxwell's equations are treated quantum mechanically, every field has a Hamiltonian similar to a quantum harmonic oscillator [3]. Even when no excitations are present, fluctuations still occur in the field's strength (conceptually similar to how the position and momentum of a ground-state quantum harmonic oscillator exhibit uncertainty about their mean values). It is these fluctuations that can drive difference frequency generation, even when the lower energy fields contain no photons initially [4]. When the pump field is weak enough that the generated photons do not interact further, the process is called SPDC.

2.2 Qualities of SPDC

SPDC is a so-called parametric process, meaning that the SPDC crystal does not absorb or supply any energy to the optical fields. The conservation of energy therefore dictates that all of the energy present in a single pump photon that down-converts must be transferred to the two new photons, usually called the signal and idler. One important result is that the signal and idler are always produced in pairs, which forms the basis of experiments that can beat shot noise statistics at very low fluxes, as well as the basis of all experiments where the detection of one photon heralds the other.

Another consequence of energy conservation is apparent when the pump laser has a narrow linewidth, implying a small uncertainty in the energy of the pump photons which are down-converted. The signal and idler are capable of taking on a wide range of energies, with the constraint that any given signal idler pair will have a total energy equal to the pump photon. While the energy of a signal photon is impossible to know until measurement, once the signal photon is detected the energy of the idler photon is heralded into a narrow wavelength range.

Furthermore, the signal and idler pair are created together within a narrow coherence time, which is inversely proportional to the frequency bandwidths of the individual fields. When SPDC is pumped with a continuous-wave (CW) laser, the emission of a pair of photons will occur at an unknown time. However, detection of a signal photon then heralds the idler photon to a very narrow time window, potentially in the femtosecond range.

These two correlations in time and energy are called time-energy entanglement, and are characterized by functions called the joint spectral amplitude (JSA) $A(\omega_s, \omega_i)$, and joint temporal amplitude (JTA) $\tilde{A}(t_s, t_i)$, which are related through a Fourier transform [5]. Assuming that the signal and idler are emitted into the same spatial mode, the state of the fields after being pumped for some amount of time is:

$$|\psi\rangle = (1 - c) |0\rangle + c \iint d\omega_s d\omega_i A(\omega_s, \omega_i) \hat{a}^\dagger(\omega_s) \hat{a}^\dagger(\omega_i) |0\rangle + \dots \quad (2.4)$$

$$|\psi\rangle = (1 - c) |0\rangle + c \iint dt_s dt_i \tilde{A}(t_s, t_i) \hat{a}^\dagger(t_s) \hat{a}^\dagger(t_i) |0\rangle + \dots \quad (2.5)$$

$$\tilde{A}(t_s, t_i) = \iint d\omega_s d\omega_i e^{-i\omega_s t_s} e^{-i\omega_i t_i} A(\omega_s, \omega_i) \quad (2.6)$$

where $\hat{a}^\dagger(\omega), \hat{a}^\dagger(t)$ are creation operators acting on the vacuum state $|0\rangle$ to produce a photon in a given frequency or time, respectively. Subscripts s, i denote the signal and idler photons, respectively. The (small) constant c represents the probability of down-conversion over the observation window, and is assumed to be small enough to neglect higher order terms of order c^2 , which will be product states of the second term of equations 2.4 and 2.5. When a narrow linewidth pump is used, $A(\omega_s, \omega_i)$ is strongly anticorrelated. If minimal dispersion is present after the source, $\tilde{A}(t_s, t_i)$ will be strongly correlated. Quantifying the entanglement present in such a state requires a Schmidt mode decomposition of $A(\omega_s, \omega_i)$, but for the purposes of most experiments using CW lasers this is not necessary since the state can be assumed to conserve energy. In an experiment, the relative probability of detecting a given pair of wavelengths or arrival times is given by $|A(\omega_s, \omega_i)|^2$ and $|\tilde{A}(t_s, t_i)|^2$, which are called the joint spectral intensity (JSI) and joint temporal intensity (JTI), respectively. These are plotted for a time-energy entangled source in Figure 2.2.

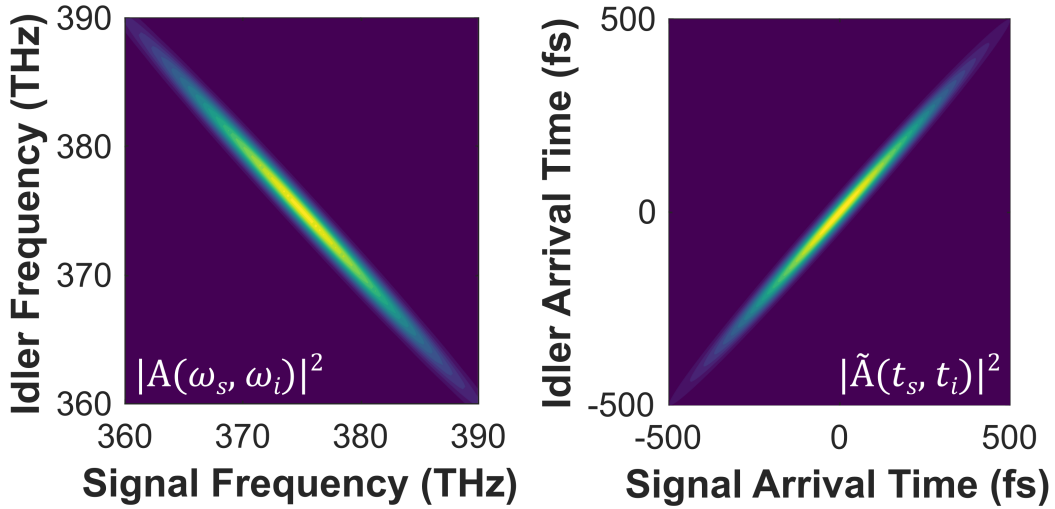


Figure 2.2: Visualization of the JSI ($|A(\omega_s, \omega_i)|^2$) and JTI ($|\tilde{A}(t_s, t_i)|^2$) of a time-energy entangled SPDC state. A signal and idler bandwidth of 40 nm generates temporal correlations of 24 fs. Dispersion has not been accounted for here, which will serve to broaden the JTI along the antidiagonal.

The wavelength distributions that are ultimately produced by SPDC are governed by phase matching relationships. The production of SPDC is maximized when the spatial wavevector of the pump is equal to the sum of the signal and idler spatial wavevectors. Momentum is therefore approximately conserved (SPDC is still produced when momentum is not perfectly conserved, with shorter crystals allowing for more momentum mismatch), as shown in Figure 2.3. For most crystals

at optical wavelengths, the wavevector of the pump will always be larger than the summed wavevectors of the signal and idler (refractive index decreases with increasing wavelength). Momentum conservation can still be achieved using the birefringence of the crystal, or by spatially modulating the orientation of the material nonlinearity, which produces a new spatial frequency that can satisfy phase matching [6]:

$$I \propto \text{sinc}^2 \left(\frac{\Delta k L}{2} \right) \quad (2.7)$$

$$\Delta k = k_p - k_s - k_i - k_{QPM} \quad (2.8)$$

$$k_{QPM} = \frac{2\pi m}{\Lambda}, \quad m = \pm 1, \pm 3, \dots \quad (2.9)$$

Here I refers to the rate of SPDC production in a given direction and wavelength, L is the length of the crystal, and k is a spatial wavevector, with subscript p denoting the pump mode. Equation 2.9 gives the calculation of the wavevector produced by a modulation in the nonlinear crystal orientation with a spatial period of Λ , which achieves quasi phase matching (QPM).

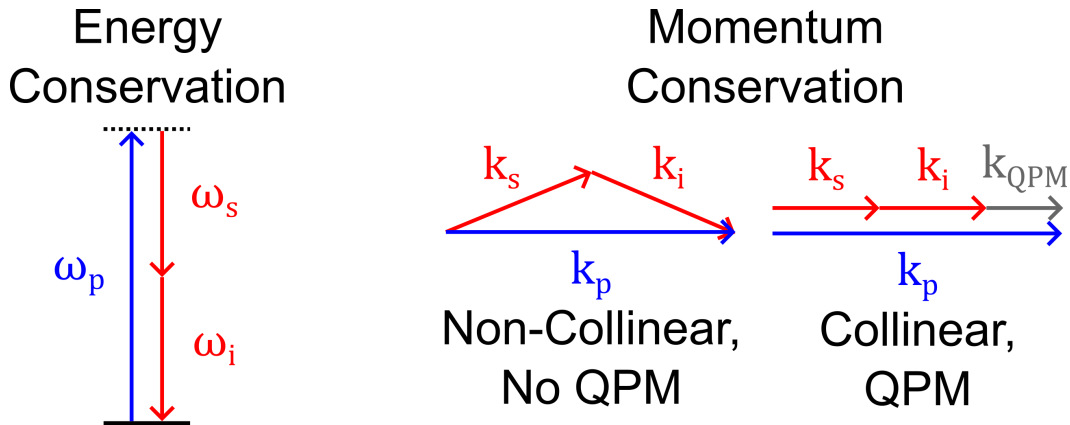


Figure 2.3: Visualization of the energy and momentum conservation properties that govern the wavelengths and emission angles of SPDC. The momentum diagram to the left shows the phase matching that can occur in a bulk crystal such as $\beta - \text{BaB}_2\text{O}_4$, and the diagram to the right shows the phase matching that is possible in a waveguide with QPM. Non-collinear QPM phase matching, and collinear non-QPM phase matching are also possible.

While all of the work in this thesis has been accomplished using minimal entanglement in the spatial and momentum degrees of freedom, a brief description is given because this type of entanglement is so important for imaging applications. As shown in Figure 2.3, the signal and idler photons tend to be emitted with opposing transverse spatial momenta. Neglecting walk-off and birefringence, this interaction is just as likely to occur at any arbitrary angle rotated about the axis of the pump wavevector, forming cones of emission. While the orientation of the emission is unknown until measurement, once the angle of the signal photon is measured, the idler is determined with a high degree of certainty in the opposing direction [7]. This is shown in one plane in Figure 2.4. In a similar vein, the location within the crystal where the signal and idler are produced is unknown, but correlated to a high degree [8]. The type of correlations that are observed in an experiment will depend on the imaging setup, the area of the pump beam, and the thickness of the SPDC crystal.

2.3 SPDC in waveguides

Due to diffraction, the length over which the pump beam stays in focus is inversely proportional to its waist radius. For intensity-dependent nonlinear processes such as SHG, this diffraction limits the effectiveness of a tightly focused pump beam as the crystal length is increased [9]. Structures such as waveguides which are capable of maintaining a confined beam over an arbitrary distance exhibit improved scaling with length for many nonlinear processes (Figure 2.5). In bulk crystals, the beam profile of the pump does not usually influence the rate of SPDC because only a single pump photon is involved and the efficiency does not depend on intensity. While this causes the picture to break down somewhat, the fact that the signal and idler modes are confined to the same location as the pump beam does result in improved efficiency [10]. In bulk crystals, the rate of SPDC in a given frequency bandwidth, integrated over all angles, scales linearly with the length of the crystal. In waveguides, this same quantity scales quadratically with length. While bulk crystals emit into a continuum of plane modes, waveguides ideally will emit into only one spatial mode. This quality enables for very efficient interfacing with single mode optical fibers, but does prevent waveguides from being useful in widefield imaging experiments due to the lack of spatial entanglement.

The derivation for the quantitative rate of SPDC is outside of the scope of this section, but is explained clearly in Reference [10]. Here, the rate of signal photon

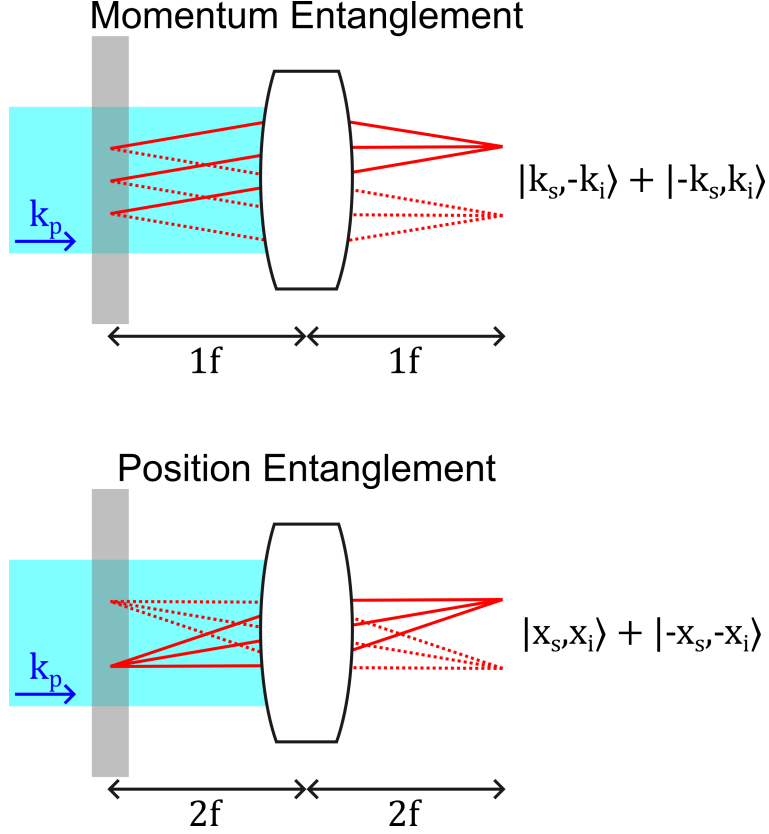


Figure 2.4: Momentum and position correlations for SPDC with a large pump beam diameter. In the top diagram, the signal is emitted along the solid lines and the idler is emitted along the dotted lines, or vice versa. In the bottom diagram, the signal and idler are both emitted along the solid lines, or are both emitted along the dotted lines. Abbreviations: f : focal length.

production W_s (with units of photons/s) with respect to a spectral bandwidth $d\omega_s$ (with units of rad/s) is:

$$\frac{dW_s}{d\omega_s} = \frac{d_{\text{eff}}^2 P_p \omega_s \omega_i}{\pi \epsilon_0 c^3 n_p n_s n_i} \frac{L^2}{A_{\text{eff}}} \text{sinc}^2 \left(\frac{\Delta k L}{2} \right). \quad (2.10)$$

Here, subscripts s, i, p refer to the signal, idler, and pump, as before. ϵ_0 is the permittivity of free space, c is the phase velocity of light, L is the waveguide length, and n is the refractive index of the respective waveguide mode. d_{eff} is the effective second order nonlinearity of the crystal, and is equal to $2d/\pi$ for first order QPM, where d is the crystal nonlinearity with units of m/V. From Reference [11], the effective area of the interaction A_{eff} is given by an overlap integral of the pump, signal, and idler mode profiles:

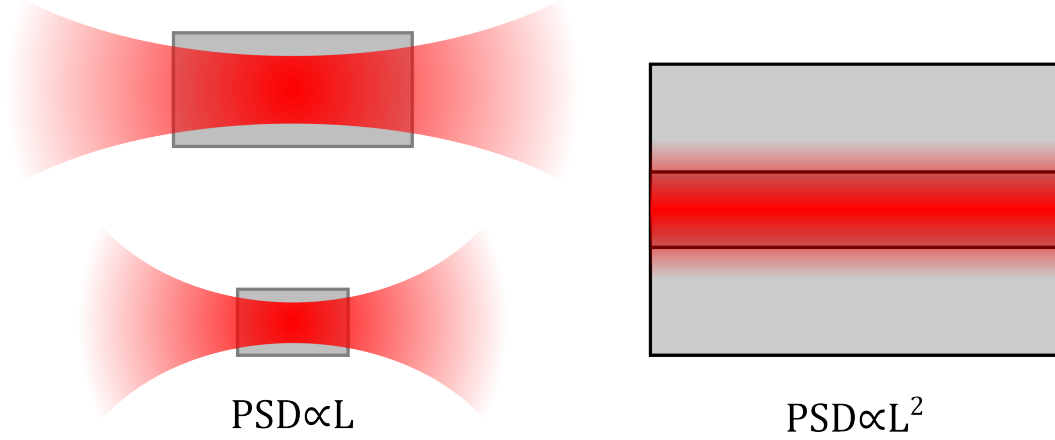


Figure 2.5: SPDC in bulk crystals and waveguides. In bulk crystals (left), the power spectral density of SPDC production scales linearly, while the same quantity scales quadratically in waveguides (right). Also shown is the pump profile focused into crystals of different lengths, for a longer crystal a pump beam with a larger area (and therefore a lower intensity) must be used. For a waveguide of any arbitrary length, the pump profile remains the same. Abbreviations: PSD: power spectral density.

$$A_{\text{eff}} = \frac{A_p A_s A_i}{\sqrt{\frac{n_p n_s n_i A_p A_s A_i}{8 Z_0^3 P^3} \left| \iint \bar{d}(x, y) E_s^* E_i^* E_p dx dy \right|^2}} \quad (2.11)$$

where A is the mode area, P is the power contained in the mode (which normalizes the result of the double integral), E is the electric field profile of the mode, Z_0 is the impedance of free space, and $\bar{d}$ is unity at locations with the optical nonlinearity, and zero elsewhere. A_{eff} is calculated numerically, and has units of m^2 .

The scaling of SPDC efficiency with many of the variables in Equations 2.10 and 2.11 is as follows. The choice of nonlinear coefficient is obviously important, with d_{33} (all fields extraordinarily polarized) being the largest by a factor of 8 in lithium niobate specifically. The rate of SPDC is more favorable at short wavelengths (scaling as λ^{-4} when measured in units of pairs/s/nm). As mentioned before, the spectral density scales with L^2 , however the efficiency only scales with L because the overall bandwidth is reduced in proportion to the waveguide length. From the mode overlap calculation, it is intuitive that the pump, signal, and idler should all be confined to the nonlinear part of the medium, overlapping with each other. Finally, smaller waveguides generate brighter SPDC due to smaller mode areas.

2.4 Applications of SPDC in spectroscopy and imaging

The photon number correlations and entanglement in various degrees of freedom between the signal and idler photons in SPDC can exhibit unique advantages over classical (coherent and thermal) light sources for a number of applications in spectroscopy and imaging. The relatively specific conditions needed to obtain a quantum advantage, coupled with high equipment costs, has prevented widespread or commercial adoption of any of the techniques shown so far using SPDC. As photon pair sources and single photon detectors mature, this might no longer be the case. A number of thorough reviews have outlined the applications of SPDC in spectroscopy and imaging [12–15], which are just a narrow subset of use cases for SPDC in quantum information science [16]. Here we review some of the proven advantages, and discuss some of the potential areas warranting future exploration.

As a first example, the paired nature of SPDC is useful for beating the shot noise limit at low fluxes. Over a given time interval, an SPDC source will produce a random number of photon pairs with Poissonian statistics, similar to how a coherent beam will contain a random number of photons over a given time interval. Unlike a coherent source, by measuring the number of signal photons produced in this interval the number of idler photons can be determined before interaction with a sample. At very low light levels, SPDC can determine the transmission or phase of a sample to a higher precision than a classical beam containing the same number of photons [17–19]. Similarly, this technique can be extended to microscopy using spatially entangled SPDC to construct images with sub-Poissonian noise [20–22]. Such correlations can also be used to perform measurements in the presence of high levels of background through coincidence detection. Compared to squeezed light experiments where the shot noise limits of high power beams can be surpassed [12], these measurements would not be competitive when compared to higher power classical light sources. However, these techniques are still beneficial for studying photosensitive samples such as biological tissues [23] or fragile quantum states in atoms [24].

In a similar vein, the detection of a signal in order to herald its idler enables SPDC to act as a source of single photons with sub-Poissonian statistics. The guarantee that the beam probing a sample only contains one photon at a time has been used to prove that photosynthesis and human vision are single photon processes [25–28] and could conceivably be applied to other areas of research where nonlinearities are suspected to have an influence on performance [29]. Control of single photon absorption is

also necessary for transferring quantum information from flying qubits to matter qubits, motivating a number of experiments that use heralded single photons to probe single cold atoms or quantum dots [30–33].

Going beyond correlations in photon number, a number of experiments have taken advantage of the Hong-Ou-Mandel effect, where indistinguishable single photons bunch at the output of a beamsplitter [34]. Due to the wavelength correlations in the pair, even-order dispersion is canceled between photons, which can allow for more accurate distance measurements in optical coherence tomography through dispersive samples [35, 36]. Furthermore, the Hong-Ou-Mandel effect is phase insensitive, which has a practical benefit over classical interferometers in that the path lengths do not need to be actively stabilized [37]. This effect has also been adapted for wide field microscopes, promising to exhibit more robust measurements in the face of vibrations and other effects that could wash out traditional interference fringes [38]. Another more exotic form of quantum spectroscopy uses the interference of two SPDC sources to obtain information about the interaction of an idler photon with a sample through measurements on the signal photon. Using the very wide difference in photon energy that can be achieved with nondegenerate SPDC, many experiments have shown spectroscopy and imaging in the mid-infrared using detection in the visible. With highly sensitive visible detectors, these experiments can perform experiments in the mid-IR with extremely low fluxes of light and high spatial resolution, both of which are difficult to achieve using standard IR detectors [39, 40].

When detected in coincidence, entangled photons acquire a phase twice as quickly as classical coherent states, and were the first photonic states used for demonstrating $N00N$ -type interference [41–43]. Such interference is useful for phase estimation in a single beam interferometer. In the spatially multimode case, this effect can surpass Rayleigh diffraction limits in microscopy. This is exciting since this is a limit that cannot be surpassed with brighter illumination or longer integration times, and has traditionally required structured illumination or the use of fluorophores to achieve super-resolution [44, 45]. First demonstrated in double-slit diffraction experiments [46], followed by microscopy and far-field imaging experiments [47–49], the spatial entanglement in SPDC allows for resolution enhancements of $1/\sqrt{2} - 1/2$, with multiphoton states promising even higher resolution [50].

Forms of spectroscopy where both photons interact with the same emitter have the fewest examples of successful demonstrations, but are potentially the most

interesting from a scientific standpoint since there is currently a large gap between theory and experiments. In such interactions, the time-energy entanglement in SPDC photons is predicted to interfere with different excitation pathways leading to selectivity in which final states are populated, as well as the ability to distinguish between different types of nonlinear light-matter interactions such as excited state absorption and stimulated emission [5, 51–54]. Because interactions of single photons with any given single emitter (be it an atom, molecule, quantum dot, exciton in a crystal, *et cetera*) are already weak, detecting the interaction of two photons with one emitter has been difficult [55–57]. Broad bandwidth entangled photon pairs are expected to arrive uncertainties in arrival time differences on the order of femtoseconds, as verified using SFG [58–60]. In spite of this, only a handful of convincing demonstrations of both SPDC photons interacting with matter have been shown. One of which has been excited state absorption in superconducting nanowire single photon detectors (SNSPDs), which exhibit very large single photon absorption to a metastable state, and have an inherently high gain readout when excited above the superconducting threshold by the second photon [61]. Another was a GaAs photomultiplier tube, again a system exhibiting high gain which facilitates detection of the relatively rare absorption events [62]. Two photon absorption of SPDC has also been shown in cesium and rubidium vapors, though at fluxes high enough that entangled pairs overlap in time [63, 64]. Finally, two photon absorption in molecules has been convincingly observed recently, which could pave the way towards ultrafast time resolved experiments [65]. These past experiments suggest that sample choice and low background detection are critical for successfully observing the interaction of both SPDC photons with a sample.

Overall, the physics of SPDC generation, interference, and detection are well understood at this point. Advancements in the field have to be made through creativity, finding new experimental setups and samples that exhibit an unexpected interaction with SPDC beyond what would be predicted with dim thermal or coherent light sources. As new SPDC sources exhibit improved purity, lower losses, higher generation efficiency, and can be detected with probabilities closer to unity, it seems inevitable that new applications will be found, and existing applications brought closer to maturity.

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*Chapter 3*FLUORESCENCE LIFETIME SPECTROSCOPY WITH
ENTANGLED PHOTONS

Fluorescence lifetime experiments are a standard approach for measuring excited state dynamics and local environment effects. Here, we show that entangled photon pairs produced from a CW laser diode can replicate pulsed laser experiments without phase modulation. As a proof of principle, picosecond fluorescence lifetimes of indocyanine green are measured in multiple environments. The use of entangled photons has three unique advantages. First, low power CW laser diodes and entangled photon source design lead to straightforward on-chip integration for a direct path to distributable fluorescence lifetime measurements. Second, the entangled pair wavelength is easily tuned by adjusting the temperature or electric field, allowing a single source to cover octave bandwidths. Third, femtosecond temporal resolutions can be reached without requiring major advances in source technology or external phase modulation. Entangled photons could therefore provide increased accessibility to time-resolved fluorescence while also opening new scientific avenues in photosensitive and inherently quantum systems.

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3.1 Introduction

Time-resolved fluorescence spectroscopy is routinely used in laboratory and clinical settings to measure excited state dynamics and, just as importantly, how changes to the lifetime provide information about the local environment surrounding the fluorophore [1, 2]. The advent of inexpensive pulsed laser diodes has led to a proliferation of time-domain fluorescence lifetime techniques in biosensing and microscopy beyond initial physical chemistry applications. Measured lifetimes are intrinsically fluorophore-specific and depend on variations in the surrounding chemical environment, such as temperature [3], pH [4], neighboring fluorophores [5], and

the quantum state [6–9]. This specificity, alongside developments in highly fluorescent tagging proteins and molecular markers, has also enabled fluorescence lifetime imaging microscopy (FLIM) to become a ubiquitous technique to visualize and understand complex biological samples [10, 11]. Autofluorescence endogenous to cellular environments has permitted label-free FLIM medical imaging applications, including clinical cancer diagnosis [12–14].

The next logical frontier for time-resolved fluorescence is highly distributable, wearable devices [15, 16]. At these spatial scales and cost targets, the same pulsed lasers that enabled proliferation of laboratory measurements become a barrier. While on-chip pulsed lasers are being developed, most still require an external power source for the diode or pulse generation [17]. Further, the short on-chip cavity lengths lead to GHz repetition rates that do not give sufficient time for fluorophores to fully relax between pulses [18]. To date, on-chip pulses are mostly in the picosecond range, although recent publications have shown pulses as short as 350 fs [19]. These integrated pulsed lasers typically have a narrow wavelength tuning range, which can make measurements of multiple fluorescent probes or dynamics from multiple local environments difficult [20].

An intriguing alternative to pulsed lasers is to leverage the inherent quantum correlations between entangled photons in a pair. When one high-energy pump photon splits into a pair of two lower-energy entangled photons through SPDC, the two single photons are deterministically correlated in time [21]. Thus, if one photon is used to excite a fluorophore, coincidence detection of the resulting fluorescence with the other entangled photon provides a measurement of the time-resolved fluorescence [22]. The uncertainty in the temporal width of the photon pair wave packet can range from tens [23–25] to hundreds [21] of femtoseconds, enabling time-resolved measurements comparable to those made with tabletop classical pulsed lasers. It is also key to note that, unlike CW phase modulation spectroscopy [26], a high frequency modulator is not needed for this technique due to its utilization of the inherent correlations between two entangled photons.

Given that classical time-resolved fluorescence instruments are also limited by detector bandwidths and timing circuits, CW entangled photon sources provide comparable experiments but with a few interesting technological advantages. First, it is straightforward to fabricate on-chip entangled photon sources that require only microwatts of power from a CW laser diode [27, 28]. Second, the wavelengths of the SPDC photons can be tuned across the transparency range of the down-conversion

crystal, usually from ultraviolet (UV) to near infrared (IR) wavelengths by varying the phase matching conditions, either by heating the crystal or by tuning the pump wavelength, enabling a range of biosensing and physical chemistry experiments [29]. Finally, femtosecond temporal resolutions can be reached without requiring major advances in external phase modulation or detection technology. Scientifically, given that the entangled photon measurements are natively performed in a single-photon-per-measurement regime, the technique is also interesting for measuring photosensitive samples [30], studying quantum systems [31], or exploring scaling behaviors of various properties against incidence flux [32, 33].

Despite early theoretical interest in utilizing entangled pairs to perform lifetime measurements [22, 34, 35], an experimental demonstration using a CW laser had not yet been shown (a similar experiment was published around the same time as ours [36]). We therefore provide a proof-of-principle experiment by measuring the fluorescence lifetime of indocyanine green (ICG). The correlation time of the entangled photon source is < 30 fs [25], but the detector used limits temporal resolution to 50 ps and minimum measurable lifetime to 365 ps [37]. The excited-state lifetimes of ICG in three solvents are measured to check the accuracy of the technique against previously published work [38]. Through a statistical analysis we show that, even though limited by the MHz detector maximum count rates and bandwidth, integration times in the minutes range provide sufficient signal for accurate lifetime determination using this configuration. Our results demonstrate that measuring time-resolved fluorescence from entangled photons is possible with properties approaching pulsed lasers, providing the proof of principle for new modalities of compact time-resolved fluorescence spectroscopy and experiments in a single-photon excitation and single-photon detection limit. Periodically poled entangled photon sources routinely approach THz pair generation rates, so commercially available picosecond detectors with GHz count rates can improve these measurements to femtosecond temporal resolution and seconds integration time. Future developments could also perform highly multiplexed measurements using the additional correlated properties of SPDC such as the momentum or angular degree of freedom, as proposed in Ref. [22].

3.2 Experimental concept

The experimental configuration for performing fluorescence lifetime measurements with entangled photon pairs is shown in Fig. 3.1, and a detailed description of all components is provided in the Experimental Details section. Briefly, 2 mW of power from a 402.5 nm CW laser diode pumps a periodically poled, Type-0 SPDC crystal

to generate entangled photon pairs spanning 720 nm to 913 nm. Here, the pump laser power is significantly reduced using neutral density filters to avoid saturating the single photon counting detectors. The periodically poled bulk source used here produces free-space pairs, adding down-stream losses due to collimation and fiber coupling. A waveguided equivalent would enable the same studies to be performed on-chip and with μW pump powers.

The energies of the photons in the entangled pair sum to that of the pump laser. For the entangled photon source used, one photon has a wavelength between 720 – 805 nm with a simultaneously produced conjugate photon between 805 – 913 nm. The resulting correlation time from this bandwidth is ~ 30 fs, comparable to the pulse width of state-of-the-art mode locked lasers [39]. The detectors used in this experiment have a larger timing jitter (3.65 ns) than the temporal characteristics of the source and ultimately determine the experimental temporal resolution, as explained later in more detail.

The entangled photon pairs are then deterministically split using a short-pass dichroic filter tuned to 805 nm. The reflected lower energy photon heralds the measurement when it is detected by a single photon counting avalanche detector (SPAD), starting the timer for a time-correlated single-photon-counting (TCSPC) circuit. The higher energy photon is sent to the sample, where it excites a single molecule that then emits a single fluorescence photon with some delay. The fluorescence photon is collected in an epifluorescence scheme and then detected by another SPAD, which stops the timer on the TCSPC board. The time delay between the heralding and fluorescence photon detections is recorded over multiple measurements to create a histogram of such time differences, from which the fluorescence lifetime can be extracted.

The molecular dye indocyanine green (ICG) is used as a proof of principle since it is commonly utilized to perform fluorescence imaging in biological and clinical settings [40, 41]. ICG also has appropriate spectral properties relative to the entangled photon source and a well-characterized lifetime dependence on the solvent environment [38]. Methanol, ethanol, and dimethylsulfoxide (DMSO) were selected as solvents due to their variation of the ICG lifetime by hundreds of picoseconds. The absorption wavelength, emission wavelength, and quantum yield change only slightly across the three solvents (Table A.1). The spectrum of the SPDC was tuned through the phase matching temperature to maximize spectral overlap with the sample (Fig. 3.2a). The resulting ICG fluorescence (Fig. 3.2b) is separated

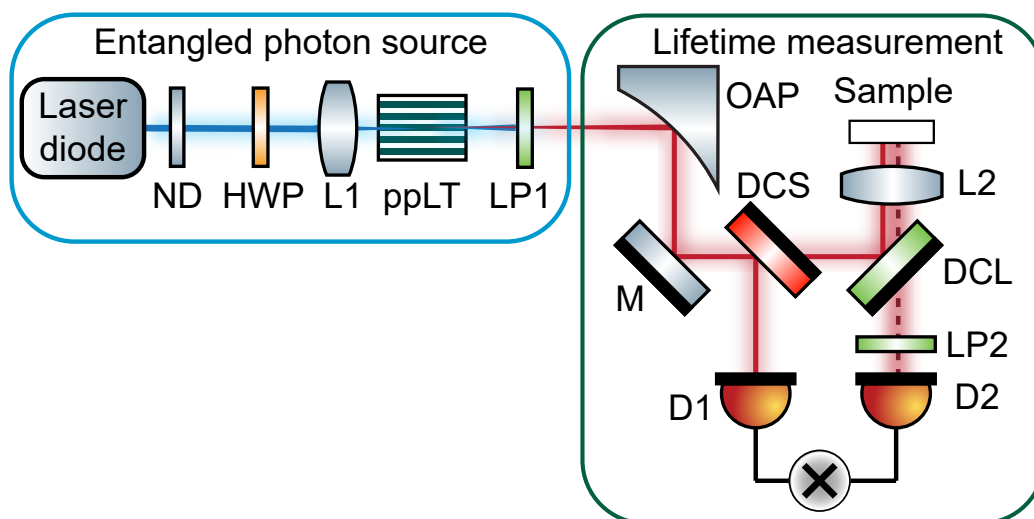


Figure 3.1: Experimental configuration for measuring fluorescence lifetimes with energy-time entangled photon pairs. The broadband entangled photon source consists of a 402.5 nm laser diode that is focused into a periodically poled lithium tantalate crystal. The resulting entangled photons (solid red lines) are collimated with an off-axis parabolic mirror and then separated by wavelength with a dichroic mirror. One photon from the entangled pair is directed to a detector to herald the measurement while the other is focused onto a molecular sample with a high numerical aperture (NA) aspheric lens. The same lens collects the emission from the sample's fluorescence (dashed red line) which is then directed through a series of long-pass filters onto a second detector. A coincidence circuit generates histograms of the arrival times between the reference and fluorescence photons. Abbreviations: ND: neutral density filters, HWP: half-wave plate, L1: UVFS focusing lens, ppLT: periodically poled lithium tantalate crystal, LP1: 500 nm long-pass filter, OAP: off-axis parabolic mirror, M: mirror, DCS: dichroic short-pass mirror with cut-on wavelength 805 nm, DCL: dichroic short-pass mirror with cut-on wavelength 810 nm, L2: high-NA aspheric lens, LP2: 808 nm long-pass filter, D1 and D2: multi-mode fiber coupled single photon avalanche photodiodes connected to a coincidence circuit.

from the excitation beam with a long-pass dichroic mirror and further filtered with an OD6 long-pass interference filter. The instrument response function (IRF, Fig. 3.2b), which characterizes the response that would be measured by a sample with an infinitely short lifetime, was obtained by replacing the sample with a mirror and removing the final long-pass OD6 filter to allow part of the excitation flux to reach the second detector. The IRF spectrum is altered from the excitation spectrum because it has been filtered by the dichroic mirror, but this alteration has minimal impact on the time-domain response due to the minimal wavelength sensitivity of the SPADs used here.

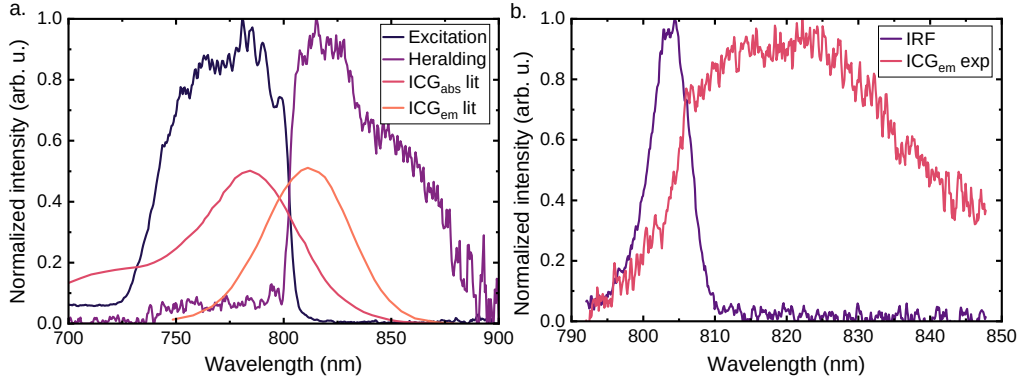


Figure 3.2: Spectral properties of the entangled photons and indocyanine green. (a) Normalized spectra of the entangled photons used for the heralding and excitation photons compared to the normalized absorption/emission spectra for ICG in methanol from Ref. [38]. The ICG spectra have been further scaled by 50% to distinguish them from the entangled photon spectra. (b) Normalized fluorescence signal from 100 μM ICG in methanol following entangled photon excitation compared to the portion of entangled photon flux that is used to characterize the instrument response function.

The timing uncertainty broadens the detection of the fluorescence photons by the total IRF. The current temporal resolution of the experiment is limited by the timing uncertainty of the detection electronics, just as with most pulsed laser experiments. The measured histograms $R(t)$ are described by a convolution of the sample's temporal response $S(t)$ with the IRF:

$$R(t) = IRF(t) * S(t) = \int_{-\infty}^t IRF(t - t')S(t')dt'. \quad (3.1)$$

After a measurement, the fluorophore lifetime is fit by the sample response function that will give the best match to the measured experimental data. Here, that is a single

exponential, but a more complex function could be used if a mixture of lifetimes is present and sufficiently fast detectors are used. Therefore, conceptually, the data produced is analogous to TCSPC with a pulsed laser.

From previous theoretical analysis, the minimum fluorescence lifetime that can be measured before deviation in the fit lifetime occurs is approximately 10% of the IRF width [37]. The IRF width in this experiment is approximately 3.65 ns, limiting our instrument to lifetime measurements greater than 365 ps. The counting circuit used here has a minimum time bin width of 4 ps with a 12 ps electrical time resolution; thus the primary factor in the 3.65 ns IRF width is the SPAD timing jitter. It should be noted that detectors with picosecond timing jitter and GHz count rates are commercially available but were not available to our lab at the time of this experiment. The central moment of the IRF drifts over time, in this case with a 50 ps standard deviation over 20 minutes; therefore, all lifetimes measured using this approach are reported with this level of uncertainty. The relevant characteristic timescales for this experiment are summarized in Table 3.1.

Parameter	Time (ns)
SPAD dead time	43
IRF width ¹	3.65
Minimum measurable lifetime ²	0.365
IRF drift (20 minutes) ³	0.050
Standard error of lifetime fit	0.003

Table 3.1: Summary of relevant experimental timescales from instrument parameters.

3.3 Results

The TCSPC histograms for ICG in three solvents, the IRFs, and the fits of the fluorescence lifetime are shown in Fig. 3.3abc. The measured TCSPC histograms for ICG in different solvents are shifted and broadened due to the nonzero lifetime. This broadening is more pronounced in DMSO compared to methanol and ethanol because of the longer ICG lifetime in this solvent. The ICG excited state lifetimes from fitting are presented in Table 3.2 and the exponential decays corresponding to

¹This IRF width is mainly due to SPAD jitter.

²Based on calculations from Ref. [37] that the minimum measurable lifetime is $\sim 10\%$ of the IRF width.

³Detector drift results in a small variation of the IRF center value that ultimately limits the temporal resolution of the measurements. The reported fluorescence lifetimes are reported with this value as the standard deviation.

these lifetimes are shown in Fig. 3.3d. The measured lifetimes agree with previously reported values [38] within error. The near-unity χ^2 values and uncorrelated weighted residuals (Fig. A.4) indicate a satisfactory fit. The standard deviation of the measurements for all experiments are reported as 50 ps due to detector drift, which is larger than the 3 ps standard errors from the fit. The curves in Fig. 3.3abc are normalized and background subtracted for clarity. The raw experimental data plotted on a logarithmic scale are also available in Fig. A.3. An experiment where the sample is replaced by a blank cuvette of methanol does not yield a measurable coincidence peak (Fig. A.1).

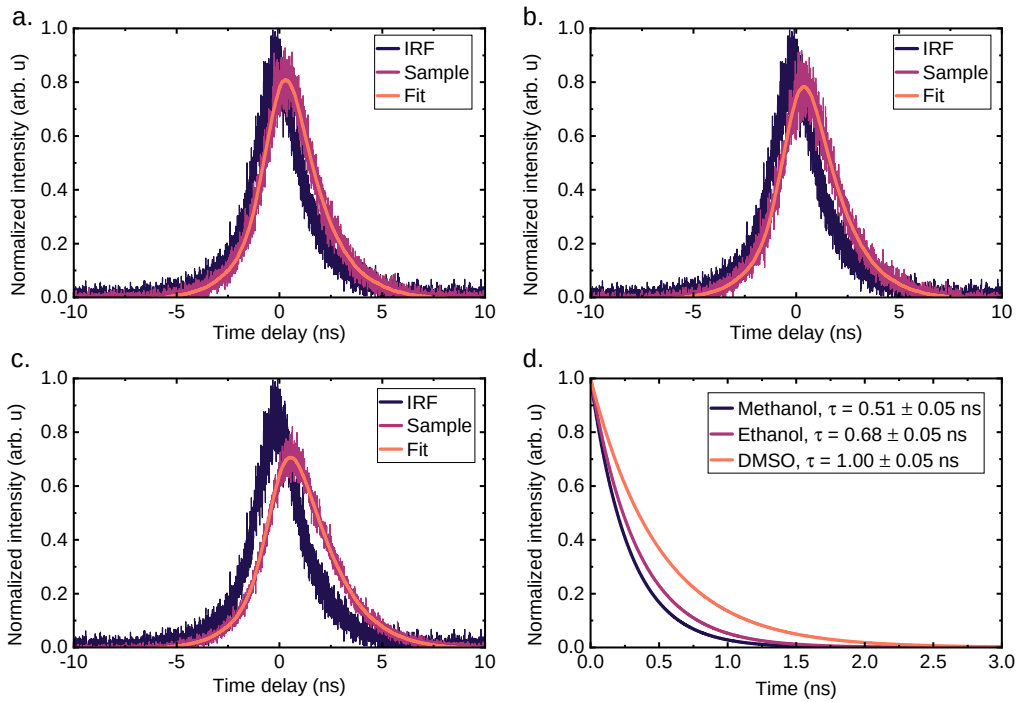


Figure 3.3: Normalized instrument response, TCSPC histogram, and fit of the histogram for ICG in methanol (a), ethanol (b), and DMSO (c). (d) Normalized fluorescence lifetime decays of ICG in each solvent reconstructed from the TCSPC fit lifetime and a single-exponential model.

The practicality of entangled photons for fluorescence lifetime measurements should also be quantified. Due to the Poissonian statistics of photon counting, the signal-to-noise ratio is expected to scale according to $\sqrt{N}$, where N is the number of true coincident photon events recorded. The number of coincidences can be increased either by increasing the SPDC flux or by increasing the integration time of each histogram. To verify the noise statistics, the fit procedure was repeated on one-

Solvent	Reported lifetime (ns)	Measured lifetime(ns)	χ^2 statistic
Methanol	0.51	0.56 ± 0.05	1.003
Ethanol	0.62	0.68 ± 0.05	0.975
DMSO	0.97	1.00 ± 0.05	1.019

Table 3.2: Fluorescence lifetimes for ICG in solutions of methanol, ethanol, and DMSO previously characterized in Ref. [38], as well as the lifetimes measured in this work and the fitting statistic.

minute subsets of a 14 hour DMSO dataset (Fig. 3.4). As expected, the uncertainty in the fitted lifetime in DMSO scales proportionally to $N^{-0.53 \pm 0.01}$, close to the expected $N^{-1/2}$ (Fig. 3.4). For each sampling interval, the dataset was binned and a fit was performed on each of the resulting histograms. The resulting standard deviation of the inferred lifetimes was recorded. The increasing uncertainty in the standard deviation at long integration times originates from the smaller sample sizes.

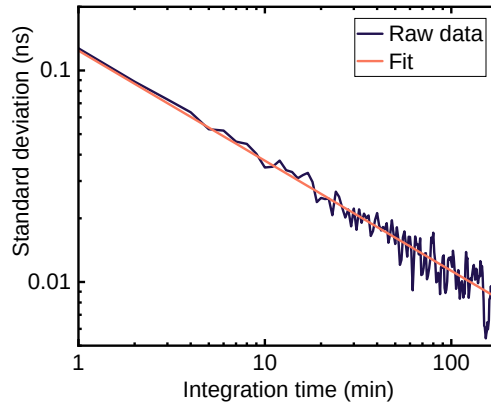


Figure 3.4: Standard deviation of the fit lifetime with respect to integration time for ICG in DMSO.

Figure 3.4 suggests that integration times on the order of several minutes would be sufficient for lifetime determination with a 10% uncertainty, based on the detectors used here that saturate at 10^6 photons/s fluxes. The integration time could be reduced to < 1 minute by using higher count rate detectors, such as those that can reach 10^9 photon/s, given that the pair rate of the experimental entangled source could have been increased by over two orders of magnitude. Theoretically, only ~ 200 coincidences are necessary for single exponential decay lifetimes to be determined with 10% uncertainty when the IRF is shorter than the molecular lifetime [42], potentially further lowering the experimental integration time to below 1 second,

closer to current microscopic techniques. Using coincidence counting also leads to rejection of background, classical photons on the order of 1,000: 1, making the scheme feasible even in sun-lit and room-lit conditions [43].

The proposed technique is therefore aptly timed with the rapidly evolving world of photon counting detector technology [44–46], especially given that THz flux entangled photon sources are already feasible. Figure 3.4 provides evidence that the use of GHz bandwidth detectors coupled with high efficiency (10^{-6}) entangled photon sources would allow for reasonable integration times even with $\sim \mu\text{W}$ power CW laser diodes. Thus, the technique presented here has multiple interesting outlooks compared to conventional pulsed laser TCSPC or CW-modulated fluorescence lifetime measurements, whether it is used for on-chip technology advances, investigation of dynamics in the single-photon excitation limit, or exploration of the ability of quantum systems and molecules to preserve incident quantum states of light.

It is important to note, however, that this method is fundamentally limited by the need to time every heralding photon, regardless of whether a fluorescence photon is detected. Practically, this means that the maximum SPDC rate is limited to the inverse of the detector dead time or molecular lifetime, whichever is larger, and the flux that contributes to the measurement will be reduced by the detector inefficiency. As a result, the count rate of fluorescence events will be restricted by the maximum SPDC flux and the probability of converting excitation photons to fluorescence detection events, which is a function of both molecular and instrumental parameters. Currently, entangled photon pair rates in the THz range can be produced, whereas state of the art photon counting detectors and molecular lifetimes imply sub-GHz pair rates are necessary. Regardless of technology advancements, this upper limit could be surpassed by multiplexing on an electron multiplying intensified charge-coupled device (EMICCD) or SPAD array as proposed in Ref. [22], which would allow the full potential of THz-rate entangled sources to be used.

3.4 Conclusion

In conclusion, we have demonstrated that molecular excited state lifetimes can be measured using the temporal correlations of entangled photons produced from a CW laser. The solvent-dependent lifetime of indocyanine green was measured in methanol, ethanol, and DMSO in agreement with previous reports using pulsed lasers. The low pump flux needed for SPDC provides a direct route to time-resolved fluorescence measurements using on-chip, CMOS compatible photonics. Multiple

waveguides and temperature tuning of phase matching can be used in the future to quickly measure a wide range of fluorophores from a single SPDC source and a photonic circuit. Overall, using a CW laser diode as a pump source opens new horizons for performing complex spectroscopic and microscopic studies with quantum light sources.

3.5 Experimental methods

Broadband entangled pairs are generated in a periodically poled crystal whose design and characterization, as well as its use in studying entangled light-matter interactions, has been reported previously [25, 47]. In short, photon pairs are generated by Type-0 spontaneous parametric down-conversion in a third-order periodically poled 8% MgO-doped congruent lithium tantalate (CLT) bulk crystal (HC Photonics). The crystal is pumped with a continuous wave diode laser with a maximum power of 400 mW at 402.5 nm and FWHM linewidth of 1 nm (Coherent OBIS). The pump polarization is conditioned with a polarizing beamsplitter (Thorlabs PBSW-405) and half-wave plate (Thorlabs WPH10M-405) before being focused through the SPDC crystal with a 40 cm focal length UV-fused silica lens (Eksma Optics). The temperature of the crystal and subsequent entangled photon bandwidth and spectrum is set and maintained using a chip heater and PID loop with an accuracy of 10mK (Covesion). For measurements of ICG (Sigma Aldrich) the crystal was heated to 75.0°C to tune the SPDC to a nondegenerate spectrum where the low-wavelength photons overlap with the ICG absorption curve. A series of 500nm OD 4 long-pass (Edmund Optics #84-706) and spatial filters (irises) remove any remaining pump photons and select the entangled photon pairs that are collinear with the pump beam.

Following the filters, the entangled photons are collimated with an off-axis parabolic mirror (Thorlabs) and directed to a short-pass dichroic mirror with a nominal cut-on wavelength of 800 nm (Edmund Optics 69-196). The incidence angle of the dichroic mirror is fine-tuned with a rotation mount (Thorlabs RP005) to increase the cut-on wavelength to 805 nm, the degenerate wavelength of the pairs, as measured with a grating spectrometer (Princeton Instruments IsoPlane SCT-320, 150 grooves/mm grating with 800 nm blaze) and EMICCD, (Princeton Instruments PIMAX4). The reflected flux (805 nm – 913 nm) is fiber-coupled into a multimode fiber (105 μ m core, 0.22 NA, M43L01) using two mirrors and a 4.51 mm focal length aspheric lens (Thorlabs C230TMD-B) and serves as the herald for the experiment. The transmitted flux is directed to a long-pass dichroic mirror with a nominal cut-on wavelength of 800 nm (Edmund Optics #69-883) and serves as the excitation for the

sample. The angle of this dichroic mirror is also fine-tuned with a rotation mount (Thorlabs RP005) such that the transmission is > 810 nm so that the passband does not overlap with that of the first dichroic mirror. A high-NA 4.51 mm focal length aspheric lens (Thorlabs C230TMD-B) focuses the excitation photons into a 1 mm path length quartz cuvette (Helma/Millipore Sigma) containing $\sim 300\mu\text{L}$ of $100\mu\text{M}$ ICG in solution. The cuvette is mounted onto a micrometer-driven linear stage to precisely control the position of the sample relative to the focus of the excitation beam. The resulting fluorescence is collected through the long-pass dichroic and coupled into a second SPAD using with two mirrors, a 9.2 mm diameter, 4.51 mm focal length aspheric lens (Thorlabs C230TMD-B), and a multimode fiber (105 μm core, 0.22 NA, M43L01). An OD6 808 nm long-pass filter (Semrock LP02-808RE-25) following the dichroic mirror filters any remaining SPDC photons and/or scatter from the fluorescence signal. For the IRF measurements, the sample cuvette was replaced with a mirror, which was positioned so the excitation beam was focused at the surface of the mirror. Differences in path length due to the missing glass of the cuvette are estimated to introduce a 5 ps error, which is below the resolution of this experiment. Black cardboard boxes are positioned to block the sample from any pump scatter and minimize background.

Spectral measurements of the heralding and fluorescence photons were performed by collimating the output of the fibers and directing the image onto the spectrometer/EMICCD. The spectrum of the excitation photons was measured similarly by replacing the sample with a multimode fiber with a micrometer-driven x/y translation mount. This same scheme was used with coincidence counting to estimate the number of heralded excitation photons arriving at the sample.

Lifetime measurements were performed by connecting the multimode fibers to SPADs (Laser Components Count) and a coincidence counting circuit (PicoQuant PicoHarp 300). For these experiments, the SPDC between 805 and 912 nm served as the heralding trigger, and the SPAD output was connected to the sync channel of the counting circuit in a forward start-stop mode. The detection events of the fluorescence SPAD served as the stop signal for the experiment, and the SPAD output was connected to the CH1 input of the counting circuit. An electronic delay of 30 ns between the arms was implemented through the counting circuit. This offset is subtracted from the time axis of Figure 3.3(abc) for clarity but is not removed from the raw data in the supplementary information. Neutral density filters were used to decrease pump power and resulting SPDC flux to minimize lost heralding

events due to the dead-time of the detectors (43 ns). For lifetime measurements, the number of singles in the heralding arm was approximately 1×10^5 counts/s, and the number of singles in the fluorescence arm was approximately 600 counts/s. Data collection consists of repeatedly collecting histograms for 60 seconds, with a series of 10 measurements of the singles rates in each channel measured between each histogram to monitor drift in the alignment. For the methanol, ethanol, and DMSO scans, 840, 840, and 960 histograms were collected, resulting in a total experiment time of 14, 14, and 16 hours, respectively. The instrument response function was measured over 240 coincidence histograms for a total of 6 hours. A custom MATLAB fitting routine is used to determine the characteristic excited state lifetime using the iterative reconvolution approach [48]. In this technique, the single-exponential sample response function is varied so that its convolution with the IRF best matches the measured histograms by minimizing the sum of squared errors.

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Chapter 4

WAVEGUIDE SOURCE OF ULTRAVIOLET SECOND HARMONIC GENERATION

On-chip UV sources are of great interest for building compact and scalable atomic clocks, quantum computers, and spectrometers. However, few material platforms are suitable for integrated UV light generation and manipulation. Of these materials, thin-film lithium niobate offers unique advantages such as sub-micron modal confinement, strong nonlinearity, and quasi-phase matching. Despite these characteristics, its utilization in the UV has remained elusive because of the substantial sensitivity of standard quasi-phase matching to fabrication imperfections, the photorefractive effect, and relatively large losses in this range. Here, we present efficient ($197 \pm 5 \text{ \%}/\text{W}/\text{cm}^2$) second harmonic generation of UV-A light in a periodically poled lithium niobate nanophotonic waveguide. We achieve on-chip UV powers of $\sim 30 \text{ }\mu\text{W}$ and linear wavelength tunability using temperature. These results are enabled with large cross section waveguides, which leads to first-order UV quasi-phase-matching with relatively long poling periods ($>1.5 \text{ }\mu\text{m}$). By varying the poling period, we have achieved the shortest reported wavelength (355 nm) generated through frequency doubling in thin-film lithium niobate. Our results open up new avenues for UV on-chip sources and chip-scale photonics through compact frequency-doubling of common near-IR laser diodes.

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4.1 Introduction

The field of integrated nonlinear optics has grown dramatically during the past decade due to the development and commercial availability of thin-film lithium niobate [1, 2]. In passive nonlinear devices, thin-film lithium niobate (TFLN) excels in efficient frequency conversion and quantum state generation from the visible to the IR [3, 4]. The strong mode confinement of single-pass, low-loss [5] nanophotonic waveguides and quasi-phase matched interactions utilizing lithium

niobate's largest second-order nonlinear optical tensor element have resulted in record-breaking efficiencies in applications such as SHG [6, 7], supercontinuum generation [8], difference frequency generation [9], parametric amplification [10], and parametric down-conversion [11]. Similarly, TFLN active devices such as modulators [12], electro-optic frequency combs [13], and femtosecond pulse generators [14] show impressive performance in compact form-factors due to lithium niobate's large electro-optic tensor elements. However, there is still significant room for lithium niobate's use in UV photonics [15], with applications such as UV-visible spectroscopy, optogenetics, high-resolution microscopy, security banknote features, laser cooling [16], atomic clocks [17], and quantum computing [18].

Although lithium niobate has been extensively studied in the IR, and comparatively less so in the visible, UV devices have remained rare to date. The few reported lithium niobate devices for UV generation have been limited to metasurfaces [19], nanoparticles [20], and large micromachined or channel waveguides [21, 22], and therefore do not take advantage of the sub-micron mode confinement and efficiency of lithium niobate in a nanophotonic platform. TFLN has yet to be well studied in the UV due to significant quasi-phase matching sensitivity to fabrication errors, the ultra-short poling periods required to overcome the high dispersion in waveguides at short wavelengths, and material and scattering loss. To date, variations in the thin film thickness of even 1 Å are sufficient to disrupt phase matching in visible SHG, limiting the effective interaction length and chip-to-chip repeatability [1, 23]. UV generation should be possible up to lithium niobate's band gap at ~ 330 nm (3.8 eV) [24], but an exponentially decaying Urbach absorption tail persists towards the visible due to defects in the crystal structure [25], and impurity ion (Cu^+ , Fe^{2+}) resonances can cause additional loss [26, 27]. Furthermore, losses at the waveguide sidewalls also increase at shorter wavelengths due to surface imperfection Rayleigh scattering, which scales as λ^{-4} [28]. In spite of these difficulties, there is much to gain by extending the spectral coverage of TFLN frequency conversion to the UV. Notably, near-IR laser diodes, which can be frequency doubled, are considerably more accessible than UV laser diodes and gas lasers [29]. Among other nanophotonic material platforms, only aluminum nitride (AlN) has been significantly investigated for waveguided second harmonic UV generation, despite AlN lacking ferroelectricity and therefore being incapable of periodic poling. The lateral polar structures used to achieve quasi-phase matching in AlN are highly scattering, resulting in much lower conversion efficiencies ($<1\%$) [30] compared to lithium niobate devices. Other potential UV platforms (lithium tantalate [31], BBO [32],

LBGO [33]) have yet to be thoroughly explored in a thin film nanophotonic platform. Lithium niobate remains superior to these materials with its combination of low-loss waveguides, high second-order nonlinear response, ferroelectric poling for quasi-phase matching, and, for the case of thin-film lithium tantalate, commercial accessibility [34].

Here, we produce 30 μW of efficient ($197 \pm 5 \text{ \%}/\text{W}/\text{cm}^2$) second harmonic generation of UV light (386.5 nm) with periodically poled TFLN rib waveguides (Fig. 4.1a). The devices exhibit wavelength tunability through temperature and poling period, and are capable of UV SHG at the lowest wavelengths tested (710 nm frequency-doubled to 355 nm).

4.2 Device design and fabrication

The waveguide geometry was designed to reduce sensitivity to the TFLN thickness without compromising the SHG bandwidth at the center wavelength of the laser used in this paper (773 nm). To quantify the phase matching sensitivity, the guided modes were simulated (Lumerical MODE) using the bulk Sellmeier coefficients of lithium niobate [35] and silicon dioxide [36] with the geometric parameters shown in Fig. 4.1b and a 60° sidewall, which is consistent with the fabrication process. Only the fundamental quasi-transverse electric (TE) modes of the first harmonic (FH) and second harmonic (SH) (Fig. 4.1b) were considered since they access lithium niobate's largest nonlinear tensor element ($d_{33} = 25 \text{ pm/V}$) [37]. Thicker waveguides (600 nm film thickness) were analyzed because they allow for reduced sensitivity to thickness errors and longer poling periods with a tradeoff of reduced efficiency and increased susceptibility to slab leakage. The first-order wavelength sensitivity and SHG bandwidth were calculated using a numerical first derivative with respect to film thickness. A 600 nm film demonstrated a significant reduction in thickness sensitivity over a 200 nm film for nearly all waveguide geometry variations (Fig. 4.1c). An etch depth of 375 nm and top width of $1.5 \mu\text{m}$ (Fig. 4.1d-e) were targeted to ensure operation within the flat region of the sensitivity plot. For these parameters, the wavelength sensitivity to film thickness is $\frac{d\lambda}{dT} = 0.08 \text{ nm/nm}$ with a 3.4 pm SHG bandwidth, and the effective refractive indices ($n_{\text{eff,SH}} = 2.32$, $n_{\text{eff,FH}} = 2.10$) result in a quasi-phase matching poling period of $\Lambda = \lambda_{\text{SH}}/\Delta n_{\text{eff}} = 1.8 \mu\text{m}$ (Fig. 4.1f). The larger cross section of the 600 nm film thickness allows for this relatively long poling period, in comparison to a $1.1 \mu\text{m}$ period for a 200 nm film with the same aspect ratio and wavelength.

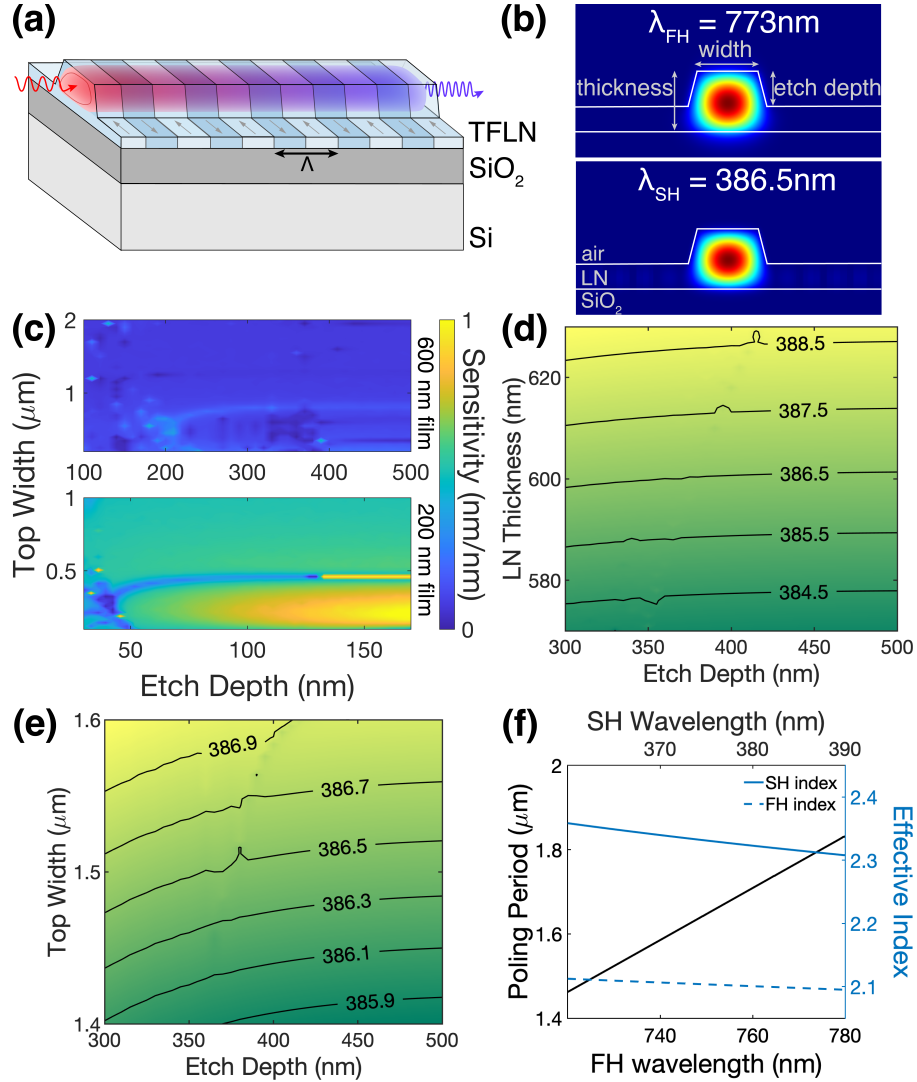


Figure 4.1: Design and sensitivity analysis of TFLN waveguides for UV SHG. (a) Schematic of the TFLN waveguide. (b) Mode profiles of the fundamental TE mode at the first and second harmonics. (c) Sensitivity of the SHG center wavelength to the thin film thickness as a function of the waveguide geometry for 600 nm (top) and 200 nm (bottom) thin film thicknesses; local areas that minimize the sensitivity also decrease the phase matching bandwidth. Two dimensional sweeps of the (d) film thickness and etch depth and (e) top width and etch depth to vary the SHG center wavelength (contour lines). Note that perturbations in the contour lines are caused by mode crossings. (f) Poling period and effective refractive indices of the first and second harmonic fundamental TE modes as a function of wavelength.

The devices were fabricated from a 5% MgO-doped X-cut thin-film lithium niobate on insulator wafer (NANOLN), which consists of 600 nm of lithium niobate bonded to 2 μm of silicon dioxide on a 0.4 mm silicon substrate. Periodically poled waveguides were fabricated following Ref. [10]. Each waveguide had a 7 mm poled length, with poling periods ranging from 1.35 to 2 μm . The waveguide etch depth and sidewall angle were verified through atomic force microscopy, and the poled domain formation was measured with second harmonic microscopy [38].

4.3 Results

The SHG from the TFLN devices was characterized using an optical setup depicted in Fig. 4.2a. The output from a tunable continuous-wave (CW) single-frequency laser (Velocity TLD-6712, 765-781 nm) passed through an optical isolator and a variable neutral density filter to adjust the input power. An achromatic half-wave plate (Thorlabs AHWP10M-980) aligned the input polarization to the optical axis of the chip to maximize SHG power. The first harmonic was coupled to the waveguide using an aspheric lens (Thorlabs C140TMD-B). The waveguide output was collimated by another aspheric lens (Thorlabs C140TMD-A) and collected by a high-OH multimode fiber (Thorlabs M122L01). The device output was monitored using an optical spectrum analyzer (Yokogawa AQ6374) with a passband bandwidth of 5 nm around the second harmonic center wavelength to remove residual first harmonic.

The off-chip power of the first harmonic was varied from 6 to 30 mW at 773.1 nm, and the resulting on-chip SHG power is plotted in Fig. 4.2b. We achieved a maximum on-chip UV power of 30 μW , and the slope of the least squares fit of the SHG output gives a power- and geometry-normalized efficiency of $197 \pm 5 \text{ } \%/ \text{W}/\text{cm}^2$ and power-normalized efficiency of $97 \pm 3 \text{ } \%/ \text{W}$. The power law scaling suggests that photorefraction and pump depletion are not significant at the maximum power tested. The calculated efficiency and on-chip powers take the coupling losses into account, which were 22% transmission per facet for the first harmonic and 10% transmission per facet for the second harmonic. These values were determined by measuring the overall transmission at 780 nm and 405 nm. Assuming that the input and output coupling losses are equal, this would result in an approximate propagation loss of 7.6 dB/cm at 405 nm.

The temperature and poling period dependence of the phase matched wavelength is plotted in Fig. 4.2c and 4.2d, respectively. To measure the temperature dependence,

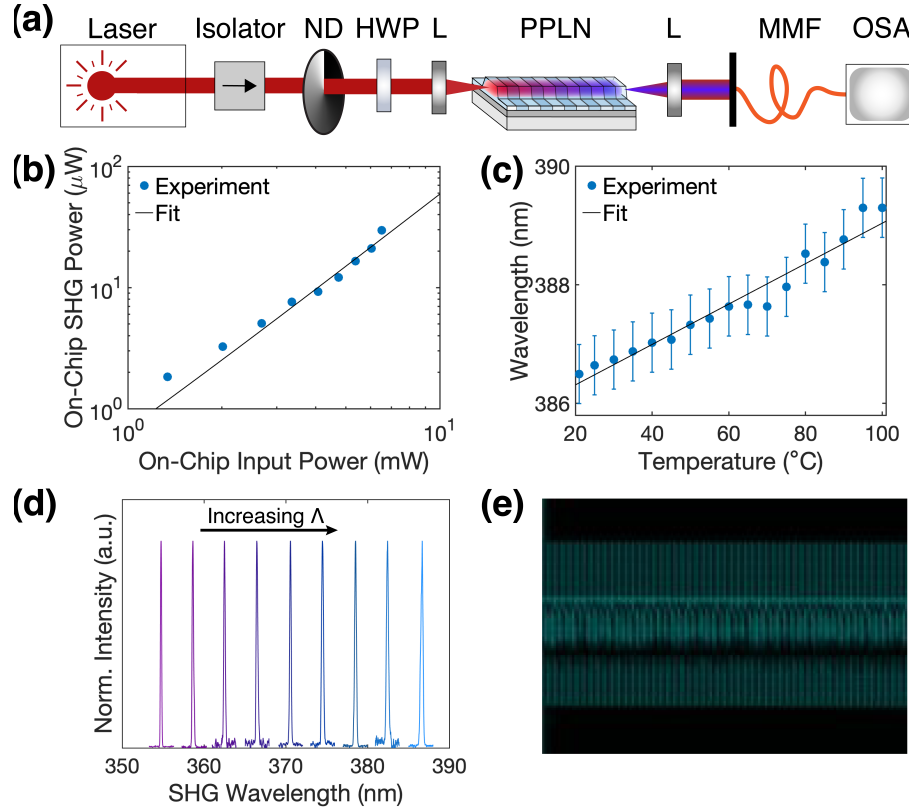


Figure 4.2: Characterization of SHG efficiency and phase matching tuning. (a) Optical setup for on-chip SHG characterization. ND, variable neutral density filter; HWP, half wave plate; L, aspheric lens; MMF, multi-mode fiber; OSA, optical spectrum analyzer. (b) On-chip SHG output power measured as a function of the on-chip input power with experimental fit to calculate the efficiency. (c) Temperature tuning of the SHG center wavelength, measured as the weighted average of the spectrum with standard deviations and experimental fit. (d) Normalized spectra of the poling period swept from 1.35 to 1.75 μm in 50 nm increments. (e) Second harmonic microscopy image of the periodically poled region.

a nonlinear crystal oven (HC Photonics TC038-PC) heated the TFLN waveguides from 21 to 100 °C. The least squares slope (34 ± 2 pm/°C) matches the theoretically calculated value of 32 pm/°C. By varying the poling period, we also obtained SHG spectra extending down to 355 nm. A tunable CW Ti:Sapphire oscillator (Spectra-Physics Tsunami, 700-1100 nm) was used in a similar scheme to Fig. 4.2a to measure the SHG from several PPLN waveguides with poling periods as short as 1.35 μ m (Fig. 4.2d). The fitted slope of the SHG center wavelength with the poling period (79.6 ± 0.2 nm/ μ m) is in close agreement with the theoretical slope of 81.1 nm/ μ m. This agreement in both the temperature and poling period demonstrate that the given Sellmeier coefficients [35] predict the temperature dependence and group velocity mismatch of lithium niobate in the UV relatively well, despite the limited refractive index data at shorter wavelengths. Unlike the initial measurements using the single-frequency laser, accurate efficiency data could not be extracted because the Ti:Sapphire oscillator linewidth (0.3 nm) is orders of magnitude larger than the phase matching bandwidth (3.4 pm). However, these spectra demonstrate that SHG is possible even closer to the 315 nm band gap of lithium niobate than what has previously been demonstrated, and that the thin film lithium niobate platform is able to phase match the full range of a Ti:Sapphire laser.

Although the SHG wavelength tunability agrees well with theory, the experimental efficiency of 197 ± 5 %/W/cm² measured from the single-frequency laser at 773.1 nm is lower than the calculated ideal theoretical efficiency [7] of 18,100 %/W/cm². An immediate explanation is the poling quality of this device, which exhibited significant domain widening due to the short poling period. The duty cycle is estimated to be 90% from second harmonic microscopy images (Fig. 4.2e), which lowers the theoretical efficiency to 1810 %/W/cm². Additional discrepancies can be explained by lateral leakage from the waveguide mode to the slab mode, second harmonic propagation loss, and asymmetry in the input and output coupling efficiency.

The experimental SHG spectrum (Fig. 4.3a) was measured by sweeping the first harmonic wavelength from 771 to 775 nm at a constant 30 mW input power. The spectrum exhibits multiple peaks over a 0.5 nm bandwidth, deviating from the theoretical sinc² line shape and 3.4 pm full-width at half maximum. The discrepancies in the efficiency, bandwidth, and spectral shape are likely caused by multimode effects, index variations, or poling variations. Although the waveguides in this work support multiple modes due to the large cross sections, the fundamental modes of the first and second harmonic are solely responsible for the phase matching of the UV

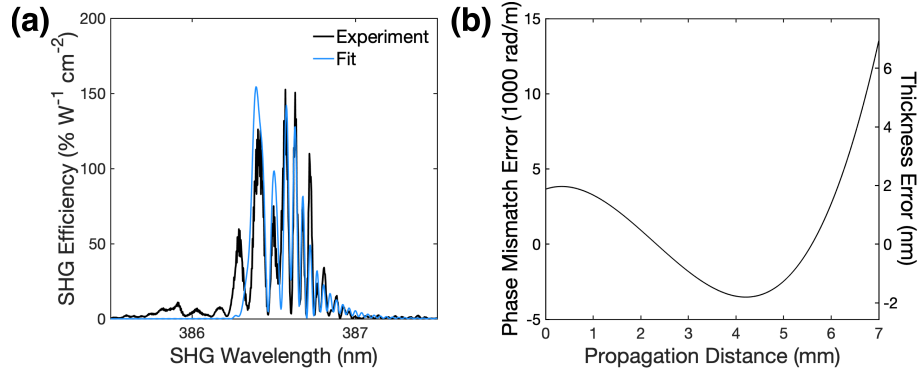


Figure 4.3: Simulation of SHG spectra in the presence of thickness variations as a potential explanation of the experimentally observed spectrum. (a) Experimental and index variation-fitted (Eq. 4.1) SHG spectra. (b) Phase mismatch error represented by Eq. 4.2 and corresponding thickness error against propagation distance.

generation due to large momentum mismatches or poor modal overlap of the higher order modes. Furthermore, collecting the second harmonic with a single-mode fiber (Thorlabs P1-305A-FC-1) does not change the shape of the transfer function, which is expected to occur if higher-order modes were present. Potential sources of index changes are thickness variations, thermal gradients, induced absorption, or photorefractive, while poling defects could be caused by stitching errors in the lithography process. Without a straightforward method of distinguishing these possibilities, we chose to focus on index variations and assume that the poling is uniform. Index variations preserve the integral of the SHG transfer function, which allows us to determine the contribution of the index variations to the experimentally lower efficiency. An integral of the spectral efficiency yields an area of $31.8 \text{ \%}/\text{W}/\text{cm}^2 \cdot \text{nm}$, and the transfer function with the same area and no index variations has a peak efficiency of $861 \text{ \%}/\text{W}/\text{cm}^2$.

The magnitude and position of the index variations cannot be directly calculated without knowledge of the SHG phase relative to the first harmonic. However, the magnitude of the index variations can be estimated by approximating the phase mismatch error as a cubic polynomial to fit the SHG spectrum, given by the following expression for $\eta(\omega)$ [39], which assumes a 50% duty cycle and constant poling period:

$$\eta(\omega) = \left| \int_0^L \exp \left(i \int_0^z (\delta\beta(\xi) + \delta\beta(\omega)) d\xi \right) dz \right|^2. \quad (4.1)$$

The coefficients of the phase mismatch error $\delta\beta(z)$ are estimated by minimizing the squared residuals between the predicted and experimental spectra using a particle

swarm optimization algorithm followed by a gradient descent [40], which yields the following expression for $\delta\beta(z)$ (Fig. 4.3b):

$$\delta\beta(z) = 0.0636z^3 - 0.578z^2 + 0.544z + 3.66 \quad (4.2)$$

where the phase mismatch error $\delta\beta$ is in units of rad/m and the propagation distance z is in μm . A thickness error of ± 5 nm throughout the waveguide explains the full spread in the experimental spectrum. A discrepancy of this magnitude is reasonable given commercial film thickness tolerances; however, this error is an upper estimate given that the index variations could be a combination of the thickness, photorefraction, UV-induced infrared absorption, and temperature gradient. Although this thickness variation could be the cause of the lowered experimental efficiency, the same amount of thickness variation in a thinner film could potentially disrupt phase matching entirely.

4.4 Conclusion

In conclusion, we have demonstrated temperature-tunable UV light generation in an integrated thin-film lithium niobate waveguide. We have measured an SHG efficiency of $197 \pm 5 \text{ \%}/\text{W}/\text{cm}^2$, with discrepancies from theory explained by the poling duty cycle and index variations. As of this publication, this is the shortest wavelength (355-386 nm) produced through second harmonic generation with CW-pumped periodically poled thin-film lithium niobate waveguides. Our work opens up opportunities to realize efficient frequency-doubled chip-scale ultraviolet laser diodes for UV integrated photonics, with applications spanning spectroscopy, atomic physics, and quantum science.

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Chapter 5

WAVEGUIDE SOURCE OF VISIBLE AND NEAR-INFRARED ENTANGLED PHOTON PAIRS

Efficient on-chip entangled photon pair generation at telecom wavelengths is an integral aspect of emerging quantum optical technologies, particularly for quantum communication and computing. However, moving to shorter wavelengths enables the use of more accessible silicon detector technology and opens up applications in imaging and spectroscopy. Here, we present high brightness $((1.6 \pm 0.3) \times 10^9$ pairs/s/mW/nm) visible-near-IR photon pair generation in a periodically poled lithium niobate nanophotonic waveguide. The degenerate spectrum of the photon pairs is centered at 811 nm with a bandwidth of 117 nm when pumped with a spectrally multimode laser diode. The measured on-chip source efficiency of $(2.3 \pm 0.5) \times 10^{11}$ pairs/s/mW is on par with source efficiencies at telecom wavelengths and is also orders of magnitude higher than the efficiencies of other visible sources implemented in bulk crystal or diffused waveguide-based technologies. Further improvements in the brightness and efficiencies are possible by pumping the device with a single-frequency laser, which would also shrink the pair bandwidth. These results represent the shortest wavelength of photon pairs generated in a nanophotonic waveguide reported to date by nearly an octave.

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Harper*, N. A., Hwang*, E. Y., Sekine, R., Ledezma, L., Perez, C., Marandi, A. & Cushing, S. K. Highly efficient visible and near-IR photon pair generation with thin-film lithium niobate. *Optica Quantum* **2**, 103. <https://doi.org/10.1364/OPTICAQ.507526> (Apr. 2024).

5.1 Introduction

SPDC has been used for decades to produce quantum entanglement in various photonic degrees of freedom, serving as a workhorse in emerging quantum optical technologies. Compared to most nonlinear processes, SPDC is relatively inefficient, requiring over one million pump photons to produce one pair of entangled photons in even the highest performing crystals. However, recent advances in nanophotonics, particularly in TFLN, have enabled significantly more efficient frequency

conversion and quantum state generation [1–3] through sub- μm interaction areas, high nonlinearities, and low material losses [4, 5]. By exploiting this platform, many recent demonstrations of SPDC in TFLN [6–9] have achieved efficiencies three orders of magnitude greater than that of bulk crystal-based sources [10] and one order of magnitude greater than that of large diffused waveguide-based sources [11]. To date, most TFLN-based photon pair sources are designed for SPDC at telecom wavelengths because of the low losses in optical fibers at 1550 nm [12, 13] and back-compatibility for applications such as quantum communication [14], computing [15], and a globally connected quantum network [16].

Although telecom photons are preferred for quantum information applications, visible and near-infrared photons are generally better suited for imaging and spectroscopy. Experiments at these wavelengths can take advantage of multi-pixel detectors such as EMICCDs and SPAD arrays, enabling the measurements needed for imaging [17–19] and characterization of high-dimensional entangled states [20, 21]. Furthermore, the electronic transitions of molecules and atoms become accessible at near-IR wavelengths, allowing for fluorescence lifetime measurements [22–24], compatibility with quantum memories [25], and fundamental studies of few-photon nonlinearities [10, 26, 27]. More generally, near-IR and visible photons can be detected with high quantum efficiency and low dark noise using existing mature silicon technology at room temperature, compared to near-IR detectors which require cryogenic cooling [28]. Despite these advantages, all demonstrations of nanophotonic pair production have resided in the telecom region, and the best near-IR and visible photon pair sources are still large-area waveguides [29–32] and bulk periodically poled crystals [10, 26, 29, 33–36]. To date, lithium niobate is the only nanophotonic platform that exhibits high transparency at near-UV pump wavelengths and support a $\chi^{(2)}$ nonlinearity. Thus, despite the known challenges, TFLN is uniquely posed to address this wavelength range. Potential reasons for the lack of visible TFLN devices stem from the difficulty in fabricating visible nonlinear circuits on thin-film lithium niobate due to factors such as the ultra-short poling periods required for quasi-phase matching and losses from material absorption [37–39] and scattering [40]. In spite of these difficulties, high-performance visible devices in thin-film lithium niobate are becoming increasingly common for classical applications such as electro-optic modulation and second harmonic generation [41–45].

Here, we extend TFLN-based SPDC sources to shorter wavelengths to produce high-brightness photon pairs in the visible and near-IR. The device produces an on-chip efficiency of $(2.3 \pm 0.5) \times 10^{11}$ pairs/s/mW, which corresponds to a per-photon conversion efficiency of more than 1 photon pair converted in every 10,000 pump photons $((1.1 \pm 0.2) \times 10^{-4}$ pairs/s/photon). This efficiency is nearly two orders of magnitude better than visible-light diffused waveguide SPDC sources [31] and is on par with the highest-performing TFLN sources in the telecom regime [8]. The SPDC from this device exhibits a broad spectrum centered at 811 nm with a degenerate FWHM bandwidth of 117 nm and an average brightness of $(1.6 \pm 0.3) \times 10^9$ pairs/s/mW/nm, a number limited by at least an order of magnitude by the pump laser linewidth (0.8 nm). Consistent with this bandwidth, we measure an ultrashort coherence time of ~ 40 fs for the entangled photons with an indistinguishability of $100. \pm 1\%$. These results are the shortest wavelength entangled photons generated in TFLN by nearly an octave to date. Our results therefore show that, although pumped at wavelengths near what would usually be considered its cutoff range, TFLN can equally be a platform for visible-near-IR entangled photon applications as it is at telecom wavelengths.

5.2 Device design and fabrication

The periodically poled lithium niobate waveguides (Figure 5.1a) were simulated in Lumerical MODE to determine the quasi-phase matching poling period. The guided modes at the design pump wavelength (406 nm) and SPDC center wavelength (812 nm) were simulated using the bulk Sellmeier coefficients of lithium niobate [46] and silicon dioxide [47] with the geometric parameters shown in Figure 5.1c and a 60° sidewall, which is consistent with the fabrication process. To take advantage of lithium niobate's largest nonlinear tensor element ($d_{33} = 28$ pm/V) [48], only the fundamental TE modes of X-cut lithium niobate were considered. An etch depth of 420 nm, a top width of $1.5 \mu\text{m}$, and a total LN thin film thickness of 600 nm were targeted for ease of optical coupling, fabrication, elimination of slab-mode leakage, and near- $2 \mu\text{m}$ poling period while providing high performance. For these parameters, the effective refractive indices ($n_{\text{eff,pump}} = 2.29$, $n_{\text{eff,SPDC}} = 2.09$) result in a quasi-phase matching poling period of $\Lambda = \lambda_{\text{pump}}/\Delta n_{\text{eff}} = 2.03 \mu\text{m}$ at the target pump wavelength of 406 nm (Figure 5.1d).

The devices were fabricated from a 1 cm by 1 cm die of a 5% MgO-doped X-cut thin-film lithium niobate on insulator wafer (NanoLN), which consists of 600 nm of lithium niobate bonded to $2 \mu\text{m}$ of silicon dioxide on a 0.4 mm silicon substrate.

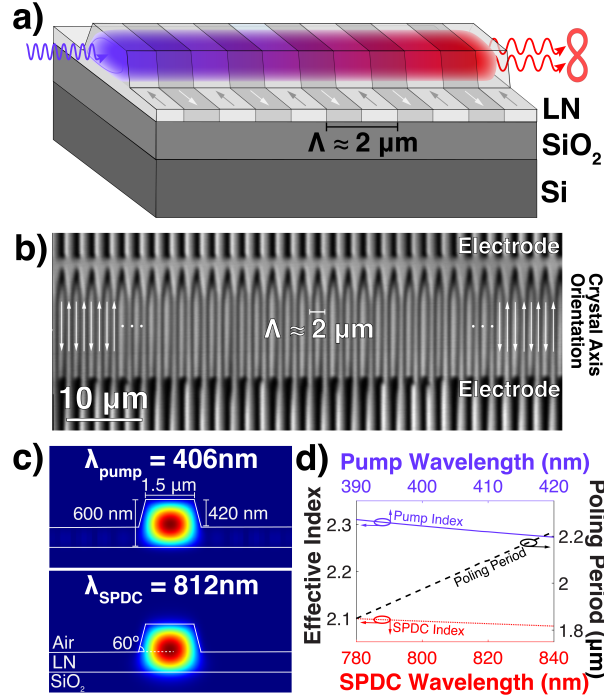


Figure 5.1: Design and fabrication of TFLN waveguides for visible and near-IR SPDC. (a) Schematic of the periodically poled lithium niobate nanophotonic waveguide. (b) Second harmonic microscopy image of the periodic poling. Note that the distance between the electrodes is $15 \mu\text{m}$ while the waveguide top width is $1.5 \mu\text{m}$, allowing for multiple waveguides in the center of the poled region where the duty cycle is 50%. (c) Mode profiles and waveguide geometry of the fundamental quasi-TE modes at the designed pump and SPDC center wavelengths. (d) Refractive indices and corresponding poling periods for a range of SPDC wavelengths.

An MgO-doped film was chosen to lower the coercive field necessary for poling [49, 50] and to reduce potential photorefractive effects from the violet laser diode [51]. MgO-doped LN has been demonstrated to lower propagation losses [38], but this doping may also result in irregular poled domains due to leakage current in the charged domain walls [50]. To quasi-phase match the SPDC sources, poling electrodes (7 mm long) were first fabricated by performing a metal lift-off through electron beam lithography with bilayer polymethyl methacrylate (PMMA) resist followed by electron beam evaporation of titanium (15 nm) and gold (55 nm). The electrodes were poled with a 490 V and $70 \mu\text{s}$ square wave, and the poled domain formation was monitored with second harmonic microscopy [52] (Figure 5.1b). After poling, waveguides were defined through an aligned electron beam lithography step with hydrogen silsesquioxane (HSQ) resist followed by argon inductive coupled plasma reactive ion etching to achieve an etch depth of 420 nm, verified through

atomic force microscopy. The chip facets were manually polished to increase coupling efficiency, resulting in a final waveguide length of approximately 8 mm. A broadband oscillator was used to verify the phase matching wavelength through second harmonic generation (Supplemental Material Section B.2) and was found to match with the computationally predicted second harmonic wavelength within ± 3 nm. This small discrepancy was likely due to fabrication tolerances, particularly in the etch depth and film thickness.

5.3 Device characterization

The spectrum, generation rate, and coherence properties of the entangled photon pairs produced from the fabricated device are characterized as shown in Figure 5.2. In these experiments, the room-temperature periodically poled waveguide is pumped with a free-running laser diode (Coherent OBIS LX 405 nm) to produce entangled pairs (Figure 5.2a). An antireflection-coated aspheric lens (NA = 0.58, Thorlabs C140TMD-A) couples the free-space pump beam to the fundamental TE mode of the waveguide. The photon pairs produced in the fundamental TE mode are collected off-chip and collimated using a similar aspheric lens (NA = 0.58, Thorlabs C140TMD-B).

The spectra of the entangled photon pairs are measured to assess the phase-matching properties and tunability of the device (Figure 5.3). Pairs collected from the waveguide are transmitted to a grating spectrometer and measured using an EMICCD camera (Figure 5.2b). To tune the SPDC emission, the center wavelength of the pump wavelength is varied from 405 to 406.4 nm by changing the drive current of the laser diode. Variable neutral-density filters are used to keep the pump power for all the collected spectra at a consistent $10 \mu\text{W}$. Each spectrum was divided by the spectrometer wavelength response and then normalized to the maximum count rate to infer the relative intensity. Three distinct phase matching regions are explored (Figure 5.3a): 1) at long pump wavelengths, the phase matching condition is not satisfied and SPDC emission is not observed; 2) from 405.6-405.9 nm, the degenerate wavelengths are phasematched; and 3) at short pump wavelengths, the spectrum splits and nondegenerate emission extending to the cutoff wavelength of the filter is observed. The dip in intensity in Figure 5.3a around 755 nm is likely due to on-chip loss, potentially from a mode-crossing [53], and is investigated in further detail with a transmission measurement (Supplemental Section B.2). Due to the linewidth of the laser used in the experiment (0.8 nm FWHM), the spectra are considerably broadened compared to the spectra expected from a single-frequency pump laser

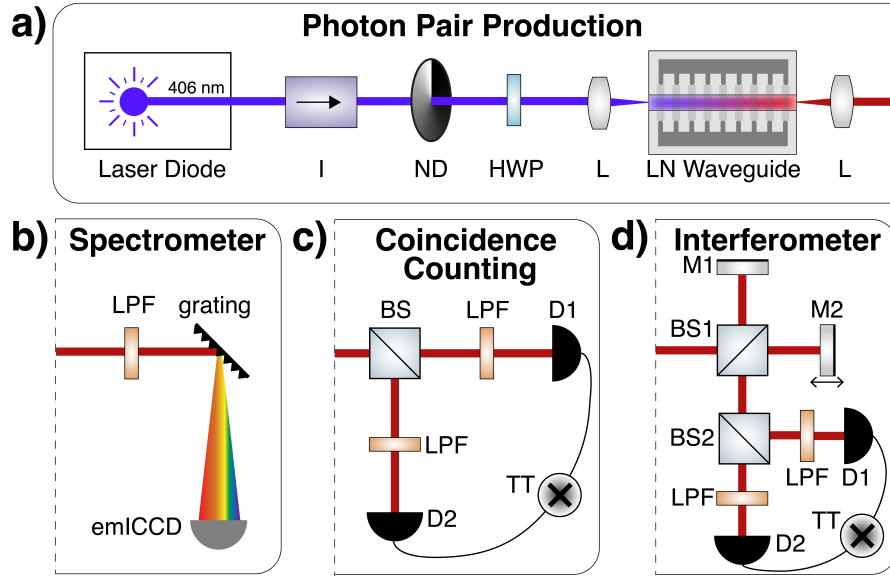


Figure 5.2: Schematic for coupling and detection of the photon pairs. I, isolator; ND, variable neutral density filter; HWP, half-wave plate; L, aspheric lens; LPF, long-pass filter; emICCD, electron-multiplying intensified charge-coupled device; BS, beamsplitter; D, single-photon avalanche detector; TT, time-tagger; M, mirror. (a) Optical setup to couple into and out of the TFLN waveguide. (b) Characterization scheme for measuring the photon pair spectra. (c) Characterization scheme for coincidence counting. (d) Optical setup for the Michelson interferometer.

(Supplemental Figure B.4). Nevertheless, experiment and theory reach qualitative agreement by accounting for the pump linewidth (Figure 5.3b), described further in Supplemental Section B.1. Further spectral broadening can also arise from propagation loss at the pump or SPDC wavelengths [54] or index variations [55–57]. For all subsequent experiments, a laser center wavelength of 405.7 nm is used for degenerate phase matching. The resulting spectrum (Figure 5.3c) is centered at 811.4 ± 0.7 nm with a FWHM bandwidth of 117 nm (53 THz) that accounts for 85% of the overall flux.

The pair generation efficiency of the device is measured through coincidence counting between two SPADs (Figure 5.2c). In this measurement, the pairs from the chip were split at a 50:50 broadband beamsplitter (Thorlabs BS014) and coupled to multimode optical fibers (Thorlabs M122L01) connected to the detectors. Coincidence detection events between the SPADs (Laser Components Count) were recorded with a time-tagger (Picoquant PicoHarp 300). Figure 5.4a shows a representative raw coincidence histogram recorded at 4.3 nW of on-chip pump power. The temporal

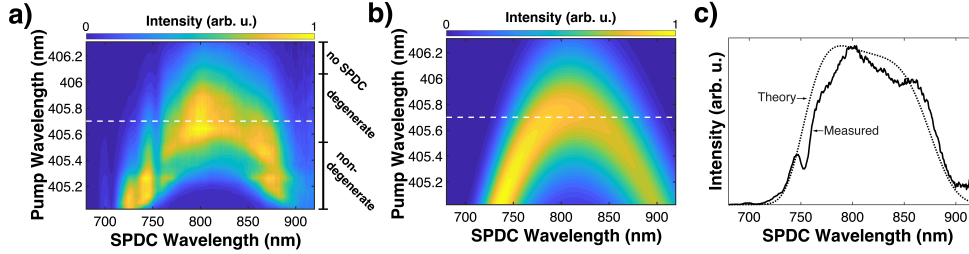


Figure 5.3: Tuning characteristics of the device with respect to the pump wavelength. (a) Measured and (b) theoretical SPDC spectra as a function of pump wavelength. Note that the arbitrary units for intensity could also be interpreted as counts per max counts due to the normalization of the spectra. (c) Lineouts of the measured and theoretical SPDC spectra at a pump wavelength of 405.7 nm, corresponding to the dashed horizontal lines in (a) and (b). Note that the frequency bandwidth per nm and the down-conversion efficiency are wavelength dependent (Supplemental Equation S1), resulting in higher intensities for shorter wavelengths. The theoretical spectra in (b) and (c) are calculated with the laser linewidth taken into account, described further in Supplemental Section B.1.

correlation in this graph (3.4 ns FWHM) is given by the response time of the SPADs and not the entangled photon correlations (see Figure 5.5 later in the text). The coincidence counts are corrected by background subtraction of the number of counts in a 9.5 ns window at the histogram peak from the number of counts in another 9.5 ns window in a background region far from the peak. Sweeping the laser power with a neutral density filter yields the curves in Figure 5.4b-c, which are linearly fit to determine the pair generation efficiency. Additional experimental details and the raw data from these measurements are given in Section B.4 and Table B.1 of the Supplemental Material. To account for the wavelength dependence of the SPAD quantum efficiency (Supplemental Section B.3), all wavelengths in the spectrum are integrated over to calculate the average detection efficiency for single photons ($\eta_1 = 0.52$) as well as the average joint pair detection probability ($\eta_{12} = 0.27$). Including a factor of 2 due to the probability of splitting pairs at the beamsplitter yields Equation 5.1 for the measured efficiency of the source:

$$E = \frac{m_1 m_2}{m_c} \frac{\eta_{12}}{2\eta_1^2}. \quad (5.1)$$

Here E is the pair generation efficiency, m_1 and m_2 are the singles rates at the two detectors, and m_c is the rate of coincidences, all in units of counts/s/mW. A derivation of Equation 5.1 can be found in Supplemental Section B.5. Accounting for the 10.2 dB transmission loss of the pump laser into the waveguide, a pair generation

efficiency of $(2.3 \pm 0.5) \times 10^{11}$ pairs/s/mW is measured, which is equivalent to a per-pump-photon efficiency of $(1.1 \pm 0.2) \times 10^{-4}$ pairs/s/photon. Over the 117 nm FWHM bandwidth of the spectrum, this efficiency translates to an average brightness of $(1.6 \pm 0.3) \times 10^9$ pairs/s/nm/mW. The uncertainties here and throughout this work are reported as one standard deviation, derived from the standard error in the fits of Figure 5.4b-c and the uncertainty in the detector quantum efficiency. The ratio of singles counts to coincidence counts suggests that the transmission of the SPDC from the waveguide to each of the two detectors is 8.4 dB and 8.0 dB, respectively, which includes losses out of the waveguide and of the free-space optics. Our theoretical efficiency (Supplemental Section B.5), including the FWHM of the pump laser, is 2.66×10^{11} pairs/s/mW, in close agreement with our experimental results.

Finally, the two-photon interference is measured (Figure 5.2d) to demonstrate the non-classical behavior of the produced photon pairs. Figure 5.5 shows the measured two-photon interferogram (Figure 5.5a) obtained from the device without subtracting accidentals, as well as the one-photon interferogram (Figure 5.5c) for comparison. Due to the aforementioned temporal resolution of the SPADs used here, the four unique paths through the interferometer are indistinguishable and combine to yield the interference pattern. The important features of the interferogram are as follows: 1) Near the zero time delay, photons are delayed within the coherence length of the source and exhibit both one- and two-photon interference. A visibility of $100. \pm 1\%$ is measured within the coherence length, with an uncertainty derived assuming Poissonian statistics. This near-perfect visibility indicates good mode overlap in the interferometer and indistinguishability of the photons within the pair. 2) Far from the coherence length of the source (delays greater than ± 20 fs), interference between two photons taking different paths disappears, which explains why the single-photon interference (Figure 5.5c) disappears in this region, shown in more detail in Figure 5.5e. Notably, interference between pairs of photons that travel together through the interferometer persists with a fringe period at half the pair wavelength (Figure 5.5d). This feature suggests quantum interference due to the energy-time entanglement of the pairs, and would not be observed if the light was generated from a coherent or a thermal source with a similar spectrum [58]. A fringe visibility of $43 \pm 3\%$ is observed in this region far from the coherence length, which is close to the theoretical maximum of 50% for this experiment due to the temporal resolution of the detectors. The uncertainty in visibility is given from the standard error in the fit of Figure 5.5d, the details of which are outlined in Supplemental Section B.7. The qualitative agreement between the measured and theoretical two-

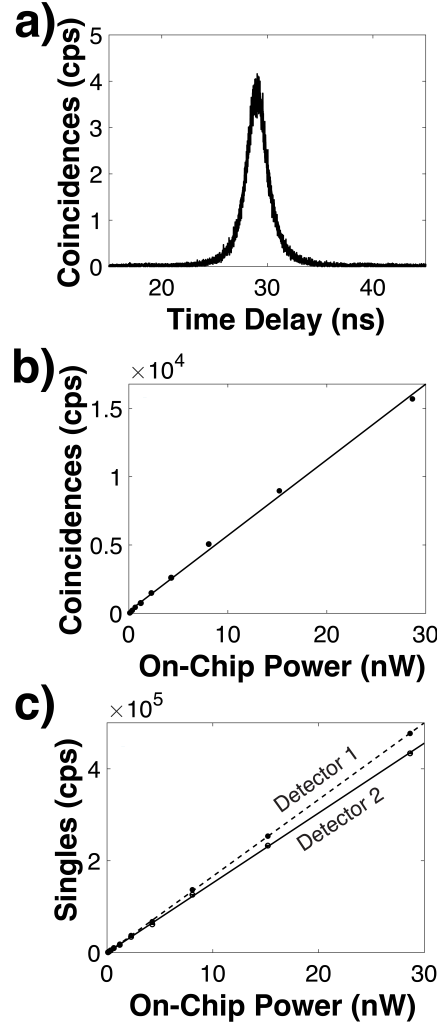


Figure 5.4: Coincidence measurements and power scaling of the SPDC device. (a) Raw coincidence histogram, including accidentals, at an input on-chip pump power of 4.3 nW. Measured (b) coincidence counts with accidentals subtracted and (c) singles counts while sweeping the input power. The vertical axes are measured in coincidence or singles counts per second (cps). The fitted slopes (lines) produce the pair generation efficiency of our device. Note that error bars are included in (b) and (c) but are smaller than the data markers. Additional experimental details and the raw data can be found in the Supplemental Material Section B.4 and Table B.1.

photon interferogram (Figure 5.5a-b) suggests that SPDC and genuine energy-time entanglement are being produced.

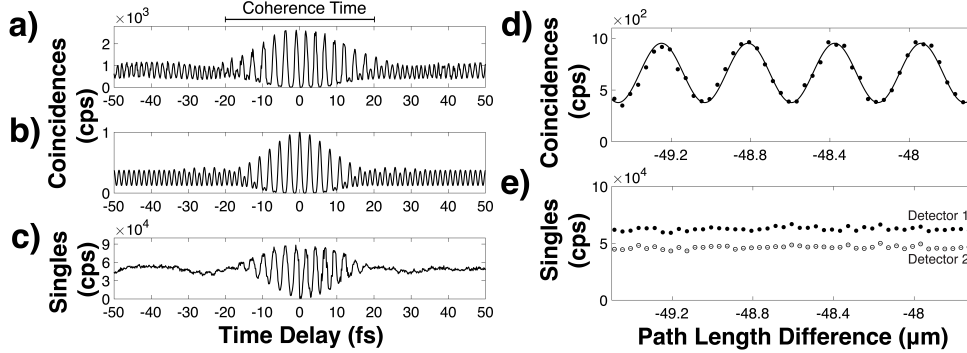


Figure 5.5: The (a) measured and (b) simulated two photon Michelson interferogram for the device. (c) Corresponding singles counts out of the interferometer, demonstrating single photon interference within the coherence length of the source. The (d) coincidence counts and (e) singles counts far from the coherence length of the source. All measured coincidence counts ((a) and (d)) do not have accidentals subtracted. Note that error bars are included in (d) and (e) but are smaller than the data markers. Details of the simulated two-photon Michelson interferogram in (b) and the sinusoidal fit in (d) can be found in the Supplemental Material Section B.7.

5.4 Discussion

Compared to the state of the art for visible photon pair sources, the device presented in this work exhibits substantially improved brightness and efficiency due to the small effective area of the nanophotonic waveguide. The device's performance against reported literature devices spanning from the visible to IR is plotted in Figure 5.6 using efficiency, brightness, and wavelength as the figures of merit. Our visible-near-IR device demonstrates improved efficiency and brightness even over other TFLN sources at the better-explored telecom band [6, 7, 9] and has comparable performance to the most efficient telecom TFLN source (Ref. [8]) to date. At short wavelengths, the phase-matching bandwidth decreases due to group velocity dispersion in lithium niobate, but the efficiency remains high because the down-conversion power spectral density scales with the inverse fourth power of the SPDC wavelength (λ_s^{-4}) [29]. Thus, in addition to the benefits of higher-energy photon pairs, decreasing the SPDC wavelength to access higher efficiencies could enable single-photon nonlinearities when integrated with a resonator[59]. The high efficiency of this device has significant implications for practical uses of entangled photons, including allowing the use of low-power laser diodes for pair generation,

reducing integration times, allowing high signal-to-noise coincidence measurements at low (nW) laser powers even with losses present, and reducing fluorescence and stray light.

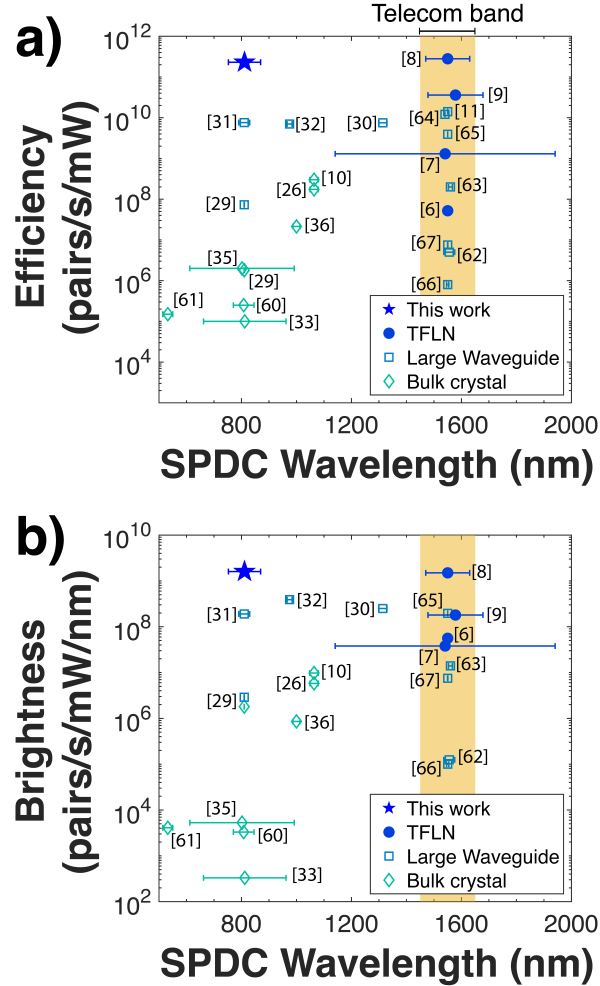


Figure 5.6: Comparison of relevant literature SPDC sources to this work with respect to (a) efficiency and (b) brightness against the SPDC wavelength. Horizontal error bars represent the reported bandwidth of the sources. Data for the efficiency, brightness, center wavelength, and bandwidth are taken from Refs. [10, 26, 29, 33, 35, 36, 60, 61] for bulk crystal sources, Refs. [11, 29–32, 62–67] for large waveguide sources (including micromachined and diffused waveguides), and Refs. [6–9] for TFLN sources. Note that Refs. [11, 64] are not included in (b) since the brightness and bandwidth were not reported. The yellow shaded region represents the typical telecommunication wavelength window.

Although the efficiency and brightness of the device compares well with literature, these values can be further improved by narrowing the bandwidth of the pump laser, as discussed further in Supplemental Section S6. A single-frequency pump is esti-

mated to shrink the phase-matching bandwidth from 117 nm to 35 nm, increasing the brightness by a comparable factor. The SPDC process is also most efficient near degeneracy because the group velocity of the signal and idler are equal to first order, so the efficiency could increase by a factor of 5. Furthermore, compared to SPDC produced with a monochromatic pump, the radiation produced here with a multimode pump will exhibit reduced time-energy entanglement (and greater separability) due to the uncertainty in the energy of the pump photons. The coherence properties of the pump laser are also transferred to the SPDC state, which can reduce the N00N state interference visibility at delays longer than the coherence length of the pump laser. Note that this negative effect is not observed here since the path length differences in Figure 5.5 cover more than the full coherence length of the SPDC source but less than the coherence length of the pump laser [68, 69], indicating that the pump laser coherence does not impair the visibilities measured in this work. Conversely, one benefit of using a multifrequency pump is that the device sensitivity to the laser wavelength is reduced, yielding a higher stability average response with greater bandwidth. Another benefit of the multifrequency pump is in time-bin entanglement, which can be generated from revivals in the biphoton interference at integer multiples of the laser cavity length [70]. For these benefits as well as for the greater accessibility of multimode lasers, a multimode pump laser was utilized in this work to represent an alternate and more applied use of photon pair sources. Furthermore, despite the aforementioned drawbacks of a multimode pump, the device was still able to achieve high efficiencies on par with the current state of the art telecom TFLN pair sources.

5.5 Conclusion

Efficient photon pair generation has been demonstrated with an integrated thin-film lithium niobate waveguide at visible and NIR wavelengths (720-900 nm). An on-chip SPDC efficiency of $(2.3 \pm 0.5) \times 10^{11}$ pairs/s/mW, which is on par with reported TFLN literature at the better-explored telecom wavelengths even with a multimode pump laser, has been produced near the usually associated cut-off wavelengths for the pump (406 nm) in TFLN. The photon pair spectra has an average brightness of $(1.6 \pm 0.3) \times 10^9$ pairs/s/mW/nm, centered at 811 nm with a 117 nm bandwidth. To date, these results are the shortest wavelength photon pairs generated in a thin film platform by nearly an octave. The work opens up opportunities to exploit the quantum advantage of integrated entangled photon circuits beyond telecom to imaging and spectroscopy applications in the visible and NIR.

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EVANESCENT SENSING ON THIN-FILM LITHIUM NIOBATE

Thin-film lithium niobate is promising for optical sensing due to its high nonlinearities, but its material properties present unique design challenges. We compare the sensing performance of the fundamental modes on a TFLN waveguide with a fluorescent dye sample. The TM mode has better overlap with the sample, with a $1.4\times$ greater sample absorption rate versus the TE mode. However, the TM mode also scatters at a $1.4\times$ greater rate, yielding less fluorescence overall. The TE mode is, therefore, more appropriate for sensing. Our findings have important implications for TFLN-based sensor designs.

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6.1 Introduction

TFLN is a promising candidate for on-chip sensing because its strong nonlinearities and low material losses allow for light generation, manipulation, and sample interaction within the same compact device [1, 2]. Lithium niobate's strong quadratic nonlinearity, sub- μm modal confinement, and ability for quasi-phase matching lead to efficient frequency conversion through second harmonic generation [3], optical parametric amplification [4], optical parametric oscillation [5, 6], and spontaneous parametric down-conversion [7, 8]. TFLN has been used to generate light spanning from the UV-A [9] to the mid-IR [10] in photonic circuits, with efficiencies unmatched in any other platform. Lithium niobate's electro-optic effect and versatile fabrication allows for the efficient modulation of light with low voltages, high bandwidths, compact footprints, and excellent insertion losses [11, 12]. Electro-optic modulators on TFLN can also be utilized as light sources, including frequency combs [13, 14], ultrafast laser pulses [15], and frequency shifters [16]. Efficient switches are useful for routing light to different sensing regions on one chip, and the electro-optic effect has been harnessed to increase the resolution of on-chip Fourier-

transform interferometers [17]. With the addition of waveguided detectors [18], the components necessary for a fully integrated optical sensor can all be fabricated on TFLN.

While frequency conversion sources and electro-optic modulation in TFLN are being widely explored, integrated sample interaction geometries for on-chip sensors are less studied. Since the evanescent field of light coupled into a waveguide extends only a few hundred nanometers past its surface, evanescent field sensing allows for highly specific analyte interrogation [19–21]. Evanescent wave sensors have been implemented in materials such as silicon, silicon nitride, and glass with multiple waveguide architectures, including fiber optic waveguides, planar waveguides, slot waveguides, rib waveguides, and strip waveguides [22–25]. For example, TE slot waveguides and TM strip waveguides have been proposed as optimal sensing geometries on silicon-on-insulator (SOI) based on the modal confinement factors and scattering losses of these waveguide configurations in the SOI platform [26]. However, the material properties of lithium niobate present additional concerns for evanescent wave sensing designs. Lithium niobate’s angled sidewall profile, which is a well known feature of the TFLN platform and arises due to redeposition from the physical nature of the waveguide etching process [27], makes slot waveguides difficult to fabricate, and its high refractive index and birefringence present unique design challenges to sample interaction geometries, warranting additional study. Evanescent wave sensing can be modeled with mode overlap calculations between the waveguide mode and the sample to investigate the efficiency of the sample excitation. However, practical devices need to account for additional sources of loss that are not easily captured by modeling, such as the scattering from sub-wavelength imperfections in the waveguide profile, scatterers in the sample, and the refractive index contrast at the material interfaces. While it is known that the TM mode exhibits larger losses than the TE mode in some bare TFLN waveguides [28], it is unknown if this relationship holds with the addition of a sample, or if the gains in the sample-mode overlap outweigh the additional scattering losses.

Here, we quantify the interaction strength of the guided modes with a sample in a model TFLN waveguide fluorescent dye sensor. The sensing region is an X-cut TFLN rib waveguide clad with a sample layer that consists of a 5 mM fluorescent dye (Coumarin-153) doped in a 60 nm thick polymethyl methacrylate polymer film. The device is pumped with a 406 nm diode laser, yielding a fluorescence signal from 450-700 nm which is detected with a camera. By measuring the fluorescence and

scatter from the dye sample along the length of the waveguide, we determine the amount of light absorbed by the sample compared to the amount of light scattered from the waveguide. Theoretical models predict that the fundamental TM mode of the rib waveguide has a nearly two-fold larger overlap with the sample than the quasi-transverse-electric (TE) mode. Experimentally, the TM mode is more efficiently absorbed by the sample than the TE mode by a factor of 1.4 (desired sample absorption of 0.95 ± 0.01 dB/cm and 0.67 ± 0.01 dB/cm, respectively). However, the scattering losses are also larger for the TM mode compared to the TE mode by a factor of 1.4 (undesired scattering losses of 31.5 ± 0.3 dB/cm and 22.4 ± 0.2 dB/cm, respectively). The TM mode thus loses its apparent advantage because of the realities of non-ideal waveguide sidewalls and sample nonuniformities. The TE mode within an X-cut TFLN film accesses the strongest optical and electro-optic nonlinearities in TFLN ($d_{33} = 27$ pm/V) since the mode is polarized along the crystal's optical axis. Therefore, the finding that the TE mode can be directly used for sensing is important for sensor compatibility with integrated frequency conversion sources and modulators. Our comparison of theory and experiment also provides important correction factors for modeling realistic waveguide properties in TFLN waveguide sensors.

6.2 Device design and characterization

The waveguide with the sample layer was modeled in Lumerical MODE before fabrication (Figure 6.1b-d). The confinement factors [29] and the propagation losses of the fundamental TE and TM waveguide modes are calculated in the presence of the Coumarin-153 (C153) dye-doped polymethyl methacrylate (PMMA) sample film. For a fixed device aspect ratio, the confinement factor is inversely proportional to the lithium niobate thickness because the mode is delocalized from the rib into the sample cladding, resulting in stronger sample absorption. This behaviour is quantified in Supplemental Material Section C.1 for thin-film thicknesses ranging from 100-600 nm. For a 406 nm pump wavelength, waveguides with total lithium niobate thicknesses <400 nm exhibit a confinement factor larger than 0.01 for the TM mode. For the waveguide geometry shown in Figure 6.1b, the confinement factors of the fundamental TM and TE modes in the PMMA/C153 film are 0.013 and 0.0073, respectively. In a 60 nm homogeneous PMMA/C153 film (as experimentally measured through profilometry), the theoretical sample absorption loss due to the presence of the dye molecules is calculated as 7.2 dB/cm for the TM mode and 4.4 dB/cm for the TE mode. The difference in sample absorption loss between

the modes arises from the difference in the electric field profile between the two fundamental waveguide modes, and is related to the aspect ratio of the waveguides relative to the polarization of the fundamental guided modes (Figure 6.1c-d).

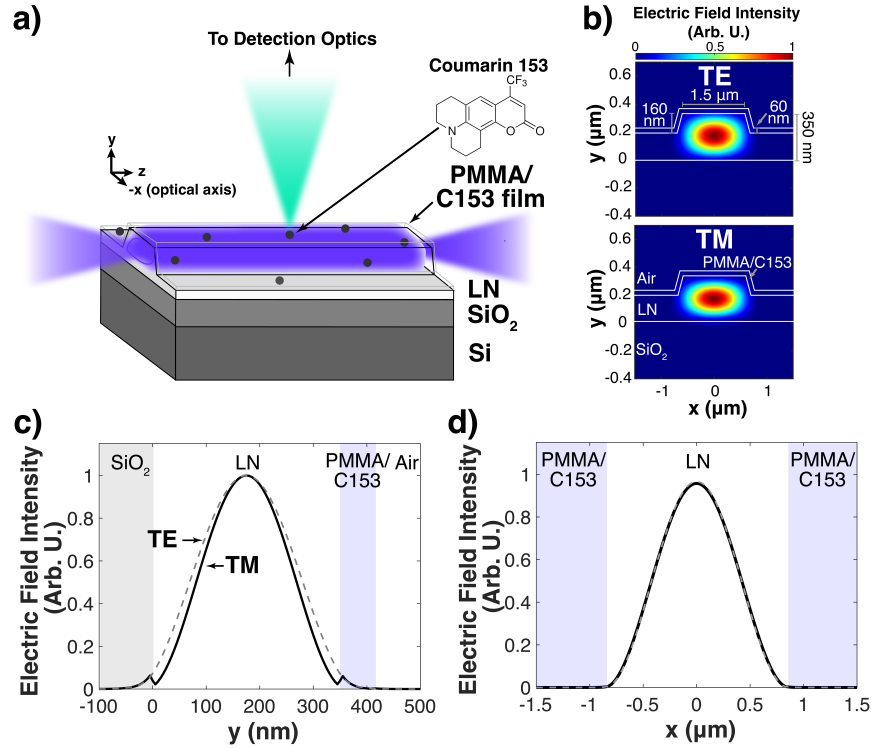


Figure 6.1: Comparison of the fundamental TE and TM modes for evanescent sensing on TFLN waveguides. (a) Schematic of the waveguide and PMMA/C153 film geometry. Note that in the coordinate system used here, the x-axis is parallel to the optical axis of lithium niobate. (b) Waveguide geometry and calculated electric field profiles of the fundamental TE and TM modes using Lumerical. Lineouts of the simulated electric field in the (c) y direction in the center of the waveguide (at $x = 0 \mu\text{m}$) and (d) x direction in the PMMA/C153 film (at $y = 200 \text{ nm}$).

The waveguides were then fabricated from an 8 mm by 12 mm die of a 5% MgO-doped X-cut thin-film lithium niobate on insulator wafer (NanoLN), which consists of 350 nm of lithium niobate bonded to 2 μm of silicon dioxide on a 0.4 mm silicon substrate. Waveguides were patterned through an electron beam lithography exposure with hydrogen silsesquioxane resist (Applied Quantum Materials Inc.) followed by argon inductively coupled plasma reactive ion etching. The final device geometry consists of a lithium niobate rib waveguide with a 1.5 μm top width and 160 nm etch depth (Figure 6.1b). The chip facets were manually polished to increase coupling efficiency, resulting in a final waveguide length of approximately 5 mm.

The PMMA/C153 films were prepared after the waveguide fabrication. To form the films, 1 μL of a 10 mM stock solution of Coumarin 153 (Millipore Sigma 546186) in dimethyl sulfoxide (Millipore Sigma 276855) was added to 99 μL of a PMMA (Millipore Sigma 182230) solution (1% in toluene; Millipore Sigma 244511). 20 μL of the PMMA/C153 solution was deposited on the TFLN chip by spin coating (MicroNano Tools BSC-100) at 300 rpm for 10 s followed by 2000 rpm for 60 s. The spin coating results in a film thickness of ~ 60 nm, confirmed through profilometry on a separate device and in good agreement with literature [30]. Assuming minimal evaporation of the dimethyl sulfoxide, the C153 concentration is approximately 5 mM in the film. A confocal fluorescence micrograph verified that the film was relatively homogeneous across the sample, though strong variations in the fluorescence at the waveguide sidewalls and surface were observed (Supplemental Material Section C.3).

The fluorescence and scatter from the PMMA/C153 film on the waveguide are characterized as shown in Figure 6.2a. In these experiments, the room-temperature waveguide is pumped with a free-running 406 nm laser diode (Coherent OBIS LX 406 nm) to excite the C153 dye, causing the sample to fluoresce from 450-700 nm (Supplemental Material Section C.2). An antireflection-coated aspheric lens ($\text{NA} = 0.58$, Thorlabs C140TMD-A) couples the free-space pump beam to the fundamental TE or TM mode of the waveguide depending on the polarization of the free-space beam, which is tuned with a half-wave plate. The total scatter from the top of the waveguides is collected using a camera lens (Edmund Optics 54691, $f = 75$ mm, operated at $f/4$ with a 300 mm working distance) and camera (Teledyne FLIR BFLY-U3-23S6M-C), with a collection efficiency of 0.025%. To measure the fluorescence, a 500 nm long pass filter (Thorlabs FELH0500) is used with an optical density >5 at the pump wavelength while rejecting only 10% of the generated fluorescence. A second aspheric lens collects the output of the waveguide into a power meter to monitor the stability of the coupling. Figure 6.2b shows an image of the device and the coupling lenses used in this setup. All images were acquired for 5 minutes and were background corrected using images recorded with the laser shuttered. The images with the longpass filter were acquired for 1000 ms at 1 FPS (300 images total), while the images without the longpass filter were acquired for 100 ms at 10 FPS (3000 images total). To avoid photobleaching the dye, the alignment into the waveguide was performed at 5 nW of free-space power and image acquisition was performed with 100 nW of free-space power (Supplemental Material Section C.5).

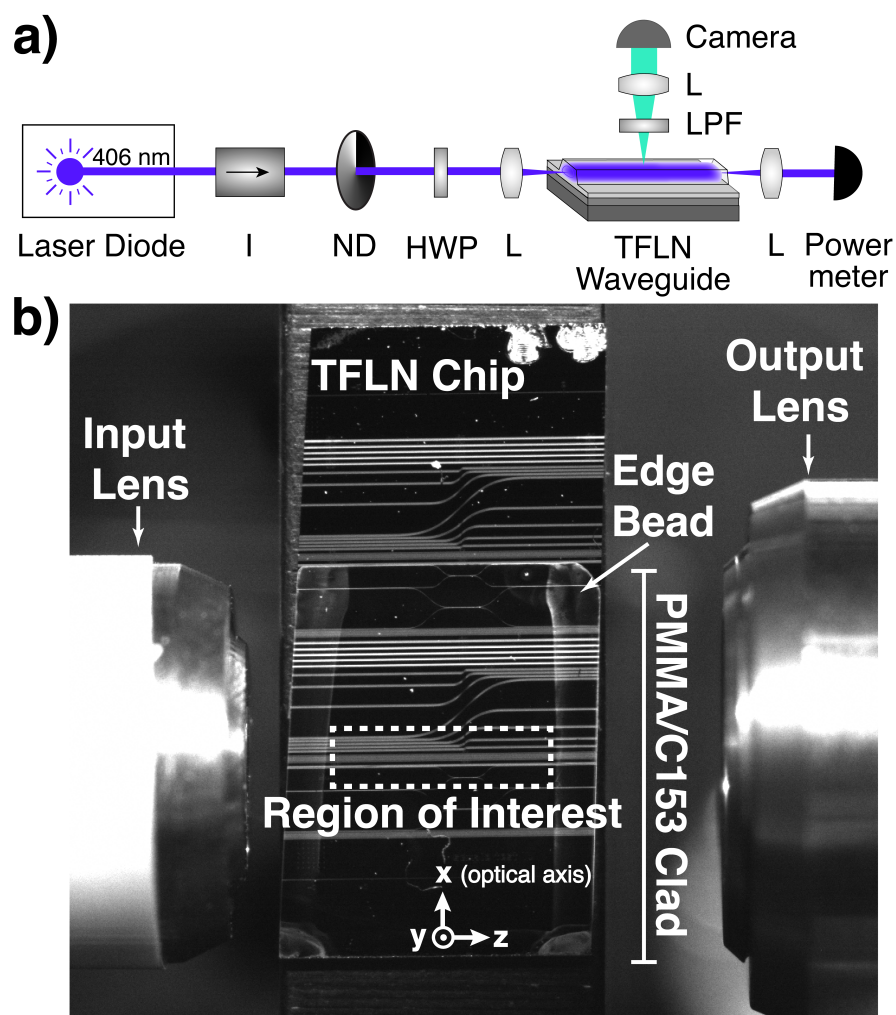


Figure 6.2: Optical setup for quantifying fluorescence from lithium niobate waveguides. (a) Simplified diagram of optical setup. I, isolator; ND, variable neutral density filter; HWP, half-wave plate; L, lens; LPF, long-pass filter. (b) Optical image of the lithium niobate chip and lens setup with the PMMA/C153 clad area, edge bead, and region of interest marked.

Due to the presence of an edge bead in the PMMA/C153 layer from the spin-coating process, a 4.3 mm section in the center of the waveguide with uniform film thickness (region of interest in Figure 6.2b) is used for data analysis. The images are processed by summing the intensity of 24 vertical pixels at each horizontal pixel along the waveguide. The fluorescence counts are scaled up by 11% to account for loss caused by the filter in the C153 emission spectrum passband (Supplemental Material Section C.2). The counts from scatter are measured by subtracting the counts due to fluorescence from the counts recorded without the filter in place. A lithographically defined feature on the device is used to infer the measurement dimensions from the camera images.

6.3 Results and discussion

Figures 6.3a and 6.3b show the intensities measured across the images of the PMMA/C153-clad waveguide when the TE and TM modes are excited. The traces are fit with a single exponential of the form $Ae^{-\alpha x}$, where x is length, α is the propagation loss of the device with units of length^{-1} , and A is a scaling term. The propagation loss of the TE mode is 23.0 ± 0.2 dB/cm, while the propagation loss of the TM mode is 32.5 ± 0.3 dB/cm, both inferred from the fluorescence images. A similar measurement using a bare waveguide determined that the propagation loss is 16.1 ± 0.5 dB/cm for the TE mode, and 18.1 ± 0.7 dB/cm for the TM mode, as summarized in Table 6.1. The PMMA/C153 cladding therefore introduces additional loss to the waveguide.

Figures 6.3a and 6.3b show that the intensity of the scattered signal is larger than the intensity of the fluorescence signal, which suggests that scattering is a more efficient loss mechanism than sample absorption in the device. The fluorescence and scattering losses show good agreement for the TE mode (23.0 ± 0.2 dB/cm and 23.4 ± 0.9 dB/cm, respectively) but show some disagreement for the TM mode (32.5 ± 0.3 dB/cm and 37 ± 1 dB/cm, respectively), most likely due to the higher sensitivity of the TM mode to sidewall scattering and PMMA film variations. Since the fluorescence intensity shows less spatial variance than the scattering intensity (Figure 6.3 and Supplementary Material Figure C.4), the loss coefficient measured via fluorescence is chosen for all subsequent results.

Equation 6.1 is a modified form of Beer's Law, which models how the individual losses of sample absorption $\alpha_{\text{absorption}}$ and scattering α_{scatter} contribute to the total propagation loss α_{total} inferred from Figure 6.3:

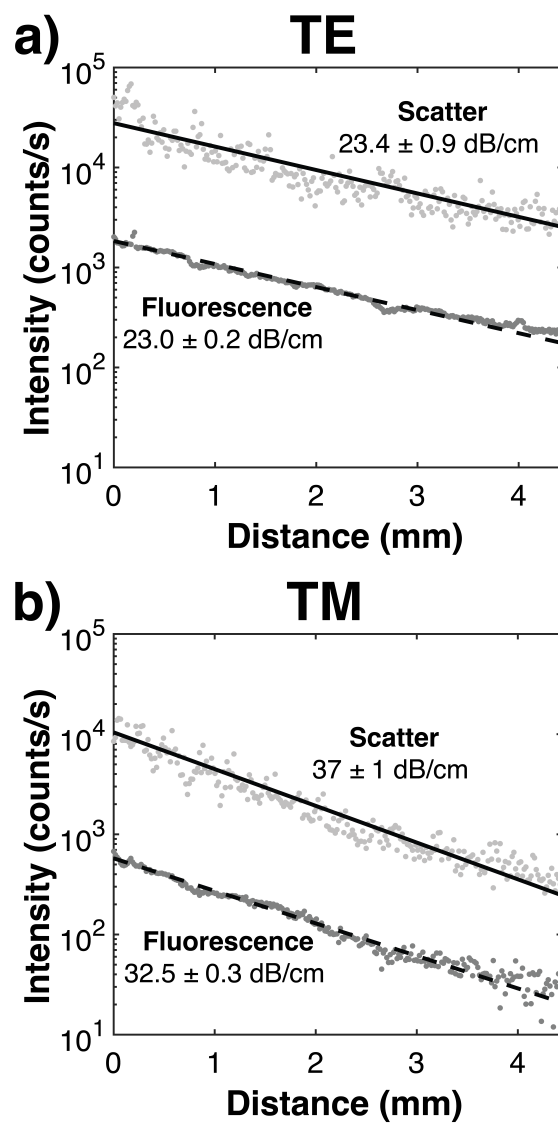


Figure 6.3: Measured fluorescence and scatter in the waveguide region of interest when coupled into the (a) TE and (b) TM modes.

$$-\frac{1}{I(z)} \left(\frac{dI(z)}{dz} \right) = \alpha_{\text{scatter}} + \alpha_{\text{absorption}} = \alpha_{\text{total}}. \quad (6.1)$$

Here, $I(z)$ is the intensity of the pump laser along the length of the waveguide. At each location along the waveguide, the number of photons lost to absorption $N_{\text{absorption}}(z)$ compared to the number of photons lost to scatter $N_{\text{scatter}}(z)$ is given by Equation 6.2:

$$\frac{N_{\text{absorption}}(z)}{N_{\text{scatter}}(z)} = \frac{\alpha_{\text{absorption}}}{\alpha_{\text{scatter}}}. \quad (6.2)$$

The number of photons lost to absorption and scatter can be inferred from the data of Figure 6.3. With the knowledge of the total propagation loss α_{total} , the individual loss coefficients of absorption and scatter are then given by Equations 6.3 and 6.4:

$$\alpha_{\text{absorption}} = \alpha_{\text{total}} \frac{N_{\text{absorption}}(z)}{N_{\text{absorption}}(z) + N_{\text{scatter}}(z)} \quad (6.3)$$

$$\alpha_{\text{scatter}} = \alpha_{\text{total}} \frac{N_{\text{scatter}}(z)}{N_{\text{absorption}}(z) + N_{\text{scatter}}(z)} \quad (6.4)$$

Since Equations 6.1-6.4 hold over the entire length of the waveguide, the total number of photons lost through the region of interest $N_{\text{absorption}}$ and N_{scatter} can be substituted for their spatially-dependent counterparts.

Over the 4.3 mm section of the waveguide used for loss measurements, the ratio of total counts due to scatter versus total counts due to fluorescence is 15.82 ± 0.01 and 15.73 ± 0.04 for the TE and TM modes, respectively. The raw integrated counts can be found in the Supplementary Material Section C.6. To relate the scatter-to-fluorescence ratio to the scatter-to-absorption ratio ($N_{\text{scatter}}/N_{\text{absorption}}$), the following factors are taken into account: 1) The collection efficiency of the system is the same for any photon radiated from the waveguide. 2) The camera quantum efficiency is 30% at 406 nm and ~70% over the emission range of C153 (500-600 nm), as reported on the camera datasheet. 3) Fluorescence from the dye has a 90% chance of transmitting through the filter based on the filter attenuation. 4) The quantum yield of Coumarin-153 in PMMA is 90%, the same as its quantum yield in nonpolar solvents such as cyclohexane [31]. 5) The PMMA film is thin enough that absorption of scatter and fluorescence reabsorption is negligible for both the TE and TM modes.

With these assumptions, the probability that a photon lost to molecular absorption generates a count through fluorescence is roughly 2.1 times as high as the probability that a photon lost to scatter generates a count. The ratios of the scatter to molecular absorption for the TE and TM modes are therefore 33.22 ± 0.02 and 33.03 ± 0.08 , respectively. The individual loss coefficients consistent with these ratios and the measured total propagation loss are displayed in Table 6.1. The measured ratios confirm that scattering dominates the overall propagation loss in both the TE and TM modes. Compared to the TE mode, the TM mode is measured to experience higher loss, but not to a degree proportional to the fluorescence. Increased scattering in the TM mode is largely responsible for the increased total propagation loss, most likely due to inhomogeneities in the sample film.

Experiment	α_{total} (dB/cm)	α_{scatter} (dB/cm)	$\alpha_{\text{absorption}}$ (dB/cm)
PMMA/C153, TE	23.0 ± 0.2	22.4 ± 0.2	0.67 ± 0.01
PMMA/C153, TM	32.5 ± 0.3	31.5 ± 0.3	0.95 ± 0.01
Bare Waveguide, TE	16.1 ± 0.5	16.1 ± 0.5	0
Bare Waveguide, TM	18.1 ± 0.7	18.1 ± 0.7	0

Table 6.1: Summary of measured and inferred propagation losses caused by scattering and C153 absorption.

The experiments confirm the theoretically predicted relative interaction strength of the TM mode compared to the TE mode with the sample (7.2 dB/cm and 4.4 dB/cm), but the measured interaction is much smaller (0.95 dB/cm and 0.67 dB/cm). The discrepancy comes from the difficulty in modeling the PMMA film parameters, especially the film profile in the vicinity of the waveguide. The PMMA/C153 layer was measured to be 60 nm on average using profilometry, but the film profile is not homogeneously 60 nm thick in the vicinity of the waveguide, as measured by confocal fluorescence microscopy (Supplementary Material Section C.3). The measured propagation loss could also be underestimated if the assumed dye quantum yield of 90% is too high, which could be the case due to the PMMA microstructure around the dye, quenching of the dye (such as self-quenching by homo-Förster resonance energy transfer), or degradation of the dye. Decreases in the dye cross-section from these effects by up to 50% have been observed in the Coumarin family [32] when dissolved in PMMA. If the dye quantum yield and film non-uniformity are included in the simulations, the absorption losses can become as low as 0.80 dB/cm for TM and 0.55 dB/cm for TE, close to the experimentally measured values in Table 6.1.

Based on our findings, future work improving TFLN-based evanescent field sensors should focus on decreasing the waveguide scattering loss imparted by the fabrication process and realistic sample interaction layers. Propagation losses of 0.002 dB/cm have been demonstrated in TFLN waveguides with methods such as post-fabrication annealing [33], ion beam milling [34], and redeposition-free etching [27]. Compared to the losses in Table 6.1, such improvements in the scattering loss will increase the fluorescence-to-scatter ratio from the 3% demonstrated here to upwards of 30,000%. A liquid sample with microfluidics will also eliminate much of the uncertainties associated with the polymer film used here.

6.4 Conclusion

TFLN rib waveguides are analyzed for their light-matter interaction strength. The thin-film thickness is found to be the primary variable for increasing the sample interaction. While the fundamental TM mode is predicted to exhibit a two-fold stronger sample interaction, increased scattering losses from the waveguide for the TM mode outweigh this factor. We demonstrate the importance of quantifying different loss mechanisms on the waveguide when measuring a LN sensor's efficacy, which we accomplish by comparing the spatially-resolved intensities of scatter and fluorescence without requiring any knowledge of the actual on-chip pump intensities. The suitability of the TE versus TM mode for sensing has important implications. The main advantage of using TFLN is the integration of a sensor with up- or downstream nonlinear frequency conversion, which utilizes the TE mode in X-cut TFLN to access the highest quadratic nonlinearity. Therefore, a sensor utilizing the TE mode in a rib waveguide is the most compatible with up- or downstream nonlinear frequency conversion. Although a polarization mode converter could be designed to convert between the TE and TM modes, any additional integrated components will likely incur more loss than is gained in interaction strength. Further improvements in the sensor performance, regardless of TE or TM mode, can be achieved with improved fabrication to decrease the scattering loss. Our work, therefore, represents a first step toward fully integrated TFLN sensors.

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PROGRESS TOWARDS CASCADED SPONTANEOUS PARAMETRIC DOWN-CONVERSION

Multiphoton states are generally useful for quantum communication and computation, but are significantly more difficult to generate compared to single photons and pairs of photons. The leading approach to this problem is to entangle multiple independent SPDC sources, then certify the production of the multiphoton state by detecting all photons involved. Alternatively, cascading two SPDC processes directly produces a multiphoton entangled state of three photons. A notable benefit of this scheme is that an entangled pair can be directly heralded by detecting one photon from the triplet. Because cascaded SPDC relies on two down-conversion events of low probability, all demonstrated examples to date have shown triplet rates too low to be useful (< 1 Hz detected). The high efficiency of SPDC on thin-film lithium niobate waveguides, as shown in Chapter 5, suggests that significant improvements to triplet generation rates are possible.

7.1 Introduction

While great progress has been made in the development of one- and two-photon sources of light, states with higher numbers of photons exhibiting entanglement are expected to be useful for specialized applications in quantum communication and computation [1–4]. While emitters such as atoms and quantum dots can generate single photons on demand, producing a multiphoton entangled state is not straightforward due to challenges in efficient collection of photons from the emitter, and the state fidelity can be limited by dephasing of the physical qubit during each emission cycle [5, 6]. SPDC on the other hand exhibits very high state fidelity, and has been the method of choice for generating multiphoton entanglement through entanglement swapping [7–9]. In this procedure, independent sources of SPDC are combined interferometrically to erase the knowledge of which source produced each photon. Because the SPDC process is not deterministic, multiphoton generation can only be determined after the fact by counting how many photons were generated in each run of the experiment, preventing further use of the state.

As an alternative, cascaded SPDC (CSPDC) can directly produce multiphoton states from one single pump photon, as has been experimentally demonstrated in several

publications [10–17]. A pump photon is first down-converted into a pair of daughter photons, one of which is down-converted using a second SPDC interaction to produce a pair of granddaughter photons. In total three photons are formed (one daughter and two granddaughters). Both SPDC processes conserve energy, which results in all three photons existing in a time-energy entangled state [11, 15]. Further engineering can yield entanglement in additional degrees of freedom such as polarization [12, 16]. A unique aspect of CSPDC is that an entangled photon pair can be heralded by detecting one of the granddaughter photons produced in the second down-conversion crystal. The remaining two photons which have not been measured can then be used for quantum information processing or communication. Such a feat is much more difficult to accomplish using entanglement swapping, which requires three independent SPDC sources to herald a single pair [18, 19].

Because CSPDC relies on two sequential processes of low efficiency, all demonstrations to date have exhibited very low triplet rates. While the pump power can be increased to generate arbitrary numbers of triplets, the practical rate that can be detected is bounded by the dead time of the single photon detectors. The flux of daughter photons is typically orders of magnitude higher than the flux of granddaughter photons, thus the detector for daughter photons will begin to saturate well before that of the granddaughter detectors. The critical parameter is therefore the system efficiency of the second down-converter, which sets the probability that a daughter successfully down-converts into granddaughters.

With the recent development of nonlinear nanophotonic platforms such as periodically poled TFLN, significant advances in SPDC production have been made. Our group has shown enhancements in visible and near-IR SPDC efficiencies by about an order of magnitude over the best large-area sources [20], and other groups have shown similar enhancements in the telecom [21–23]. Here, we show a proof of principle measurement of efficient triplet generation using dispersion engineered TFLN waveguides. Specifically, we show that one daughter photon can herald the presence of a granddaughter photon, observing coincidence rates of 0.20 ± 0.03 counts/s which implies a triplet production rate of 24 ± 4 triplets/s for an on-chip efficiency of $(130 \pm 20) \times 10^3$ triplets/s/mW.

As an aside, an alternative method to directly produce entangled photon triplets is third-order SPDC [24, 25]. Here, a single pump photon is down-converted to triplets in one four wave mixing step. The efficiency of this process is set by the $\chi^{(3)}$ tensor of the crystal, which is orders of magnitude lower than $\chi^{(2)}$. While

many theoretical proposals have been put forth, this process has only ever been observed experimentally when one of the three daughter fields is seeded with a coherent state, which does not yield a usable triplet [26, 27]. For this reason CSPDC is more likely to be fruitful. An alternative approach to generating entangled triplets is to combine two photons from independent SPDC sources through sum frequency generation, which offers many of the same benefits as CSPDC in terms of generating heralded entangled pairs without postselection. This scheme suffers from low success probability due to the low ($10^{-7} - 10^{-8}$) efficiencies of single photon sum frequency generation in large area waveguides, but could also be an interesting future target for TFLN waveguides (a recent work [28] has shown success probabilities as high as 4×10^{-5} using integrated semiconductor microdiscs) [29, 30].

7.2 Device design and fabrication

Previous demonstrations of CSPDC have used two physically separate SPDC sources, giving access to the photons produced in the first down-conversion step before they reach the second SPDC source. While such an arrangement allows for filtering between the sources, any losses that occur in coupling photons from one source to the next reduce the triplet rate that can ultimately be produced. Without spot size converters, insertion losses in excess of 3 dB are common among TFLN waveguides. For this reason, both down-converters are located on the same waveguide (Figure 7.1). Down-converter 1, phase matched for nondegenerate SPDC at 407.8 nm, produces a wide spectrum of daughter photons centered at 796 nm and 836 nm. Down-converter 2, phase matched for degenerate broadband SPDC at 796 nm, probabilistically splits the lower-wavelength daughter photon into a pair of grand-daughter photons centered at 1592 nm. The longer-wavelength daughter photon also propagates through Down-converter 2 with low loss, yielding all three photons in the fundamental mode of the waveguide. While any of the three photons can be used to herald the remaining two, the unused daughter photon from Down-converter 1 will be referred to as the herald for the rest of this chapter for clarity.

The limiting factor in the detectable triplet rate is the efficiency of Down-converter 2, which will be a product of the device length, brightness, and down-conversion bandwidth (see Section B.1 for the relationship between some of these parameters). While the down-conversion bandwidth is normally set by the crystal indices when working with bulk and large-area waveguides, the geometric dispersion present in high confinement TFLN waveguides gives an opportunity to engineer the indices

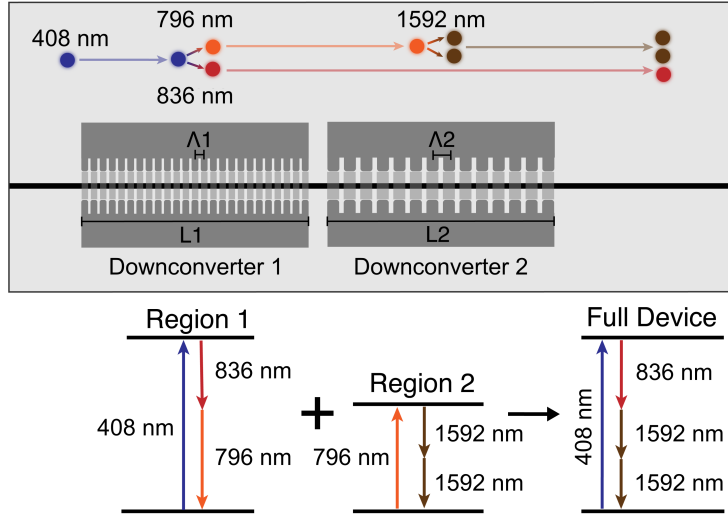


Figure 7.1: Conceptual overview of the CSPDC device and experiment. Down-converter 1 produces a pair of daughter photons through SPDC, one of which then produces a pair of granddaughter photons through SPDC in Down-converter 2. All photons are confined to one waveguide. The energies of the photons are constrained by energy conservation due to the narrow linewidth of the pump laser used in the experiment as shown in the energy diagrams. Momentum conservation further restricts the wavelengths that are phase matched, with nominal center wavelengths for each photon shown throughout. Abbreviations: L: down-converter length, Λ : poling period.

of the waveguide modes. As shown previously by other groups, the bandwidth of SPDC can be maximized by tailoring the waveguide geometry to minimize the group velocity dispersion (GVD) at the degenerate wavelength [22, 31]. For an X-cut TFLN waveguide on SiO_2 , a top width of approximately $2.1 \mu\text{m}$ minimizes GVD when the film thickness is 610 nm and the etch depth is 520 nm (chosen to suppress lateral leakage of the 408 nm pump photons). Such a device was fabricated using procedures similar to those outlined in Chapter 5. Due to fabrication tolerances a nonzero GVD ($-8 \text{ fs}^2/\text{mm}$) is realized in the fabricated device when the waveguide parameters are measured with AFM, which is sufficiently small to generate SPDC with a 3-dB bandwidth of 825 THz ($1.3\text{-}2.0 \mu\text{m}$), as shown in Figure 7.2. For comparison, the GVD and resulting SPDC spectrum are also shown for a previous iteration of the CSPDC device with a narrower top width.

The lengths of the individual down-converters provide one final parameter for tuning the device performance. The TFLN dies that were available at the time are 10 mm in width, yielding approximately 7 mm of usable length for poling when edge beads

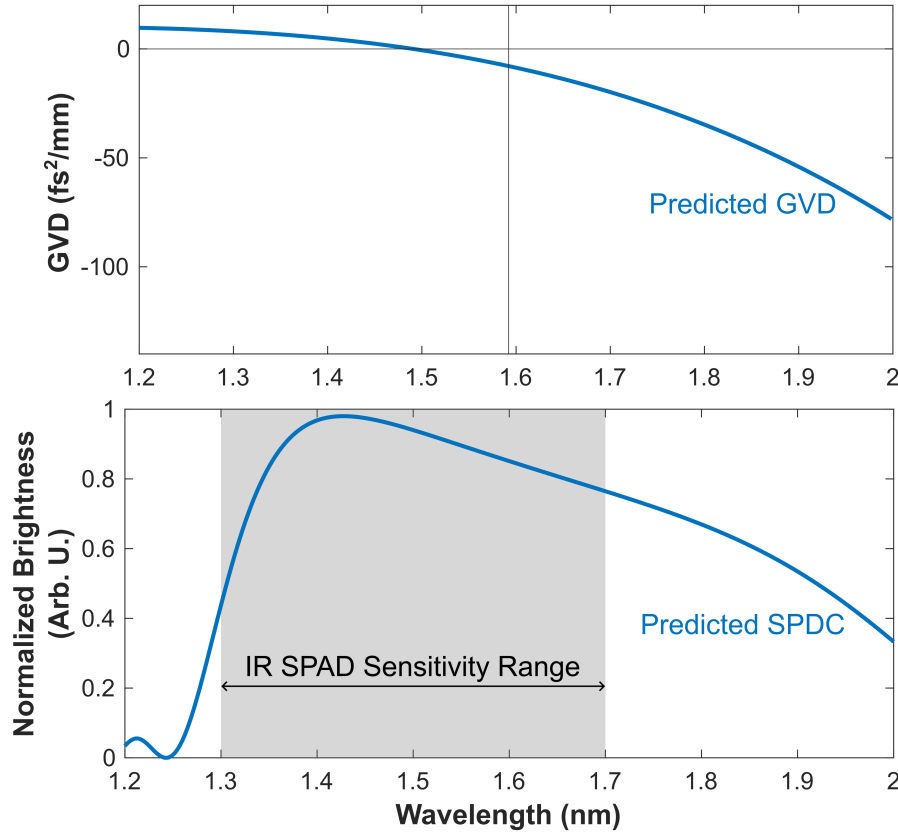


Figure 7.2: Simulated wavelength dependence of the waveguide GVD (top) and predicted SPDC spectral brightness (bottom). Simulations for Device 2, the focus of this Chapter, were calculated using a film thickness of 610.9 nm, etch depth of 520 nm, top width of $2.12\ \mu\text{m}$, sidewall angle of 64° , and poled length of 3.5 mm all estimated from AFM scans.

in the lithography process and polishing are taken into account. The efficiency of an SPDC source scales as L (brightness scales as L^2 , while the bandwidth scales as L^{-1}). At the same time, the acceptance bandwidth scales as L^{-1} , which reduces the bandwidth of daughter photons from Down-converter 1 that can efficiently pump Down-converter 2 [32]. For simplicity, down-converters of equal lengths (3.5 mm each) were chosen, yielding an acceptance bandwidth of 3.6 nm for Down-converter 2. While more optimization could certainly be done, this acceptance bandwidth matches well with the filter bandwidth of 4 nm on the heralding arm as described later.

7.3 Device characterization

The individual down-converters exhibit exceptional brightness when pumped at their respective wavelengths. Figure 7.3 shows the spectral brightness produced

by Down-converter 1 when pumped with a narrow linewidth (1 MHz) frequency doubled titanium sapphire laser. Integrating over the full bandwidth gives a total efficiency of 200 GHz/mW, which is equivalent to a per-photon down-conversion probability of 10^{-4} for the 407.8 nm pump photons. When normalized for device length, the brightness is approximately 5 times as high as the device shown in Chapter 5, most likely a result of the narrower pump linewidth. To calculate the spectrum shown in Figure 7.3, the spectrum of Down-converter 1 was scaled to match a brightness measurement conducted at 836 nm, the details of which are given in the Methods section (Section 7.7).

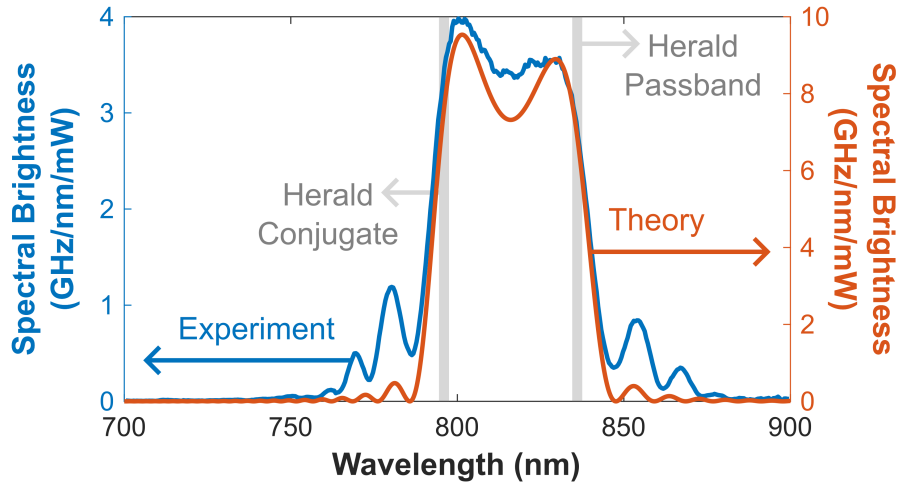


Figure 7.3: Measured (left axis) and theoretical (right axis) brightness of Down-converter 1. The relevant wavelengths for pumping Down-converter 2 and heralding CSPDC are highlighted as well.

Only the photons in the vicinity of 796.1 nm are useful for CSPDC (shaded regions of Figure 7.3), we estimate that about 10% of the bandwidth produced by Down-converter 1 can effectively pump Down-converter 2. At this wavelength the brightness is 3.5 GHz/nm/mW, slightly below the peak brightness experimentally observed (4.0 GHz/nm/mW), and approximately 40% of the value that would be theoretically expected. The device is operating with a slight detuning from optimal phase matching due to the Fabry-Perot resonances of the waveguide arising from the nearly parallel facets, which produce oscillations in the transmission spectrum of the pump. We have chosen to operate at a maximum of one of these fringes to ensure the largest coupling and lowest susceptibility to drift from slight changes in chip temperature. The discrepancy in theory and experiment could be caused by variations in the thin-film thickness, which are the most likely cause for the minor

differences in the shapes of the theoretical and experimental spectra. Another cause could be an overestimation of the on-chip power, which we calculated assuming a 4.7 dB (34%) coupling efficiency from free space to the waveguide (half of the total 10.2 dB transmission experimentally measured when accounting for 0.9 dB of propagation loss). This analysis implies equal input and output coupling efficiencies, though it is more likely for the input coupling to be worse than the output coupling due to mode matching considerations. Overall, the order of magnitude agreement between theory and experiment suggests a nearly ideal first down-converter.

The discrepancy between theory and experiment for the brightness of Down-converter 2 is 65%, similar in magnitude to that seen in Down-converter 1. A brightness of 0.22 GHz/nm/mW is measured from 1535-1565 nm, assuming a 45% coupling efficiency at the 796 nm pump. At the time of this writing, the spectrum of SPDC generated by Down-converter 2 has yet to be measured. If the spectrum is similar in shape to that simulated in Figure 7.2, an efficiency of 210 GHz/mW would be expected, equivalent to a per-photon conversion efficiency of 4×10^{-5} .

7.4 Results

Photons of the correct wavelength from Down-converter 1 are expected to produce granddaughter photons in Down-converter 2 with a low but measurable probability. The experiment shown in Figure 7.4 is designed to experimentally measure signatures of CPSDC, namely coincidences between the 836 nm herald daughter photon and either of the two granddaughter photons. The device is pumped at 407.751 nm, with the wavelength of the laser stabilized to the pm-level. SPDC from Down-converter 1 and CSPDC from Down-converter 2 are collected with high efficiency ($\approx 50\%$) using an aspheric lens. The daughter and granddaughter photons are separated with a shortpass dichroic filter. The granddaughter photons are further filtered with two 1300 nm longpass filters before being coupled to a graded index multimode fiber (OM1) and detected with the InGaAs SPAD. The SPDC produced by Down-converter 1 is filtered with an angle-tuned narrow bandpass filter, discarding all photons outside of a 4 nm range centered at 836 nm. This filter ensures that the daughter photons which are detected have the highest probability of heralding the granddaughter photons. Two additional longpass filters at 700 nm and 808 nm suppress any residual pump photons before multimode fiber coupling and detection with the Si SPAD. A time tagger (PicoQuant PicoHarp 300) measures coincidence histograms between the two SPADs. During the experiments a photodiode records the amount of free space pump power in the experiment using the reflection from

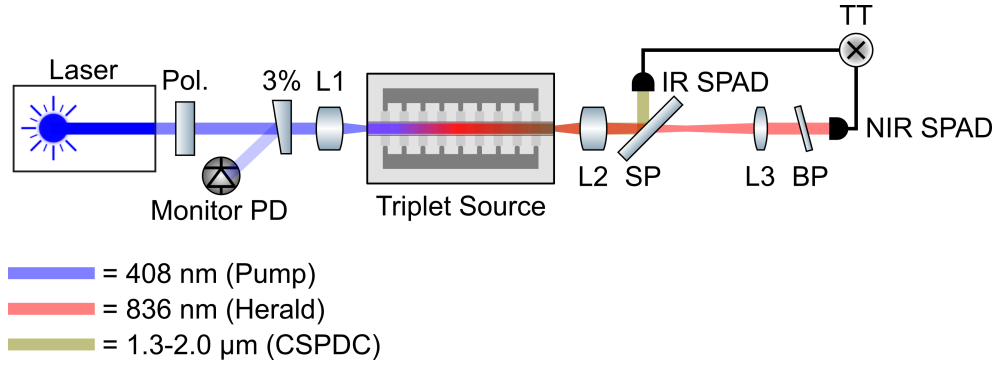


Figure 7.4: Simplified experimental setup used to measure CSPDC generation efficiency. For clarity, a half wave plate and shortpass filter ($\lambda = 500$ nm) on the pump is not shown, in addition to longpass filters in front of the NIR and IR SPAD fiber couplers and all mirrors. Abbreviations: Pol.: polarizer, 3%: 3% pickoff wedge, PD: photodiode, L1, L2: aspheric lens, SP: dichroic shortpass ($\lambda = 1180$ nm), L3: achromatic doublet, BP: angle-tuned bandpass ($\lambda = 836$ nm), TT: time tagger.

an uncoated wedge. Coincidence histograms are collected over 1 minute intervals, followed by a measurement of the SPAD detection rates over a 10 second interval. Data is then recorded to a computer over a 19 hour experiment, corresponding to 16 hours of histogram data.

Figure 7.5 shows a histogram recorded by the experiment shown in Figure 7.4, with a clear coincidence peak rising above the accidental background at 73.5 ns (SNR = 7). A programmable delay of 60 ns between the NIR and IR SPAD timing signals has been applied within the time tagger, with the remaining 13.5 ns offset occurring due to differences in discriminator lag within the two different SPADs. In this experiment the pump power on-chip is estimated to be 188 nW, yielding a coincidence rate of 0.20(3) Hz when the histogram is integrated over a 3.3 ns window and accidentals are subtracted. Taking into account the probabilities that a daughter or granddaughter photon produced in the waveguide are ultimately detected (13.8% and 6.0%, respectively), an ultrahigh triplet production efficiency of 130 ± 20 kHz/mW is inferred. In this experiment the singles rate of the herald detector is 300 kcps, which implies a conversion efficiency of a (heraldable) daughter photon into granddaughter photons to be approximately 10^{-5} , very well in line with the estimated efficiency of the second down-converter when the finite acceptance bandwidth of the source and the limited wavelength detection range of the SPADs (≈ 1300 -1600 nm) are accounted for.

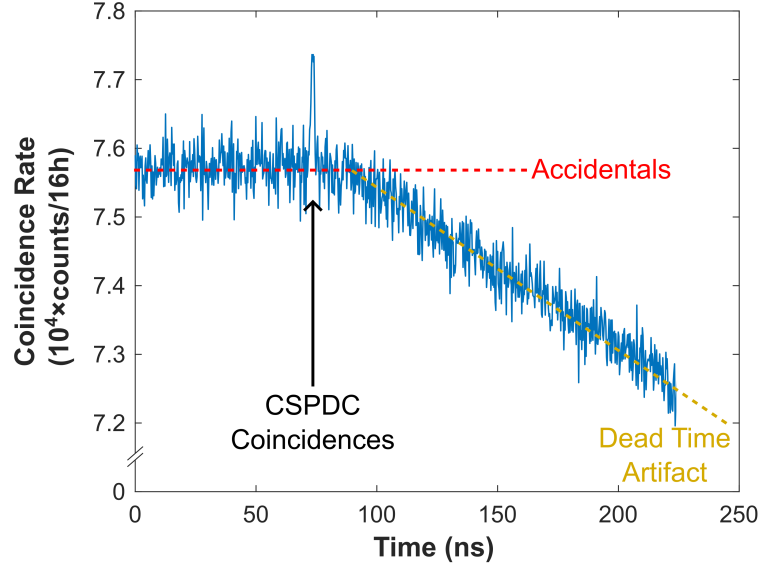


Figure 7.5: Coincidence histogram recorded over 16 hours without accidental subtraction. The histogrammer resolution is 4 ps, with the data post-processed into 256 ps bins. Lines are drawn as a guide to the eye. A decrease in coincidences after ≈ 90 ns is observed due to the dead time of the histogrammer channels.

Further evidence that the coincidences measured in the experiment are due to CSPDC is provided in Figures 7.6 and 7.7. Here, the experiment is repeated when the angle of the heralding bandpass is stepped, changing the center wavelength of the filter. This causes the wavelength of the photons conjugate to the herald to fall outside of the acceptance bandwidth of Down-converter 2, reducing the likelihood of detecting a daughter-granddaughter pair. Figure 7.6 shows zoomed in views of the histograms with accidentals subtracted, the coincidence peak at 73.5 ns clearly disappears into the noise floor for the most extreme heralding wavelengths. The data are then processed to determine the probability that a detection event of the NIR SPAD successfully heralds a coincidence event with the IR SPAD, which accounts for any differences in pump powers and singles rates among the different experiments. This effect is what causes differences in the noise levels of each histogram of Figure 7.6. As shown in Figure 7.7, the heralding probability closely tracks with the acceptance spectrum of Down-converter 2 as expected.

While the actual rate of triplet generation efficiency in our experiment is very efficient compared to previous experiments, long integration times were required to accurately determine the triplet rate due to a high level of background at the wavelengths of the IR SPAD. While the estimated count rate at the IR SPAD due to CSPDC photons is 1.4 cps, the measured count rate is 17 kcps. The origin of these

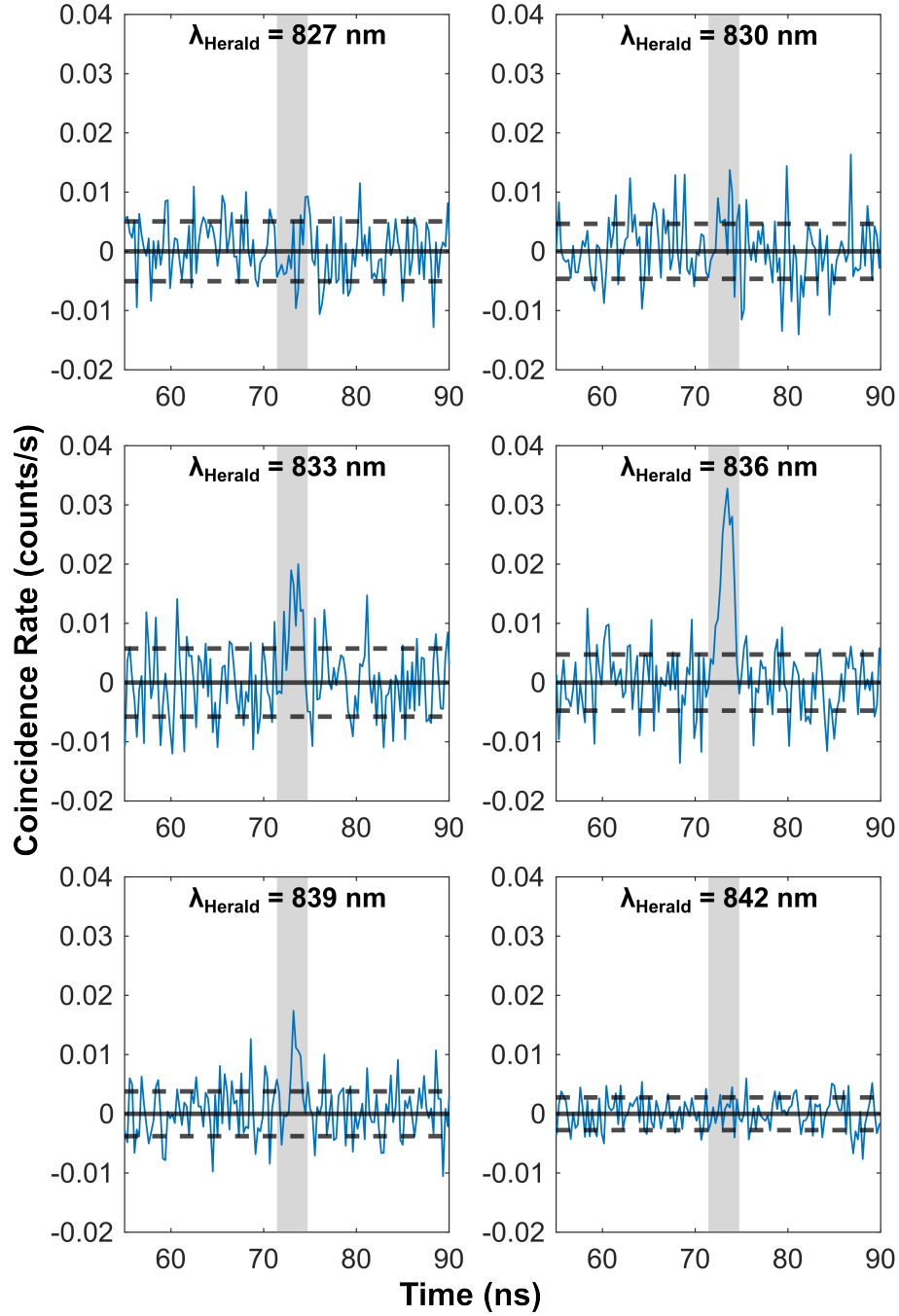


Figure 7.6: Accidental-subtracted coincidence histograms at six different heralding wavelengths. Highlighted regions in gray show the time bins used for integrating coincidences, and dotted lines show the 1σ uncertainties of the accidental floor. The center wavelength of the heralding bandpass filter is shown for each plot. Due to the $\approx 4 \text{ nm}$ bandwidth, each scan has some wavelength overlap with its neighbors.

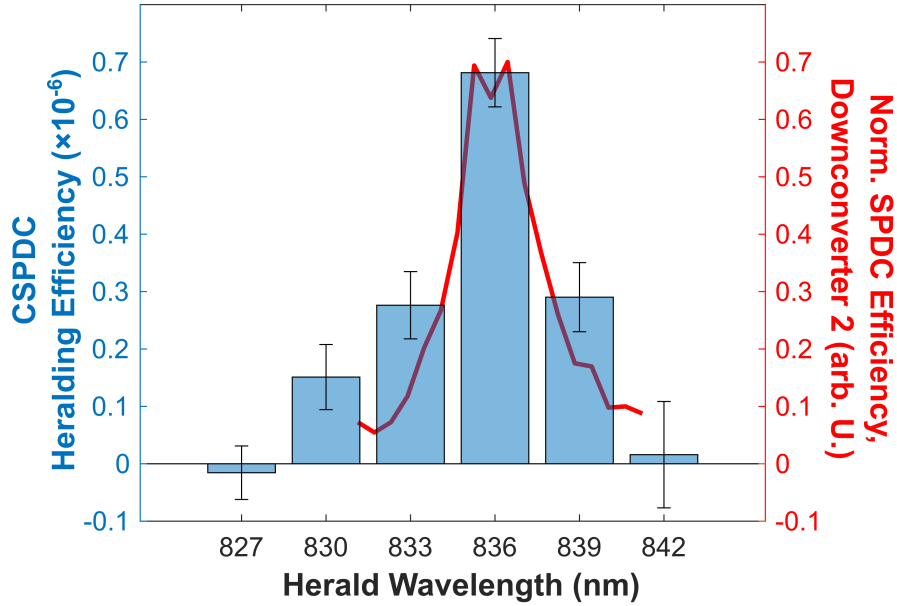


Figure 7.7: Heralding probabilities of CSPDC events, as described in main text (blue bars, left axis). Also shown is the relative efficiency of Down-converter 2 at 1550 nm for different pump wavelengths, converted to conjugate wavelengths according to energy conservation (red line, right axis).

uncorrelated counts is likely from nondegenerate SPDC of the pump, producing a visible signal and IR idler photon pair. Figure 7.8 shows the spectrum produced by the device in the visible region. As shown in the contour plot of Figure 7.8a, many peaks are present and depend on the horizontal position of the input coupler. Figure 7.8b shows the spectrum recorded when the coupler is centered on the waveguide (white dotted line of 7.8a). A single peak at 570 nm is visible, which would correspond to idler partners at 1440 nm that are readily detected by the IR SPADs used here. More peaks could be possible with longer integration. The modes involved in the SPDC, as well as the effective poling period producing that causes the SPDC, have yet to be determined. The pattern of nodes and antinodes for each of the peaks shown in Figure 7.8a suggests that many different pump modes can be phase matched, and these have been labeled to the right of the figure. Unfortunately, the peak most likely to cause issues in the experiment appears to be from the TE₀ pump mode. Fixing this issue will necessitate a filter between the down-converters. If the emission originates from Down-converter 1, a shortpass filter that cuts off below 1300 nm will prevent these photons from interfering with the CSPDC of the second down-converter. If the emission originates from Down-converter 2, a longpass filter that cuts off above 450 nm will be used to prevent the production of

the spurious SPDC in the first place. A potentially simpler alternative would be to use a notch interference filter in free space after the device to block these photons from reaching the IR SPADs, at the expense of losing some CSPDC. A final strategy could be to change the waveguide geometry to shift the SPDC peaks away from the spectral region of the IR SPADs.

7.5 Discussion

Compared to CPSDC experiments that used two separate down-converters, and therefore incur losses in the coupling to and from the separate waveguides, the probability of transferring photons in this device is limited only by the propagation loss of the waveguide. Losses as low as 6 dB/m have been shown at 637 nm, though on waveguides without periodic poling (which tends to introduce additional propagation loss due to corrugations) [33]. The other comparable figure of merit is the efficiency of the second down-converter. While TFLN waveguides exhibit significantly larger per-length efficiencies, very long diffused waveguides are possible. Most of the comparable CSPDC literature has used 30 mm long diffused waveguides to achieve efficiencies on the order of $10^{-5} - 10^{-6}$, efficiencies which have only been matched on TFLN in one example [23]. One drawback however is that long devices exhibit small acceptance bandwidths, limiting the effective efficiency of the first down-converter. Table 7.2 gives the relevant metrics of comparable experiments in comparison to ours.

Ref.	$\eta_{1,2}$	η_{DC2}	$\eta_{1,2} \times \eta_{DC2}$	Efficiency (Hz/mW)
[10]	0.3	1×10^{-5}	2.7×10^{-6}	1.8*
[11]	0.3	1×10^{-5}	2.7×10^{-6}	0.06*
[12]	0.5	7×10^{-6}	4×10^{-6}	0.17*
[13]	1×10^{-3} *	1×10^{-6}	1×10^{-9} *	2.5
[14]	≈ 1	3×10^{-7}	3×10^{-7}	810
[15]	0.5	7×10^{-6}	4×10^{-6}	0.15*
[16]	0.3*	1×10^{-6}	3×10^{-7}	0.03*
[17]	0.18*	1×10^{-6}	2×10^{-7}	1.2*
This work	≈ 1	1×10^{-5}	1×10^{-5}	1.3×10^5

Table 7.1: Summary of relevant metrics of comparable CPSDC experiments. Values that were not directly given and were indirectly calculated are indicated with *. All publications on this list use long large-area PPLN waveguides for the second down-converter. $\eta_{1,2}$: Transmission efficiency from Down-converter 1 to Down-converter 2, η_{DC2} : Down-converter 2 per-photon efficiency.

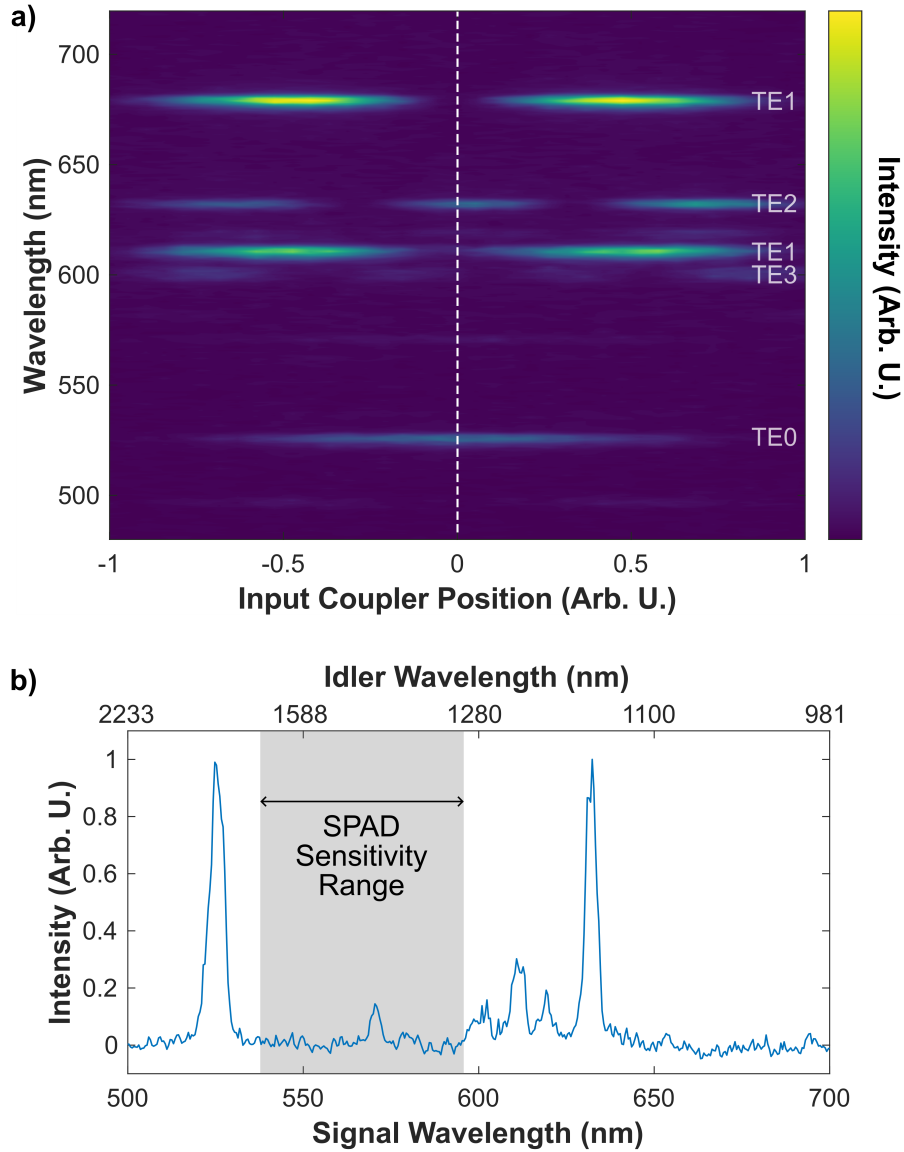


Figure 7.8: Visible spectrum of device when pumped at 408.5 nm and a temperature of 55°C. (a) Spectra measured at different horizontal locations of the input coupler with arbitrary scaling. The dotted white line at $x = 0$ denotes the approximate center of the waveguide. (b) Lineout of the spectrum measured at the center of the waveguide. The bottom wavelength axis is the wavelength axis of the spectrometer, the top wavelength axis has been calculated for nondegenerate SPDC conserving energy with the pump wavelength.

Increasing the practical detection rate requires increasing the efficiency of the second down-converter. Adapted poling to combat index variations of the 3.5 mm devices shown here could potentially reach the theoretical performance of such devices, but would only represent a modest 35% improvement [34]. Longer down-converters could be used instead, which will certainly require adapted poling since index variations become more severe over longer distances. A potential solution based on a meandering waveguide is shown in Figure 7.9, where the efficiency of the second down-converter scales with the number of meanders, but will ultimately be limited by propagation losses of the 796 nm daughter photon. Alternatively, an approach that uses a resonator to circulate the 796 nm daughter photon many times through the same Down-converter 2 could be very promising, and is shown in Figure 7.9b. Here, the finesse of the resonator determines the effective number of round trips and therefore the enhancement over a single-pass source. Embedding the first down-converter inside the resonator ensures that the 796 nm daughters will circulate automatically, with their spectrum consisting of a comb of wavelengths resonant with the cavity [35]. If the first down-converter lies outside of the cavity, as would occur with separated SPDC sources, only a small fraction of the daughter photons could be coupled to the cavity. The primary difficulty of such a device will be to reduce the loss and to engineer the cavity couplers so that only one of the daughter photons resonates and the other can be efficiently extracted. Straight waveguides with high reflectors, either implemented as Bragg gratings or dielectric coatings on the facet, could be used for a more spectrally selective response instead [36].

7.6 Conclusion

A fully integrated source of photon triplets using CSPDC has been produced using the TFLN platform. Compared to previous demonstrations which have used long periodically poled diffused waveguides, our device is able to execute the second down-conversion step with comparable efficiency (10^{-5} conversion probability) and minimal loss between down-converters. By using two highly efficient SPDC sources on the same waveguide, the triplet generation efficiency has been improved by 5 orders of magnitude over experiments using two physically separate sources. With an appropriate method to filter the SPDC directly produced at telecom wavelengths, this device is a step towards high triplet generation rates with few accidentals.

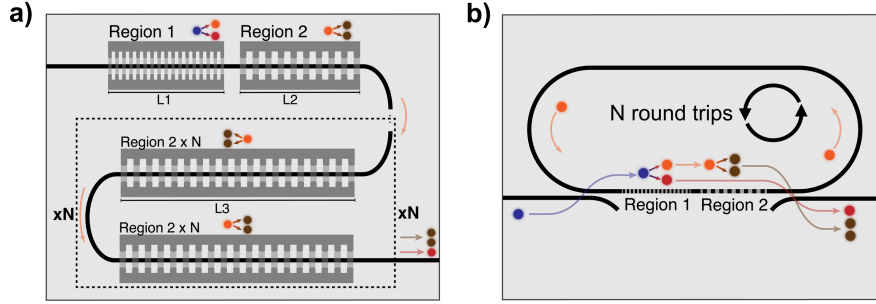


Figure 7.9: Potential future devices to increase the efficiency of the second down-converter. (a) N -fold improvement in down-conversion efficiency by increasing the length of the down-converter by a factor of N . Straight waveguides on long TFLN dies could be used, or a waveguide could be meandered many times on a smaller footprint as shown. (b) N -fold improvement in down-conversion efficiency by recycling the daughter photons N times in a cavity surrounding Down-converter 2.

7.7 Methods

Similar to Chapter 5, a free space end-fire coupling setup has been used to minimize fluorescence from the near-UV pump wavelengths and for convenience of working over a wide wavelength range for the CSPDC experiments (400-1700 nm). All experiments use high-NA aspheric lenses for the single-wavelength input coupling. Except for the actual CSPDC experiments, an aluminum reflective objective (NA = 0.5) was used for collecting light from the waveguide without chromatic aberration. The central obscuration of the objective introduces significant loss to the output ($\approx 35\%$ transmission relative to an asphere). For this reason, an aspheric lens with a broadband AR coating (NA = 0.52) is used for the CSPDC experiment shown in Figure 7.4. Due to chromatic aberration at 836 nm the herald photons are focused approximately 5 cm after the asphere, and need to be collimated by a second plano-convex lens ($f = 100$ mm).

The setup is pumped with a single-frequency CW Ti:Sapphire laser on a separate optical table, the wavelength of which is corrected for long term drifts with a wavemeter. The laser is frequency doubled with a BBO crystal, filtered with two OD 5 shortpass filters, and then spatially filtered with a single mode polarization maintaining fiber which delivers the pump to the chip table. Any fluorescence produced in the fiber is suppressed with an additional shortpass filter. A polarizer and half wave plate then produce a linear polarization state aligned to the waveguide crystal axis. The collimated beam ($1/e^2 \phi = 1$ mm) is focused to an estimated 775 nm spot size at the waveguide by the 1.5 mm asphere. For experiments where

the second down-converter is pumped directly, a similar setup is used to deliver the first harmonic of the laser to the table followed by spectral and polarization conditioning.

The chip studied here is maintained at a temperature of 25 °C by a crystal oven. Over 150 waveguides are present with varying top widths and poling periods. The specific waveguide studied was chosen for its high transmission and SPDC spectrum with few sidelobes indicating relatively low thickness variations. Total transmissions of 8.5 dB and 10.2 dB are measured at 800 nm and 405 nm, respectively, suggesting high coupling efficiencies and low propagation losses. Fabry-Perot measurements and images of the waveguide scatter are currently being conducted to get the most accurate estimate of input coupling and propagation loss [37]. As of the time of this writing, only the loss at 407 nm has been estimated (to be at least 0.9 dB/cm), using the camera-based method described in Chapter 6.

All characterization measurements on the waveguide output are conducted with filters suppressing the pump by at least an OD of 10. The SPADs and EMICCD all use multimode fibers for light delivery. Due to the single spatial mode output of the waveguide SPDC, high fiber coupling efficiencies (85-90%) are routinely measured, limited mainly by the reflectivity of the coupling optics and fiber facets. The NIR SPAD(s) (Laser Components Count 10) have a quantum efficiency of approximately 50% at 836 nm. The IR SPADs have a detection efficiency measured to be 20% at 1550 nm, determined in a measurement with respect to a calibrated photodiode. A similar measurement over a wider wavelength range is in progress, which will be necessary to determine the probability that a given broadband granddaughter photon is detected. Spectral measurements of Down-converter 1 have been conducted with a grating spectrometer with an EMICCD detector. The wavelength axis of the spectrometer is corrected with respect to the more accurate wavemeter over the bandwidth of the Down-converter 1 SPDC (725-850 nm). The relative sensitivity of the spectrometer has also been corrected with respect to a calibrated compact grating spectrometer using a fiber coupled thermal lamp. Spectral measurements of the second down-converter will be conducted with a scanning grating optical spectrum analyzer, sensitive from 700-1700 nm. The previous device was measured in this way without the need for any spectral corrections when a single mode optical fiber (SMF-28) was used for delivery.

Brightness measurements can be accurately conducted without knowledge of the SPAD efficiencies or the individual transmission of chip output and downstream

component. Here, we use the fact that the SPDC is always produced in pairs exhibiting energy conservation with respect to the pump. Pairs are split with a 50:50 beamsplitter in free space and sent to two different SPADs, one of which acts as a herald for the detector which will be used in the brightness measurement. A bandpass at the conjugate wavelength of the desired wavelength for brightness measurements is placed in front of the herald SPAD. A coincidence circuit then measures the rate of heralding events and the rate of coincidence events. Such a measurement then gives the probability that a coincidence is recorded given that the herald detector fires, which is equal to the probability that a photon is measured given that its partner is present (when dark counts and dead time corrections are applied). For example, a bandpass filter centered at 796 nm was used to infer that the detection probability of 836 nm photons is 13.8%, which includes all sources of loss and detector inefficiency. Similar measurements were conducted on a different waveguide to determine a detection probability of 6.0% for the Down-converter 2 SPDC photons at 1550 nm. Both of these measurements suggest high collection efficiencies ($\approx 50\%$) for photons from the waveguide when the other losses are taken into account. The brightness can then be determined by inserting a bandpass filter at the desired wavelength in front of the now "calibrated" SPAD and measuring the singles rate. The effective bandwidth (equivalent to the spectral width of a perfectly flat-topped filter) is then used to determine the per-nm brightness of the source. Critical to these measurements is that the output of the setup remains the same between experiments, and that the variation in detector performance is small over the range of the filter bandwidth. Filter bandwidths of 10 nm, 4 nm, and 30 nm were used for measurements at 796 nm, 836 nm, and 1550 nm, respectively. The detection probabilities determined here were also used for estimating the triplet performance of the CSPDC process.

The CSPDC experiments were challenging due to the high level of background ($\approx 12,000:1$) of spurious photons relative to granddaughter photons produced through CPSDC. While coincidence detection allows the correlated detection events to be separated from the uncorrelated background events, the probability of detecting an accidental still dominates the probability of detecting a coincidence from CPSDC in our experiments. This necessitated long integration times (> 15 hours) to obtain reasonable signal to noise, even though a CPSDC coincidence is measured every 5 seconds. To determine uncertainties in the coincidence rate due to CPSDC, we need to know the uncertainty of the coincidence rate over the detection window, in addition to the accidental rate over this same window. The uncertainties in the

accidentals were determined by measuring the mean and standard deviation in the coincidence rate per bin over 0-60 ns, which is in the region of the histogram where artifacts due to the histogrammer dead time are not present. The accidental rate uncertainty over the window was then scaled by $\sqrt{N}$, where N is the number of bins in the range (14 bins of 256 ps duration here). The uncertainty in the total number of coincidences in the window was calculated using standard Poissonian statistics, $\sigma = \sqrt{RT}$, where σ is the uncertainty, R is the coincidence rate, and T is the integration time of the experiment. The uncertainty in the coincidence rate of true coincidences is then determined by adding these uncertainties in quadrature.

Running long experiments without a way to correct for chip coupling drifts necessitated a stable experiment. The chip coupling setup is located on an optical table with air bearings to minimize vibrations, and experiments were conducted overnight when foot traffic in the room is minimized. A cardboard box around the setup reduces stray light, air currents, and temperature fluctuations. The stages housing the input and output lenses have been found to be very stable over long periods of time, but the chip position has been found to drift over hour long time scales. One important source of drift is the cable connected to the crystal oven, which should be clamped to the table without introducing too much strain in the connector. Locking the chip stages with set screws and waiting several hours has been found to minimize drift to a level acceptable for the experiments done here (see Figure 7.10). Future setups could be made even more stable using dovetail stages and clamping the chip to the setup using clips similar to the stages used on electron beam lithography tools. Students from the Marandi group at Caltech have mentioned that the room temperature can also have a significant impact on chip alignment. It would be interesting to measure the temperature stability of our room to verify this. While the alignment of the chip input needs to be stable to the ≈ 10 nm and ≈ 10 μ rad level, the alignment of the output is much more forgiving if multimode fibers are used, so long as all optical components are rigidly mounted to the table.

A table of best estimates for the device parameters are given in Table 7.2. This table also indicates the measurements that have yet to be completed to fully determine the device parameters, such as the poling duty cycle, and propagation losses at the daughter and granddaughter wavelengths.

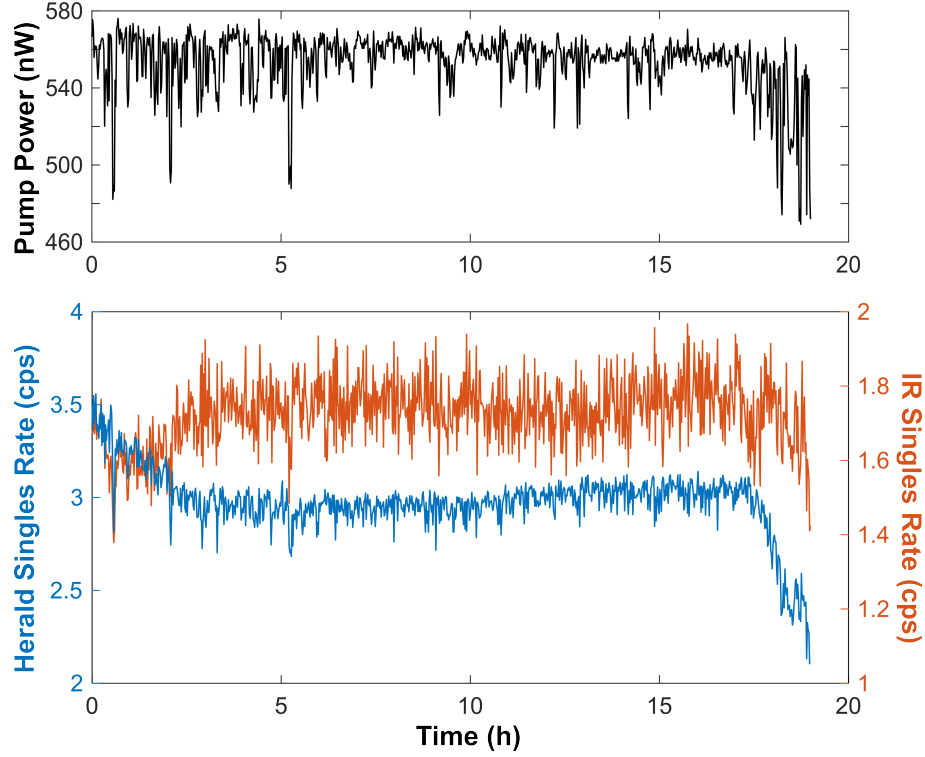


Figure 7.10: Stability of the CSPDC experiment over time, showing the singles counts at the NIR and IR detectors in comparison to the pump power in the experiment. Drifts in the chip coupling of $\approx 15\%$ are seen in the first few hours, as evidenced by the NIR count rate. Drifts in the IR count rate are not as obvious because multiple pump modes are capable of generating IR photons through non-degenerate SPDC.

Parameter	Experimental Estimate	Theoretical Estimate
Top Width	2.120 μm	—
Film Thickness	0.6109 μm	—
Etch Depth	0.520 μm	—
Sidewall Angle	64 $^{\circ}$	—
Poling Duty Cycle, DC1	*	—
Poling Duty Cycle, DC2	*	—
Propagation Loss, 408 nm	> 0.9 dB/cm	—
Propagation Loss, 796 nm	*	—
Propagation Loss, 1592 nm	*	—
Facet Reflectivity, 796 nm	—	17%
Facet Reflectivity, 1592 nm	—	17%
Input Coupling, 408 nm	34%	—
Input Coupling, 796 nm	45%	—
Output Coupling, 796 nm	46%	—
Output Coupling, 1592 nm	48%	—
Brightness, 796 nm	3.1×10^9 Hz/mW/nm	10.0×10^9 Hz/mW/nm
Brightness, 1592 nm	2.2×10^8 Hz/mW/nm	3.4×10^8 Hz/mW/nm
Efficiency, DC1	200 GHz/mW	401 GHz/mW
Efficiency, DC2	*	208 GHz/mW
Acceptance Bandwidth, DC2	3.3 nm	3.6 nm
Detection Probability, 836 nm	13.8%	—
Detection Probability, 1550 nm	6.0%	—
Triplet Efficiency	1.3×10^5 Hz/mW	*

Table 7.2: Summary of measured and estimated parameters for determining triplet efficiency. Relevant values that have yet to be obtained experimentally are denoted by *.

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Appendix A

SUPPLEMENTARY INFORMATION FOR FLUORESCENCE LIFETIME SPECTROSCOPY WITH ENTANGLED PHOTONS

A.1 Select optical properties of ICG

Solvent	Peak absorption/emission wavelength (nm)	$\varepsilon \text{ cm}^{-1} \text{ mol}^{-1}$ at λ_{max}	Φ
Methanol	784/809	221,000	0.09
Ethanol	787/811	167,000	0.11
DMSO	794/817	170,000	0.12

Table A.1: Select optical properties of ICG in methanol, ethanol, and DMSO from Ref. [1].

A.2 Confirmation of fluorescence

While the results presented in the main text of the chapter suggest that the coincidences observed with the sample present originate from fluorescence due to the good agreement between the observed histograms and fits, a control experiment as additional evidence was performed to rule out the role of scatter from the excitation beam. Additionally, a blank scan was performed, where the dye solution was replaced with only methanol. Figure A.1 displays this histogram, as well as a side-by-side comparison of the histograms observed with and without the dye. The lack of an obvious coincidence peak suggests that the SPDC flux is sufficiently filtered from the fluorescence detector, and that the coincidences observed in the experiment originated from fluorescence of the sample.

A.3 Experimental stability and background

Over the course of the 14-16 hour scans presented in Fig. 3.3, minimal drift or sample degradation was observed. Figure A.2 shows the singles and coincidence count rates over the course of the experiment. Coincidence count rates were obtained by summing all coincidence counts between 24 and 34 nanoseconds and subtracting the product of accidentals per bin and the number of bins in this window. The accidental rate per bin was obtained by averaging the number of coincidences observed from 50 to 70 ns, far from the coincidence peak. While a slight decrease in the heralding channel (Channel 0) is observed in the DMSO data over time likely due to drift in the alignment, this change in intensity is about 1% of the original value.

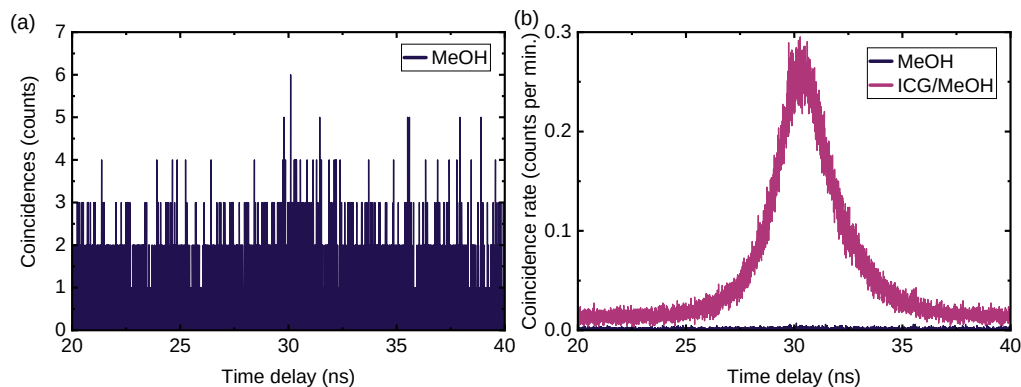


Figure A.1: Coincidence histograms of pure methanol and methanol/indocyanine solutions. (a) Coincidence histogram from methanol blank experiment. (b) Coincidence rates for blank methanol and ICG/methanol solutions.

The singles rate in the fluorescence arm (Channel 1) as well as the coincidence rate appear to remain steady over time. While ICG is known to exhibit degradation over time due to a number of factors, we do not observe a loss in coincidence counts likely because the sample is exposed to low light levels, and the sealed cuvette containing the dye had minimal headspace. The observed fluctuations in the coincidence data is not due to technical noise, but rather the Poissonian statistics of a shot-noise limited system, as the variance of the observed rates is nearly equivalent to the mean of the rate (Table A.2).

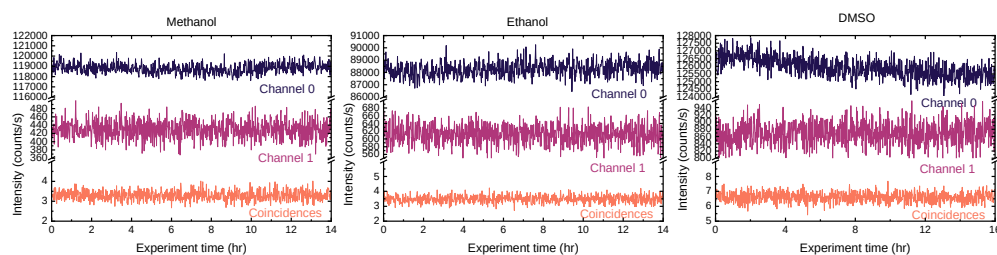


Figure A.2: Count rates in Channel 0 (reference photons), Channel 1 (fluorescence photons), and coincidences from 100 μ M ICG in methanol, ethanol, and DMSO experiment over the course of the scan.

The background of the experiments presented here are low, but some stray light is likely still present. From the blank experiment, the singles rate at the fluorescence detector was 28 ± 5 counts per second, slightly higher than the specified dark count rate of the detectors at 10 counts per second. Regardless, the fluorescence counts

Parameter	Mean rate (counts per second)	Rate variance (counts/second) ²
Heralding singles	12600	39300
Fluorescent singles	870	880
Raw coincidences	8.3	8.0
Accidental coincidences	0.78	0.77
True coincidences	7.5	8.7

Table A.2: Count rate means and variances demonstrating nearly shot-noise limited statistics.

observed during experiments with dye are substantially higher, suggesting that these counts are mostly fluorescence and not background.

A.4 Lifetime fits with residuals

Fits of the raw histograms are shown in Fig. A.3 on a logarithmic scale to show the accuracy of the fit extending to the tails of the coincidence peaks over several decades of intensity.

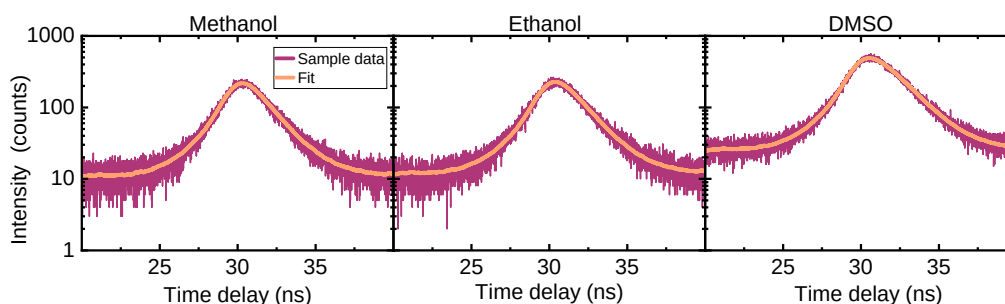


Figure A.3: Raw coincidence data and fits for ICG in methanol (left), ethanol (center), and DMSO (right) on a logarithmic scale.

The weighted residuals are shown in Fig. A.4, the lack of obvious trends in the data suggest that the model used for fitting the data is reasonable. Here, the residuals are weighted by the inverse square of the fit value at each timepoint, as the uncertainty of the counts is proportional to this value for Poissonian data.

A.5 Fitting algorithm

The fits presented in this work were performed in a custom Matlab program using the iterative reconvolution technique. First, the accidentals present in the IRF, as obtained by averaging the histogram coincidence counts from 50-70 ns, were subtracted from the raw data, and the data were truncated to a 20-40 ns window to reduce the amount of baseline present in the fit. The resulting true coincidence curve

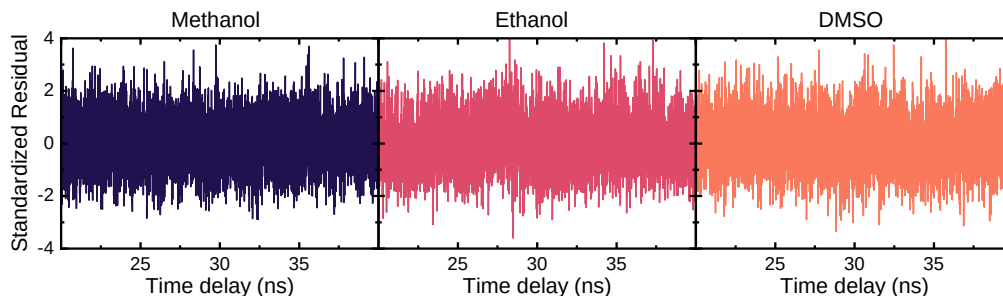


Figure A.4: Weighted residuals of the fits from Fig. A.3.

was then scaled so that the sum of counts over the IRF was unity. The experimental data from each sample were also truncated to a 20–40 ns window. The accidental counts were not subtracted from the sample coincidence curve, as these were treated as a fit parameter. The accidental data was also normalized so that the sum of counts was equal to unity. The sample response model functions were of the form:

$$R(t_i) = c(e^{-t_i/\tau} + A) \quad (\text{A.1})$$

where τ , the fluorescence lifetime, and A , a factor accounting for accidentals, are the fit parameters. The constant c is used to normalize the area of the sample response to unity. The normalization in all three cases is necessary because the convolved response of two functions has an area equal to the product of the areas of the original functions. The experiment response function was calculated as a discrete convolution of the sample response and the IRF, truncated to the length of the experimental data, and normalized to an area of one. Then, a trust-region nonlinear regression algorithm was performed to estimate the parameters τ and A that minimize the sum of squared errors between the experimental data and the fit.

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Appendix B

SUPPLEMENTARY INFORMATION FOR THE WAVEGUIDE SOURCE OF VISIBLE AND NEAR-INFRARED ENTANGLED PHOTON PAIRS

This appendix chapter serves as supplemental information for Chapter 5 . Here we outline the background theory for simulating SPDC in waveguides. Additional details of the broadband oscillator characterization, coincidence raw data and detection probabilities, multimode pump theory, and theoretical Michelson interferogram are also presented here.

B.1 SPDC theoretical calculations

The theory of parametric down-conversion in waveguides is well established. Here, the equations used in the simulations of the main text are reviewed. We consider a strong, undepleted pump wave at frequency ω_p , stimulating the production of a signal photon with frequency ω_s and idler photon with frequency $\omega_i = (\omega_p - \omega_s)$. From B.1, the rate of down-conversion W is given by [1]:

$$\frac{dW}{d\omega_s} = \frac{d_{\text{eff}}^2 P_p \omega_s \omega_i}{\pi \epsilon_0 c^3 n_p n_s n_i A_{\text{eff}}} \frac{L^2}{A_{\text{eff}}} \text{sinc}^2 \left(\frac{\Delta k L}{2} \right) \quad (\text{B.1})$$

where d_{eff} is the effective nonlinear coefficient of the interaction, P_p is the power of the pump, ϵ_0 is the vacuum permittivity, c is the speed of light, and $n_{p,s,i}$ are the respective effective refractive of the modes. The momentum-mismatch Δk is

$$\Delta k = k_p - k_s - k_i - k_{QPM} \quad (\text{B.2})$$

where $k_{p,s,i}$ are the respective propagation constants of the modes and k_{QPM} is the wavevector due to quasi-phase-matching. k_{QPM} and d_{eff} both take the order of the phase-matching m into account, which is unity for the device used in this work:

$$k_{QPM} = \frac{2\pi m}{\Lambda} \quad (\text{B.3})$$

$$d_{\text{eff}} = \frac{2d}{\pi m}. \quad (\text{B.4})$$

Here Λ is the poling period and d is the nonlinear tensor element of the interaction. The largest nonlinear tensor element of lithium niobate is the d_{33} element; the remaining elements are approximately an order of magnitude or more smaller. To maximize the SPDC efficiency in this work, we utilized $d_{33} = 28.4$ pm/V (for 5% MgO-doped lithium niobate at 852 nm) [2] to obtain $d_{\text{eff}} = 18.1$ pm/V through Equation B.4.

In the waveguide, the effective area A_{eff} is given as a mode overlap calculation of the three interacting waves mediated through the nonlinear tensor of the crystal[3]. For the device used in this work, the effective area can be simplified as:

$$A_{\text{eff}} = \frac{A_p A_s A_i}{\sqrt{\frac{n_p n_s n_i A_p A_s A_i}{8 Z_0^3 P^3} \left| \iint \bar{d}_{33} E_s^* E_i^* E_p dx dy \right|^2}}. \quad (\text{B.5})$$

Here $A_{p,s,i}$ are the effective areas of each mode, Z_0 is the free space impedance, P is the power in each mode (normalized to 1 W here), $\bar{d}_{33}$ is the normalized d_{33} nonlinear tensor element, and $E_{p,s,i}$ are the electric field profiles of each mode. The mode profiles are evaluated in Lumerical MODE to find that $A_{\text{eff}} = 0.7 \mu\text{m}^2$.

To modify B.1 to accommodate a multi-frequency pump, the pump power P_p can be replaced with the spectral intensity of the pump $P(\omega_p)$ and integrated over all frequencies:

$$\frac{dW}{d\omega_s} = \int \frac{d_{\text{eff}}^2 \omega_s \omega_i}{\pi \epsilon_0 c^3 n_p n_s n_i} \frac{L^2}{A_{\text{eff}}} \text{sinc}^2 \left(\frac{\Delta k L}{2} \right) P(\omega_p) d\omega_p. \quad (\text{B.6})$$

For the simulations given in the main text, the pump spectral intensity is approximated as a Gaussian distribution (Equation B.7) with a mean μ and standard deviation σ such that the FWHM is 0.8 nm, as measured experimentally, and is normalized to an total intensity of 1 mW.

$$P(\omega_p) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\omega_p - \mu}{\sigma} \right)^2 \right] \quad (\text{B.7})$$

Because the signal and idler are indistinguishable, and thus both detected in our experiment, the expected total number of counts at a given frequency for the spectrally resolved experiments (Figure 5.3 of the main text) of is:

$$\frac{dW}{d\omega} = \left. \frac{dW}{d\omega} \right|_{\omega=\omega_s} + \left. \frac{dW}{d\omega} \right|_{\omega=\omega_p-\omega_s}. \quad (\text{B.8})$$

Finally, it is useful to have an equation for the probability of jointly detecting a signal photon at ω_s and an idler at ω_i . This distribution is typically called the Joint Spectral Intensity (JSI) and is obtained from B.6 by replacing the pump frequency by sum of the signal and idler frequencies:

$$\text{JSI}(\omega_s, \omega_i) = C \frac{\omega_s \omega_i}{n_p n_s n_i} \text{sinc}^2 \left(\frac{\Delta k L}{2} \right) P(\omega_s + \omega_i). \quad (\text{B.9})$$

Here, C is a normalization constant chosen such that

$$\iint \text{JSI}(\omega_s, \omega_i) d\omega_s d\omega_i \equiv 1. \quad (\text{B.10})$$

Thus, the JSI represents a two-dimensional probability distribution, and is symmetric with respect to exchange of the variables ω_s and ω_i .

B.2 Broadband oscillator characterization

A broadband oscillator (Coherent Vitara) is used to test the phase matching and simulate the SPDC transmission of the device. In this characterization scheme, the oscillator output is sent into a single mode polarization-maintaining tapered fiber (OZ Optics Ltd.) to couple into the waveguide. A second identical tapered fiber collects the output of the waveguide and is sent into a grating spectrometer and electron-multiplying intensified camera, similarly to Figure 5.2b of the main text. The spectrum of the oscillator (Figure B.1a), although broad with an 85 nm FWHM bandwidth, aids in finding phase-matching over a wide wavelength range and also mimics the spread of the SPDC spectrum (main text Figure 5.3c) for transmission measurements.

The phase matching of the device was tested through second harmonic generation (SHG), which should have similar phase matching to SPDC. Several sets of electrodes with varied poling periods near the computationally predicted value ($2.03 \mu\text{m}$, Section 2 of the main text) were fabricated to compensate for possible fabrication imperfections that could disrupt phase matching. Three waveguides with different poling periods were tested to verify that the SHG was phase matched (Figure B.1b). The waveguide chosen for further measurements from the SHG measurements has a poling period of $1.988 \mu\text{m}$. This poling period had a computationally predicted

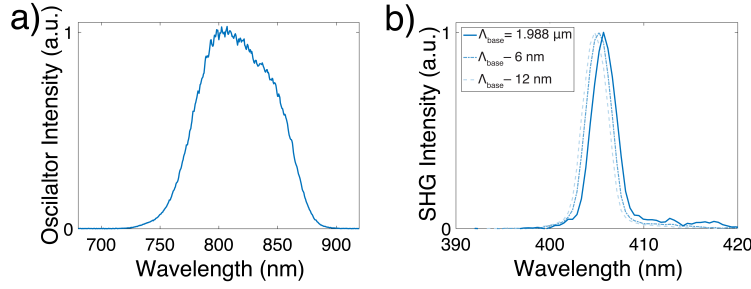


Figure B.1: Oscillator and second harmonic generation spectra. (a) Spectrum of the broadband oscillator. (b) Second harmonic generation spectra corresponding to waveguides with three different poling periods. The waveguide corresponding to the spectrum denoted with $\Lambda_{\text{base}} = 1.988 \mu\text{m}$ was chosen for the measurements in the main text.

degenerate wavelength of 403 nm, which is under 3 nm from the experimentally measured degenerate wavelength of 405.7 nm. This <3 nm discrepancy is likely due to variations in the thin film thickness or etch depth.

The transmission spectra of these same three devices show an approximately 5 dB dip in transmittance near 755 nm (Figure B.2a-b), which corresponds with the dip in the SPDC spectra seen in Figure 3a of the main text. These spectra suggest that the source of loss occurs downstream of the SPDC pair production and the loss occurs on-chip as opposed to in free space. If the dip was caused by a discontinuity in the phase-matching, a similar dip would be seen in the conjugate spectrum of the idler photon near 874 nm. Since different optical paths are used for the transmission spectra in Figure B.2 and the SPDC spectra in Figure 5.3 of the main text, the loss occurs on-chip. It is also clear that this loss is systematic, as it is observed in all three waveguides tested. While slab mode leakage can be an issue for the TE waveguide modes in TFLN, this mechanism is unlikely because the transmission recovers at lower wavelengths, whereas slab mode leakage is expected to occur for all wavelengths below a certain cutoff, which is not true here as the transmission and SPDC both recover below 755nm. One potential source of loss could be a mode-crossing [4] at 755 nm that transfers power from the fundamental TE mode to a higher-order mode, demonstrated by the calculated modal refractive indices in Figure B.2c. Such higher-order modes would be collected inefficiently by the aspheric lenses, which already suffer from chromatic aberrations, and the single-mode tapered fibers, which act as mode filters. Future mode-crossings could be avoided by careful selection of the waveguide top width, thickness, and etch depth.

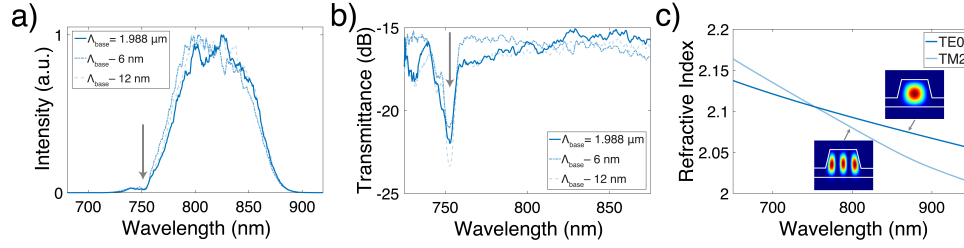


Figure B.2: Transmission spectra measured through three different waveguides in units of (a) normalized intensity and (b) transmittance in dB with respect to the oscillator spectrum from Figure B.1a. Loss at approximately 755 nm can be observed in both (a) and (b), indicated by the arrows. (c) Simulated mode refractive indices, demonstrating a mode-crossing near 755 nm between the TE0 and TM2 modes.

B.3 Single and joint detection probability

The SPADs used in this study (Laser Components COUNT-10C) exhibit a spectrally-dependent quantum efficiency with a peak at 680 nm (Figure B.3). This wavelength dependence complicates the prediction of detection probabilities due to the large SPDC bandwidth.

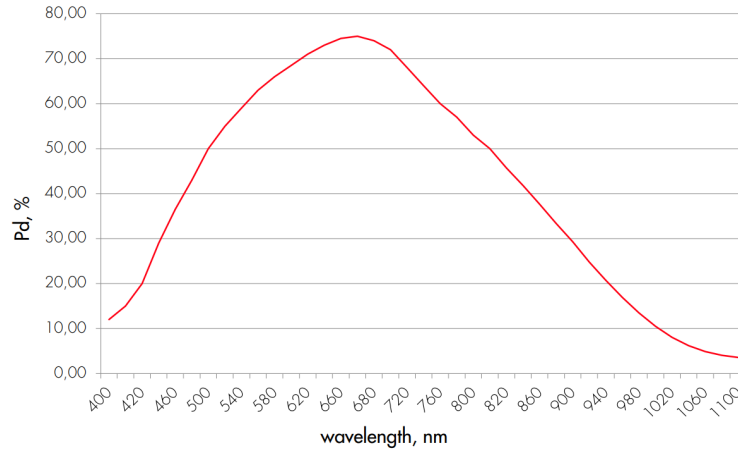


Figure B.3: Spectrally-dependent quantum efficiency $QE(\omega)$ of the SPADs used in this work, from [5].

The quantum efficiency curve from the manufacturer specifications can be interpolated to obtain a continuous quantum efficiency $QE(\omega)$, which ranges from 0 to 1. From this distribution, the probability of detecting both the signal and idler (i.e., a coincidence) is an expectation value given as:

$$\eta_{12} = \iint \text{JSI}(\omega_s, \omega_i) \text{QE}(\omega_s) \text{QE}(\omega_i) d\omega_s d\omega_i. \quad (\text{B.11})$$

The probability of detection given the presence of a single photon is also given as an expectation value. Here, we use the quantum efficiency weighted by the probability distribution of the signal photon frequency, which is obtained by integrating over all possible idler frequencies:

$$\eta_1 = \iint \text{JSI}(\omega_s, \omega_i) \text{QE}(\omega_s) d\omega_s d\omega_i. \quad (\text{B.12})$$

Given that two near-identical SPAD detectors are used, the quantum efficiency of both detectors are assumed to be equal ($\eta_1 = \eta_2$). As a result, only η_1 appears in the following equations, as well as Equation 5.1 of the main text. These probabilities are calculated as $\eta_1 = 0.522$ and $\eta_{12} = 0.266$. In this case, $\eta_{12} \approx \eta_1^2$, which would not be generally expected given the wide range of wavelengths and large variations in the quantum efficiency. However, due to the linearity of $\text{QE}(\omega)$ in the vicinity of our experiment, an increase in the quantum efficiency of the signal photon at shorter wavelengths is balanced by the decreased probability of detecting the idler photon at longer wavelengths.

B.4 Power sweep experimental details and raw data

The raw data obtained from the power swept coincidence counting experiment are displayed in Table B.1. On-chip inferred powers are determined by multiplying the free-space laser power by the 10.2 dB transmission of the input coupler. For each power, the singles rate and a coincidence histogram are recorded. The mean singles rates of the two detectors are calculated from 10 consecutive measurements with a 1 s integration time. Each coincidence histogram is recorded with a 100 s integration time. Raw coincidence rates are calculated by integrating the number of coincidence counts in a 9.5 ns interval at the coincidence peak. This coincidence interval is centered at a time delay of 29.43 ns, which accounts for the electronic delay applied within the timing circuit and any mismatches in the electrical cabling from the detectors. Accidental counts are integrated from a time delay of 50 ns until the end of the histogram recording, 262.14 ns. This large range is chosen to minimize the uncertainty in the determination of the accidental rate at low pump powers. To be consistent with the coincidence rates, the accidental rates are scaled to give the count rate over a 9.5 ns window, which are reported in Table B.1. True coincidences are calculated by subtracting the inferred accidental rate from the

raw coincidence rate. The coincidence to accidental ratio (CAR), defined as the ratio of true coincidences to accidentals, is also tabulated. The uncertainty in the singles rate is given as the standard deviation of the 10 singles measurements. The uncertainties in the raw coincidence and accidental rates are reported as standard deviations calculated assuming Poisson statistics. Here, the standard deviation in the total counts N is calculated as $\sqrt{N}$. The uncertainties in the count rates are then scaled by the integration times. Uncertainties in the true count rates and the CAR are determined using standard error propagation.

B.5 Power scaling equations

The scaling of the single and coincidence detection rates are useful for estimating the device efficiency and transmission efficiency of pairs through the system. A simple model is used to estimate these quantities, similar to Ref. [6]. First, the rate of singles counts at detectors 1 and 2 (S_1, S_2) are modeled as:

$$S_1(P) = 2EP\mu_1 R\eta_1 + \text{Dark}_1 \quad (\text{B.13})$$

$$S_2(P) = 2EP\mu_2 T\eta_1 + \text{Dark}_2 \quad (\text{B.14})$$

where E is the pair production efficiency, P is the on-chip power, $\mu_{1,2}$ are the transmission of the path to detectors 1 and 2, R and T are the beamsplitter reflection and transmission probabilities, η_1 is the average detector quantum efficiency given by Equation B.12, and $\text{Dark}_{1,2}$ are the dark counts of detectors 1 and 2. This can be interpreted as $2EP$ photons being produced by the device (the factor of 2 is from the two photons produced in each SPDC pair), then suffering losses of $\mu_1 R\eta_1$ or $\mu_2 T\eta_1$ in the setup before being detected by the respective SPADs.

Similarly, the rate of coincidences ($S_{cc}(P)$), which requires the detection of both photons, is:

$$S_{cc}(P) = EP\mu_1\mu_2 2RT\eta_{12} \quad (\text{B.15})$$

where the factor of $2RT$ accounts for the two possible paths through the beamsplitter that result in a coincidence.

The slopes of Equations B.13-B.15 with respect to power, as shown below in Equations B.16-B.18, can be experimentally measured:

On-chip Power (nW)	Singles Rate Detector 1 (cps)	Singles Rate Detector 2 (cps)	Raw Coincidence Rate (cps)	Accidental Rate (cps)	True Coincidence Rate (cps)	CAR
0.096	$(8.1 \pm 0.5) \times 10^2$	$(7.4 \pm 0.4) \times 10^2$	$(3.10 \pm 0.06) \times 10^1$	$(3.8 \pm 0.4) \times 10^{-2}$	$(3.09 \pm 0.06) \times 10^1$	$(8.2 \pm 0.9) \times 10^2$
0.18	$(2.3 \pm 0.3) \times 10^3$	$(2.2 \pm 0.3) \times 10^3$	$(8.81 \pm 0.09) \times 10^1$	$(1.32 \pm 0.08) \times 10^{-1}$	$(8.80 \pm 0.09) \times 10^1$	$(6.7 \pm 0.4) \times 10^2$
0.34	$(5.20 \pm 0.06) \times 10^3$	$(4.84 \pm 0.6) \times 10^3$	$(2.17 \pm 0.01) \times 10^2$	$(2.3 \pm 0.1) \times 10^{-1}$	$(2.17 \pm 0.01) \times 10^2$	$(9.5 \pm 0.4) \times 10^2$
0.64	$(1.049 \pm 0.005) \times 10^4$	$(9.72 \pm 0.07) \times 10^3$	$(4.40 \pm 0.02) \times 10^2$	$(9.4 \pm 0.2) \times 10^{-1}$	$(4.39 \pm 0.02) \times 10^2$	$(4.7 \pm 0.1) \times 10^2$
1.2	$(1.83 \pm 0.02) \times 10^4$	$(1.68 \pm 0.01) \times 10^4$	$(7.55 \pm 0.03) \times 10^2$	$(2.86 \pm 0.04) \times 10^0$	$(7.52 \pm 0.03) \times 10^2$	$(2.63 \pm 0.03) \times 10^2$
2.3	$(3.71 \pm 0.03) \times 10^4$	$(3.42 \pm 0.01) \times 10^4$	$(1.498 \pm 0.004) \times 10^3$	$(1.15 \pm 0.07) \times 10^1$	$(1.486 \pm 0.004) \times 10^3$	$(1.288 \pm 0.009) \times 10^2$
4.3	$(6.73 \pm 0.03) \times 10^4$	$(6.15 \pm 0.03) \times 10^4$	$(2.641 \pm 0.005) \times 10^3$	$(3.76 \pm 0.1) \times 10^1$	$(2.604 \pm 0.005) \times 10^3$	$(6.92 \pm 0.03) \times 10^1$
8.1	$(1.368 \pm 0.006) \times 10^5$	$(1.260 \pm 0.006) \times 10^5$	$(5.221 \pm 0.007) \times 10^3$	$(1.547 \pm 0.002) \times 10^2$	$(5.067 \pm 0.007) \times 10^3$	$(3.276 \pm 0.007) \times 10^1$
15	$(2.535 \pm 0.009) \times 10^5$	$(2.329 \pm 0.008) \times 10^5$	$(9.50 \pm 0.01) \times 10^3$	$(5.295 \pm 0.005) \times 10^2$	$(8.96 \pm 0.01) \times 10^3$	$(1.692 \pm 0.002) \times 10^1$
29	$(4.771 \pm 0.006) \times 10^5$	$(4.337 \pm 0.007) \times 10^5$	$(1.752 \pm 0.001) \times 10^4$	$(1.833 \pm 0.001) \times 10^3$	$(1.569 \pm 0.001) \times 10^4$	$(8.561 \pm 0.008) \times 10^0$

Table B.1: Raw coincidence data used to calculate the pair generation efficiency of the device. Note that the true coincidence rate and the two singles rates are plotted against on-chip power in Figure 5.5b-c of the main text.

$$m_1 = 2E\mu_1 R\eta_1 \quad (\text{B.16})$$

$$m_2 = 2E\mu_2 T\eta_1 \quad (\text{B.17})$$

$$m_{cc} = 2E\mu_1\mu_2 RT\eta_{12}. \quad (\text{B.18})$$

These equations are then rearranged to solve for the efficiency and loss of the setup, given that R , T , η_1 , and η_{12} are known.

$$E = \frac{m_1 m_2}{m_{cc}} \frac{\eta_{12}}{2\eta_1^2} \quad (\text{B.19})$$

$$\mu_1 = \frac{m_{cc}}{m_2} \frac{\eta_1}{R\eta_{12}} \quad (\text{B.20})$$

$$\mu_2 = \frac{m_{cc}}{m_1} \frac{\eta_1}{T\eta_{12}} \quad (\text{B.21})$$

The parameters measured in the experiment as well as the parameters necessary for calculating the device loss are displayed in Table B.2.

Parameter	Value	Description
m_1	$(1.670 \pm 0.005) \times 10^{10}$ photons/s/mW	Detector 1 Singles Rate
m_2	$(1.521 \pm 0.007) \times 10^{10}$ photons/s/mW	Detector 2 Singles Rate
m_{cc}	$(5.5 \pm 0.1) \times 10^8$ pairs/s/mW	Coincidence Rate
R	$47 \pm 10\%$	Beamsplitter Reflectance
T	$47 \pm 10\%$	Beamsplitter Transmittance
η_1	$52 \pm 5\%$	Average Quantum Efficiency
η_{12}	$27 \pm 4\%$	Average Joint Quantum Efficiency
E	$(2.3 \pm 0.5) \times 10^{11}$ pairs/s/mW	Device Efficiency
μ_1	$15 \pm 4\%$	Transmission to Detector 1
μ_2	$14 \pm 4\%$	Transmission to Detector 2

Table B.2: Parameters used to determine SPDC device efficiency. Uncertainties of the photon count rates are obtained from standard error of a linear fit. Beamsplitter and detector uncertainties are obtained from the manufacturers. Derived parameter (E , μ_1 , μ_2) uncertainties are obtained through standard uncertainty propagation.

B.6 Pump linewidth comparison

The measured SPDC efficiency of the device $((2.3 \pm 0.5) \times 10^{11}$ pairs/s/mW) is on par with the efficiencies of telecom regime TFLN sources and an order of magnitude or greater than the efficiencies of other visible SPDC sources, as shown in Figure 6 of the main text. However, this efficiency is significantly lowered by the bandwidth of the pump laser used in this work, which was experimentally measured to be 0.8 nm FWHM.

As shown in Figure B.4a, the calculated SPDC efficiency for a single frequency pump demonstrates a strong peak at the degenerate wavelength. The SPDC from a multimode pump can be understood as a convolution of the pump lineshape with Figure B.4a. For the same total input power, the spread in the spectral density of a multimode pump results in only a fraction of the total power overlapping with this peak in the efficiency, while a single frequency pump can be tuned to the maximum efficiency. Therefore, as shown in Figure B.4b, the maximum brightness of the SPDC spectrum from a single frequency pump is an order of magnitude higher than the spectrum for a multimode pump for the same input power.

To further quantify the enhanced device performance with a single frequency pump, the theoretical efficiencies of SPDC from single frequency pump and a multimode pump can be calculated. Approximating the pump as a Gaussian distribution with a FWHM of 0.8 nm (Equation B.7), theoretical efficiency of 2.66×10^{11} pairs/s/mW is obtained using Equation B.6. However, using Equation B.1, the theoretical efficiency using a single frequency pump is calculated to be 1.28×10^{12} pairs/s/mW. Therefore, approximately an order of magnitude of enhancement is expected by using a single frequency pump over a multimode pump.

B.7 Michelson interferogram

Two-photon interference in a Michelson interferometer has been demonstrated in several previous works. Equation 16 from Ref. [7] is used here to predict the shape of the experimentally measured interferogram shown in Figure 5a of the main text:

$$R_{cc}(\tau) = \iint d\omega_s d\omega_p \text{JSI}(\omega_s, \omega_p - \omega_s) [1 + \cos(\omega_s \tau)] [1 + \cos((\omega_p - \omega_s) \tau)]. \quad (\text{B.22})$$

Here τ is the path-length difference of the interferometer, which is twice the physical difference in the path lengths due to the reflection at the translating mirror. The cosine terms in Equation B.22 can be expanded as:

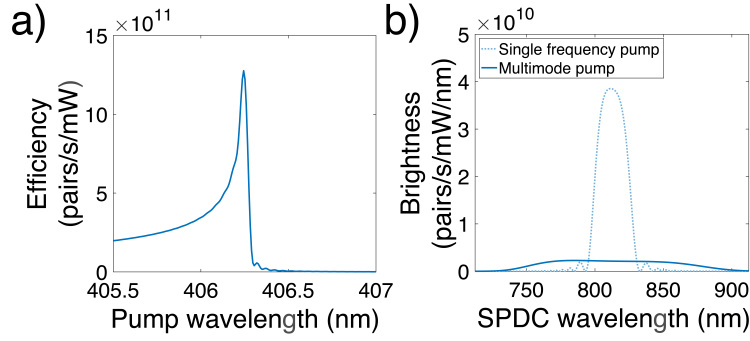


Figure B.4: Predicted effect of pump linewidth on observed spectra and efficiency. (a) Theoretical single-frequency SPDC efficiency while varying the pump wavelength. The lack of symmetry in the efficiency can be explained by non-degenerate phase-matching at wavelengths shorter than the degenerate wavelength (here designed to be 406.25 nm), as shown by Figure 3 of the main text. (b) Theoretical SPDC spectra for a single frequency pump and a broadband pump, both with 1 mW of power.

$$[1 + \cos(\omega_s \tau)][1 + \cos((\omega_p - \omega_s) \tau)] = 1 + \cos(\omega_s \tau) + \cos((\omega_p - \omega_s) \tau) + \frac{1}{2} \cos(\omega_p \tau) + \frac{1}{2} \cos((\omega_p - 2\omega_s) \tau) \quad (\text{B.23})$$

At large delays, the cosine terms dependent on ω_s average to zero, and the interference is dominated by $1 + \cos(\omega_p \tau)$, explaining the oscillation at the pump frequency with a theoretical 50% visibility. The predicted inteferogram from Equation B.22 can be seen in Figure 5b of the main text.

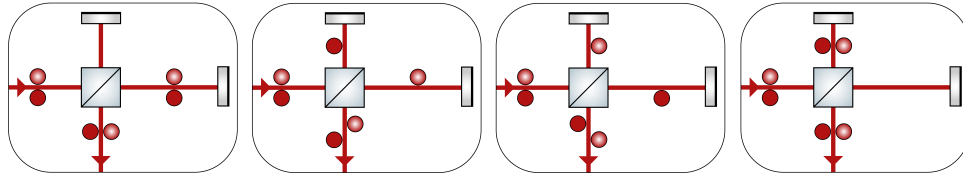


Figure B.5: Schematic of the four unique paths a photon pair can take through the Michelson interferometer.

To assess the visibility at large delays, a subset of the interferogram (Figure 5d of the main text) was selected. A sinusoid of the following form was fit to the data with a nonlinear least squares algorithm:

$$A + B \cos(\omega \tau) + C \sin(\omega \tau). \quad (\text{B.24})$$

The parameters derived from the fit are $A = 665 \pm 5$ cps, $B = 186 \pm 7$ cps, $C = 219 \pm 7$ cps, and $\omega = 4.13 \pm 0.02$ rad/fs. The visibility of the signal, which is defined as $\frac{[\max(R_{cc}(\tau)) - \min(R_{cc}(\tau))]}{\max(R_{cc}(\tau))}$, is given in terms of the fit parameters as:

$$V = \frac{\sqrt{B^2 + C^2}}{A}. \quad (\text{B.25})$$

The uncertainty of the visibility was given by uncertainty propagation of the standard errors of each of the fit parameters. Reporting the visibility through the fit gives a more conservative estimate of the visibility compared to the raw data.

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Appendix C

SUPPLEMENTARY INFORMATION FOR EVANESCENT SENSING ON THIN-FILM LITHIUM NIOBATE

C.1 Electric field simulations

All simulations were performed in Lumerical MODE. The confinement factor provides a measure of the modal confinement in the PMMA/C153 sample layer and can be expressed as [1]:

$$\Gamma = \frac{n_g}{\text{Re}\{n_{\text{clad}}\}} \frac{\iint_{\text{clad}} \varepsilon |\mathbf{E}|^2 dx dy}{\iint_{-\infty}^{+\infty} \varepsilon |\mathbf{E}|^2 dx dy}. \quad (\text{C.1})$$

The confinement factor varies with the waveguide geometry, particularly the thin film thickness (Figure C.1a).

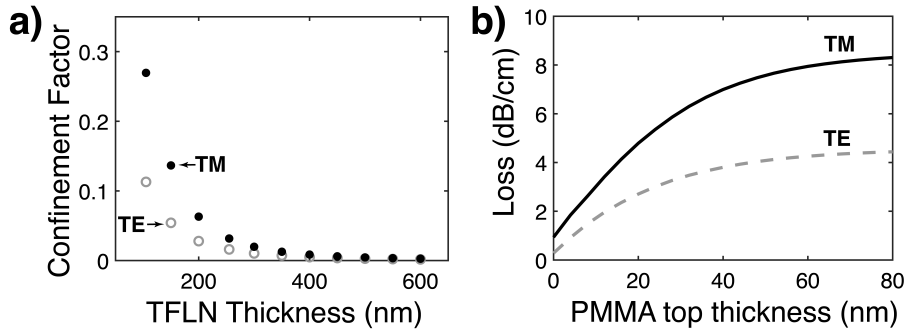


Figure C.1: Predicted performance of the TE and TM modes for evanescent sensing. (a) Confinement factor Γ against TFLN thickness with a fixed waveguide aspect ratio and conformal 60 nm PMMA/C153 layer. (b) Theoretically predicted loss of the TE and TM modes with varying PMMA thickness on the top of the waveguide with the waveguide profile in Figure 6.1b of the main text.

To simulate the absorption of Coumarin-153, the dye loss can be incorporated into the simulated material parameters, where the refractive index of the PMMA/C153 is represented as $n' = n + i\kappa$. The real component of the refractive index is the index of bulk PMMA at the excitation wavelength, or $n = 1.5$. The imaginary index κ incorporates the properties and concentration of Coumarin-153:

$$\kappa = \frac{\alpha \lambda_0}{4\pi} = 2.303 \frac{\varepsilon c \lambda_0}{4\pi} = 0.000743 \quad (\text{C.2})$$

where the cross section ε is $20,000 \text{ cm}^{-1}\text{M}^{-1}$ for Coumarin-153 in toluene, the predicted dye concentration c is 5 mM based on the solution concentrations, the excitation wavelength λ_0 is 406 nm, and the factor of 2.303 comes from the change of base. Incorporating the dye loss κ in the simulation material parameters, the theoretical propagation loss due to the presence of the dye molecules is 4.4 dB/cm for the TE mode and 7.2 dB/cm for the TM mode with a 60 nm conformal PMMA/C153 film thickness. As discussed in the main text, these predicted losses do not match with the experimentally measured losses of 0.67 dB/cm for TE and 0.95 dB/cm for TM. The discrepancy in the predicted and measured losses likely arises from the unknown PMMA/C153 film quality, particularly the film profile near the waveguides. Consistent with this uncertainty, confocal fluorescence microscopy indicates that the PMMA/C153 layer is not uniform over the waveguide profile (Section C.3), particularly the top surface of the waveguides. Varying the PMMA/C153 thickness on top of the waveguides but maintaining 60 nm thickness elsewhere (Figure C.1b), the predicted losses decrease to 1.1 dB/cm for TE and 1.6 dB/cm for TM, much closer to the measured values. The losses can be further decreased by incorporating a lower C153 quantum yield, which could be the case due to the PMMA microstructure around the dye, quenching of the dye (such as self-quenching by homo-Förster resonance energy transfer), or degradation of the dye. Decreasing the quantum yield to 50% produces theoretical losses of 0.80 dB/cm for TM and 0.55 dB/cm for TE, much closer to the experimentally measured losses of 0.95 dB/cm for TM and 0.67 dB/cm for TE. The remainder of the discrepancy can be attributed to uncertainties in the dye cross section, uncertainties in the dye concentration, and potential dye aggregation.

C.2 Dye properties

UV-vis absorption spectra were recorded with a Varian Cary 500 spectrophotometer (Agilent). Fluorescence emission spectra were recorded with an RF-6000 fluorimeter (Shimadzu). Spectra were acquired with a $10 \mu\text{M}$ stock solution of C153 in dimethyl sulfoxide (DMSO), and are shown in Figure C.2.

To estimate the percentage of the fluorescence that is able to transmit through the 500 nm longpass filter $T_{\text{fluorescence}}$, the following integrals over the emission intensity $I(\lambda)$ are numerically evaluated. The limits to these integrals are determined by the wavelength range of the instrument and the filter cutoff.

$$T_{\text{fluorescence}} = \frac{\int_{500 \text{ nm}}^{928 \text{ nm}} I(\lambda) d\lambda}{\int_{405 \text{ nm}}^{928 \text{ nm}} I(\lambda) d\lambda} = 0.90 \quad (\text{C.3})$$

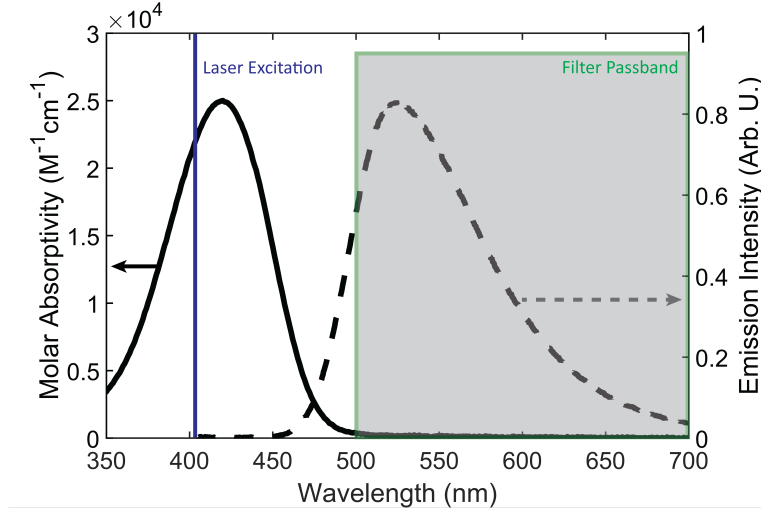


Figure C.2: Absorption and emission spectra of Coumarin-153 in DMSO with the laser excitation and filter passband wavelengths marked.

C.3 Fluorescence microscopy

Fluorescence images of the device were recorded with a commercial scanning confocal microscope (Zeiss LSM 880). The sample was excited with a 405 nm laser diode in an epifluorescence scheme with a 20x dry objective. An image of the PMMA/C153 cladded device is shown in Figure C.3a. The top-most straight waveguide is of the same dimensions as the waveguide investigated in the main text, though it is not the same waveguide due to concerns over photobleaching. A lineout of the intensity collected across the waveguide is shown in Figure C.3b. Each data point is the mean count value at each vertical pixel acquired by integrating the image in the horizontal direction, and the error bars represent one standard error of the mean, calculated from the variance in the counts at each vertical pixel. From Figure C.3b, it appears that the thickness of the PMMA film is not constant across the waveguide profile due to the strong variance in fluorescence as a function of position. Notably, the fluorescence is strongest near the etched areas of the waveguide, and lowest at the top surface of the waveguide. While the fluorescence profile could be explained by variations in the PMMA/C153 thickness, it could also be the result of differences in excitation and collection efficiencies from thin-film interference

effects. We therefore suggest that the PMMA thickness might be spatially varying, but do not attempt to make any quantitative claims.

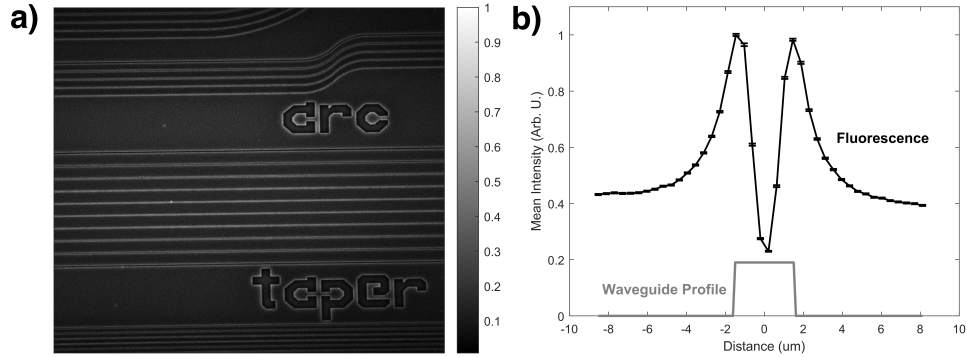


Figure C.3: Evidence for nonuniformities in PMMA film thickness due to waveguide profile. (a) Fluorescence microscope image of the PMMA/C153 film on the waveguides. (b) Lineout of the fluorescence intensity across a waveguide.

C.4 Raw data from images

The raw data from the imaging experiments are displayed in Figure C.4. Uncertainties are given as one standard error of the mean. The uncertainties from each figure are directly comparable as each experiment has the same total integration time of 5 minutes, and all images are acquired with the same digitizer gain (30 dB). The fluorescence datasets are acquired at 1 FPS with an integration time of 1 s, while the scatter datasets are acquired at 10 FPS with a 100 ms integration time to avoid saturating the camera. The uncertainty of the fluorescence data is larger than the scatter data due to the low light intensity, and is especially apparent at the end of the waveguide where the pump is most attenuated.

As discussed in the main text, the propagation loss measured from the fluorescence and the scatter shows good agreement for the TE mode (23.0 ± 0.2 dB/cm and 23.4 ± 0.9 dB/cm, respectively) but show some disagreement for the TM mode (32.5 ± 0.3 dB/cm and 37 ± 1 dB/cm, respectively), most likely due to the higher sensitivity of the TM mode to sidewall scattering and PMMA film variations. Potential reasons for the disagreement in the loss measurements of the TM mode are underestimations in the fit error or the presence of higher-order modes in the waveguide. The spatial variance in the scattering data of Figure C.4 and Figure 6.3 of the main text is larger than that of the fluorescence, most likely due to uneven distribution of scattering sites or speckle interference from the narrow laser bandwidth.

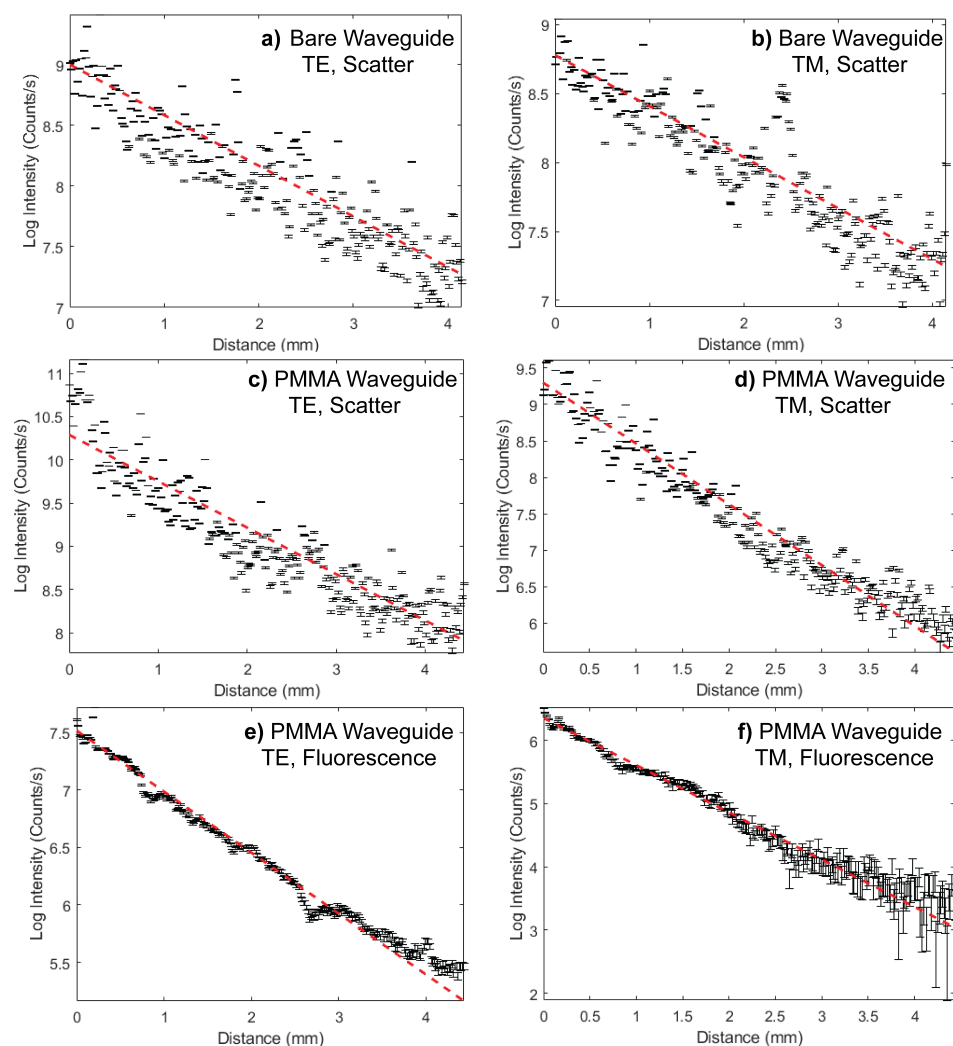


Figure C.4: Raw intensities for (a)-(b) pump scatter from the bare waveguide, (c)-(d) pump scatter from waveguide with PMMA cladding, (e)-(f) fluorescence from waveguide with PMMA cladding. Each data point represents a 17 μm section of waveguide. The red dashed line is a linear fit to the logarithmic data.

C.5 Photobleaching analysis

The incident free space power into a waveguide was increased to determine the appropriate measurement settings with minimal photobleaching. Note that a different waveguide with identical dimensions to the one presented in the main text was tested here to avoid photobleaching the dye in the main device of interest. After coupling to the TM mode of the waveguide using 5 nW of incident power, the laser was set to the desired power, and fluorescence data were recorded for 100 s, followed by a 100 s background with the laser off. This process was repeated a total of five times, with the power level increasing by a factor of 10 for each measurement. A time series of the total amount of fluorescence collected over a 4 mm section of the waveguide are displayed in Figure C.5. While it is difficult to determine if any photobleaching occurs at 10 nW or 100 nW due to the signal-to-noise of the measurement, photobleaching is apparent at 1 μ W, and increases in strength at 10 μ W and 100 μ W. A power of 100 nW was chosen for the experiments in this work to maximize signal while keeping photobleaching to a relatively low level.

C.6 Raw data from aggregated counts

Experiment	Total Count Rate in ROI (kcps)
Bare Waveguide, TE, Scatter	799.8 ± 0.3
Bare Waveguide, TM, Scatter	890.5 ± 0.3
PMMA/C153, TE, Scatter	3091 ± 1
PMMA/C153, TM, Scatter	735.9 ± 0.3
PMMA/C153, TE, Fluorescence	185.3 ± 0.1
PMMA/C153, TM, Fluorescence	43.7 ± 0.1

Table C.1: Summary of the total signal recorded for each experiment, integrated over a 4.3 mm section of the waveguide.

The total count rate over the entire device is summarized in Table C.1. Uncertainties are given as standard errors of the mean. These total counts are proportional to the amount of pump power in the ROI, in addition to the scattering and fluorescence loss rates. Since the pump power in the ROI region is dependent on the chip coupling efficiency and any losses in the edge beam region of the device, these numbers cannot be directly compared to each other.

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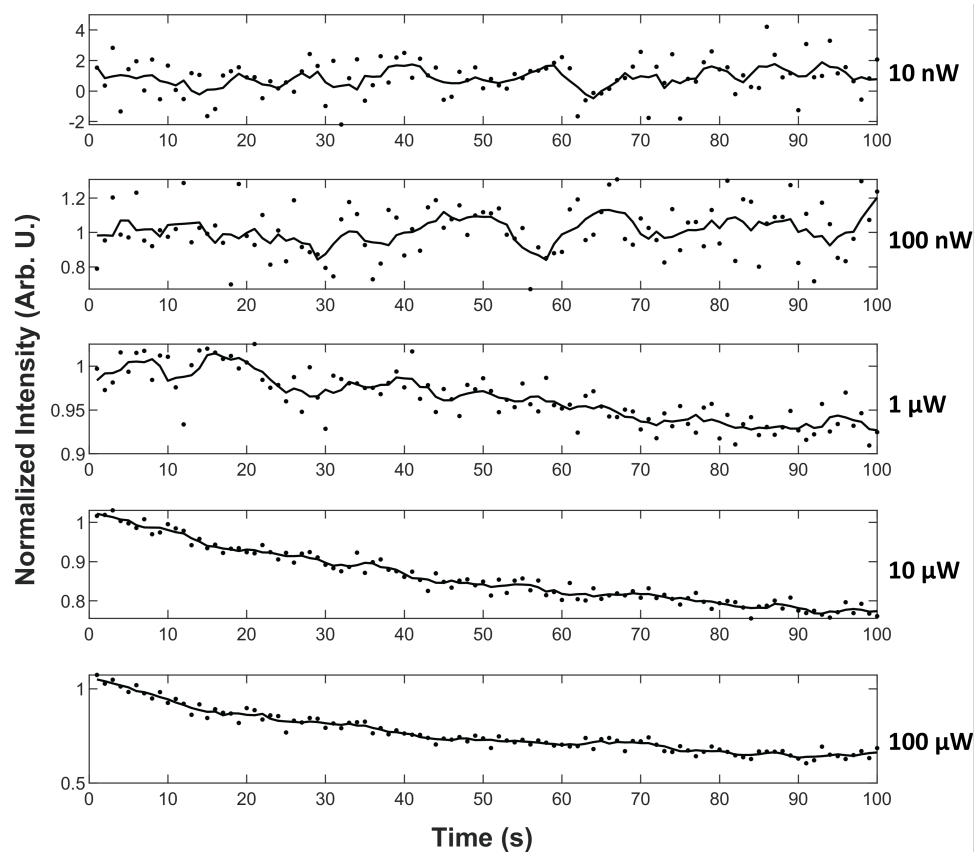


Figure C.5: Integrated fluorescence intensity over time for increasing values of free-space power. Data points show the raw intensity at each time point, and lines are a 5 s moving average. Intensities have been normalized relative to the mean intensity of the first 10 data points.

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