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Decay-Associated Fourier Spectroscopy: Visible to Shortwave Infrared Time-Resolved Photoluminescence Spectra

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Supporting Information

ABSTRACT: We describe and implement an interferometric approach to decay-associated photoluminescence spectroscopy, which we term decay-associated Fourier spectroscopy (DAFS). In DAFS, the emitted photon stream from a substrate passes through a variable path length Mach–Zehnder interferometer prior to detection and timing. The interferometer encodes spectral information in the intensity measured at each detector enabling simultaneous spectral and temporal resolution. We detail several advantages of DAFS, including wavelength-range insensitivity, drift-noise cancellation, and optical mode retention. DAFS allows us to direct the photon stream into an optical fiber, enabling the implementation of superconducting nanowire single photon detectors for energy-resolved spectroscopy in the shortwave infrared spectral window ($\lambda = 1\text{--}2\ \mu\text{m}$). We demonstrate the broad applicability of DAFS, in both the visible and shortwave infrared, using two Förster resonance energy transfer pairs: a pair operating with conventional visible wavelengths and a pair showing concurrent acquisition in the visible and the shortwave infrared regime.

INTRODUCTION

Time-correlated single photon counting (TCSPC) provides an invaluable background free method to quantify time-resolved photoluminescence (TRPL) from emitters in both ensemble and microscopic contexts. TCSPC has been extensively applied in range of disciplines, such as semiconductor physics,^{1,2} nanomaterial science,^{3,4} optoelectronic device engineering,^{5,6} photochemistry,⁷ and cellular imaging,^{8,9} and in the characterization of photoactive materials. TCSPC is typically performed using silicon single photon avalanche detectors (SPADs), which limit the range to photons with energies in the visible and near-infrared. However, many technologically relevant species luminesce in the shortwave infrared (SWIR, $1\text{--}2\ \mu\text{m}$), i.e., below the bandgap of silicon, ($E_g^{\text{Si}} = 1.1\ \text{eV}$). This spectral region includes telecom relevant semiconductor single photon emitters,^{10–12} deep tissue imaging dyes,^{13–16} and singlet oxygen,¹⁷ all of which have broad physical, chemical, and biological importance. By combining spectral and temporal resolution of the emitted photon stream we can probe complex photophysics and influence new materials development.

Typically, SWIR detection requires InGaAs photomultiplier tubes or avalanche photodiodes to sense and time photons. Yet, these detectors suffer from either low relative efficiencies, high dark count rates, or long reset times.¹⁸ Commercialized

SWIR sensitive superconducting nanowire single photon detectors (SNSPDs) have recently overcome these limitations. In an SNSPD, a photon impinges on a superconducting nanowire, creating a transient resistance that can be amplified and timed using traditional TCSPC electronics. SNSPDs detect photons with near unity quantum efficiency¹⁹ and less than 20 ps timing resolution²⁰ in the SWIR, but this method requires that the photon stream be coupled into a single or few mode optical fiber. Consequently, SNSPDs' use has been limited to telecommunication studies,²¹ quantum key distribution²² and characterization of the spectra or antibunching properties of SWIR emitters.^{12,23,24} Combining spectral resolution with TRPL using SNSPDs will greatly increase the potential applications of this exciting technology.

Spectrally resolved TRPL (commonly named decay-associated spectroscopy or DAS) quantifies the population dynamics of multiple emissive states. Separating luminescent states by photon energy provides direct insight into energy transfer among states⁴ and hot carrier dynamics² or enables new channels for multiplexed signal processing.^{25,26} In this

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manuscript, SNSPDs and silicon SPADs are implemented in concert to develop decay-associated Fourier spectroscopy (DAFS), which we use to extend DAS across the visible and SWIR. We employ a Mach–Zehnder interferometer (MZI) with TCSPC using multiple detectors to interferometrically sort and time-resolve the emitted photon stream. We outline the theory and implementation of DAFS, demonstrate the method on several Förster resonant energy transfer (FRET) emissive systems, and describe how it provides several advantages over traditional approaches to decay-associated emission spectroscopy—focusing on its application in the SWIR.

■ ANALYSIS AND RESULTS

Theory of Decay-Associated Fourier Spectroscopy.

An idealized Mach–Zehnder interferometer is illustrated in Figure 1. Photons emitted from the sample are directed

Figure 1. Schematic of a conventional Mach–Zehnder interferometer showing the propagation of the photon as a wave function from a sample, $|x\rangle$. Shown are the corresponding operations from each component, and the wave functions of each arm, and outputs produced by the MZI. The variable geometric phase delay component corresponds to our linear delay stage in our setup. BS: beamsplitter.

through a beamsplitter, and a geometric phase shift is introduced on one path. The beams then recombine at a second beamsplitter, resulting in an interference between transmitted and reflected paths. Unlike a Michelson interferometer, commonly employed in FTIR measurements, both path combinations are collected after the second beamsplitter. A typical MZI measurement introduces a sample along one interferometer arm, and the resulting phase-shift between reflected and transmitted beams changes the relative intensities in each output path. In our system, we control the phase-shift by scanning a delay stage and thus the interferometer retardation, δ , allowing us to modulate the photon's relative phase in each arm of the interferometer. Following conventions from FTIR spectroscopy, when $\delta = 0$, each path length is equal, and the beams fully interfere, resulting in the “centerburst,” i.e., the delay stage position of maximum phase coherence.

Following is a semiclassical derivation of the action of a scanning MZI on a photon emitted from a sample. We make the simplifying approximation that each emitted photon possesses a single wavevector, k , and has a normalized wave function, $|x\rangle$ (i.e., $\langle x|x\rangle = 1$).²⁷ When a 50:50 beamsplitter reflects $|x\rangle$, it induces a $\pi/2$ phase shift, $\hat{R}|x\rangle = \frac{i}{\sqrt{2}}|x\rangle$, or transmits $|x\rangle$, $\hat{T}|x\rangle = \frac{1}{\sqrt{2}}|x\rangle$. Within the reflective path, we

introduce a variable path geometric phase retardation, $\hat{\phi}$, (experimentally from a delay stage). The phase delay operator is expressed as,

$$\hat{\phi}|x\rangle = e^{i\delta k}|x\rangle \quad (1)$$

where $k = \frac{\omega}{c} = \frac{2\pi}{\lambda}$ describes the wavevector of the photon and δ is the scanned interferometer retardation. Therefore, the probability of detecting the self-entangled photon in a detector in the output path $|a\rangle$ is given by

$$P_a = \langle a|a\rangle = [\langle x|(\hat{R}\hat{T})^* + \langle x|(\hat{T}\hat{\phi}\hat{R})^*][\hat{R}\hat{T}|x\rangle + \hat{T}\hat{\phi}\hat{R}|x\rangle] \quad (2)$$

which resolves into

$$P_a = \frac{1}{2}(1 + \cos(\delta k)) \quad (3)$$

Similarly, the probability of detecting the photon in a detector in the output path $|b\rangle$ is

$$P_b = \frac{1}{2}(1 - \cos(\delta k)) \quad (4)$$

recovering the equivalent result of the purely classical electric field derivation.²⁸ Hence the idealized signal, $S_{a,b}^{ideal}(\delta)$, from a stream of identical photons in each detector is

$$S_{a,b}^{ideal}(\delta) = \dot{N}P_{a,b} = \frac{\dot{N}}{2}(1 \pm \cos(\delta k)) \quad (5)$$

where $\dot{N}$ is the rate of sample photon emission. Notice that the spectral component of the signal, $\cos(\delta k)$, from detector a will be anticorrelated to the signal from detector b while scanning across δ .

For photons with various wavelengths, if we assume photons only interfere with themselves (i.e., first order correlation only), the signal is a weighted sum of cosines

$$S_{a,b}^{ens}(\delta) = \sum_i \frac{\dot{N}_i}{2}(1 \pm \cos(\delta k_i)) \quad (6)$$

and the ideal anticorrelated signal is

$$S^{AntiCor}(\delta) = S_a^{ens}(\delta) - S_b^{ens}(\delta) = \sum_i \dot{N}_i \cos(\delta k_i) \quad (7)$$

where now $\dot{N}_i$ corresponds to the rate of photon emission of photons with wavevector, k_i . By using time correlated detection, we obtain the photon arrival time relative to laser pulse excitation time, or delay time, τ . So, eq 7 becomes

$$S^{AntiCor}(\delta, \tau) = \sum_i \dot{N}_i(\tau) \cos(\delta k_i) \quad (8)$$

By Fourier transforming $S^{AntiCor}(\delta, \tau)$ along the interferometer retardation domain, δ , we recover the distribution of photons at each corresponding wavevector at each delay time, i.e., our DA spectrum, $I(k, \tau)$.

Implementation of DAFS. We use a custom all-reflective epifluorescence spectrometer to colocalize excitation and collection. The excitation is filtered from the sample photon stream, which passes through the scanning MZI and is selectively directed toward SPADs and/or SNSPDs, as illustrated in Figure 2. We define a Mach–Zehnder interferometer as having two inputs (in this case one input is null) and two anticorrelated outputs. DAFS data are obtained by tagging photon arrival times relative to the laser synchronization pulse

Figure 2. Excitation and emission are colocalized in all-reflective off-axis parabolic epifluorescence setup. After passing through the MZI, the photons are separated, using a 700 nm hot mirror and selectively directing them to either the Si SPADs or SNSPDs.

(Hydraharp time-tagged time-resolved or TTTR mode). The signals are globally correlated to the position of the linear translation stage while it scans across the PL's coherence length, yielding a time-resolved interferogram. Each photon arrival time is histogrammed into a two-dimensional matrix with one axis representing stage position, δ' , and the other arrival time relative to the pulsed excitation laser, t (details in the Supporting Information section 1, parts a and b).

Processing DAFS Spectra. Balanced Detection. We establish how an MZI removes shared fluctuations and drift from the spectral measurement. The signal at the single photon detector with noise is

$$S_{a,b}(\delta') = \frac{\eta_{a,b}}{2} (S_{a,b}^{\text{ens}}(\delta') + S^{\text{CorNoise}}(\delta'(T))) + S_{a,b}^{\text{StatNoise}} \quad (9)$$

In eq 9, $\eta_{a,b}$ incorporates respective detector quantum efficiency and losses from the setup, and $S_{a,b}^{\text{StatNoise}}$ represents the static noise from dark counts and constant background scattered light unique to each detector. The $S^{\text{CorNoise}}(\delta'(T))$ refers to the fluctuation/drift noise, in global time, T , common to both detectors, e.g., a moving baseline observed in Figure 3a.

In the region where δ' is outside the coherence length of the photon stream, such that $S^{\text{AntiCor}}(\delta') = 0$, we express the ratio of detector signals as

$$\frac{S_a(\delta')}{S_b(\delta')} = \left(\frac{\eta_a}{\eta_b} \right) \left(\frac{(1 + S^{\text{CorNoise}}(\delta'(T))) + S_a^{\text{StatNoise}}}{(1 + S^{\text{CorNoise}}(\delta'(T))) + S_b^{\text{StatNoise}}} \right) \quad (10)$$

Hence by fitting a linear regression to the correlated data (blue dots in Figure 3b) $S_a(\delta')$ vs $S_b(\delta')$ we extract the slope, $\left(\frac{\eta_a}{\eta_b} \right)$. We define the correlated data as the shared set of points that

Figure 3. (a) Integrated raw interferometric trace from each SNSPD detector collected from a sample of colloidal PbS NC in hexanes (532 nm excitation). (b) Correlated signal (blue dots) from SNSPD a vs SNSPD b was fit with a line and its slope corresponding to $\left(\frac{\eta_a}{\eta_b} \right)$ was extracted (eq 10). We define the correlated data as the shared set of points that are within one standard deviation of the mean of each respective detector's interferogram. The rest of the points are counted as uncorrelated (red dots) and do not affect our fit. (c) Corrected anticorrelated signal as determined by eq 12. (d) PL spectrum of the colloidal PbS NC in hexanes under a 532 nm excitation obtained from the apodized and zero-padded Fourier transform of the anticorrelated signal in with Mertz correction (black solid) and without (gray dashed). The signal shows negligible chirp which accounts for the minimal difference. The red line shows the emission as obtained from a side-illuminated grating spectrometer with an InGaAs detector. The discrepancy in the peak shape/width is attributed to the hexanes absorption (blue dashed).

are within in one standard deviation of the mean of each respective detector's interferogram, $\text{Mean}[S_{a,b}(\delta')]$. Further details found in the Supporting Information.

Taking the difference of the two detectors' signals weighted by their respective efficiency terms (i.e., the slope extracted from eq 10), $\left(\frac{\eta_a}{\eta_b} \right)$, we obtain a postprocessed balanced signal. This eliminates the drift/fluctuation term, $S^{\text{CorNoise}}(\delta'(T))$:

$$\begin{aligned} S_a(\delta') - \left(\frac{\eta_a}{\eta_b} \right) S_b(\delta') \\ = S^{\text{AntiCor}}(\delta') + S_a^{\text{StatNoise}} - \left(\frac{\eta_a}{\eta_b} \right) S_b^{\text{StatNoise}} \end{aligned} \quad (11)$$

We can further eliminate the static noise terms by subtracting the mean of eq 11:

Figure 4. (a) PL spectra of CdSe NC (donor) and PIC-Cl (acceptor) as isolated and mixed solutions. In the presence of PIC-Cl the NC emission is strongly quenched while the PIC-Cl emission is enhanced. (b) Plot of the time-resolved interferogram of the CdSe NC and PIC-Cl mixed solution after application of eq 12 to balance the detectors. The left-hand panel shows the result of summing along the time delay axis to give the time-averaged interferogram. (c) DA spectrum obtained by Fourier transforming and applying the Mertz correction each delay. Spectral features corresponding to the CdSe NCs at ~ 2.15 eV (light blue) and to the PIC-Cl at ~ 1.95 eV (red). The left-hand panel gives the time-averaged PL spectrum from the Fourier transform, compared to the grating base measurement. The bottom panel shows the TRPL traces corresponding CdSe NC and PIC-Cl. (d) TRPL traces corresponding to an isolated CdSe NCs (black) and CdSe NCs PIC-Cl (blue). (e) TRPL traces corresponding to an isolated PIC-Cl solution (black) PIC-Cl in the FRET pair mixed solution obtained from the DA spectrum summing from 1.9 to 2.0 eV.

$$S(\delta') = S_a(\delta') - \left(\frac{\eta_a}{\eta_b} \right) S_b(\delta') - \text{Mean} \left[S_a(\delta') - \left(\frac{\eta_a}{\eta_b} \right) S_b(\delta') \right]_{\delta'} = \sum_i \dot{N}_i \cos(\delta k_i) \quad (12)$$

Hence, we recover eq 7's idealized anticorrelated signal as seen in Figure 3c. Uncorrelated drift/fluctuations and shot noise are still present in the signal. However, upon Fourier transforming eq 12, the uncorrelated drift/fluctuations contributions fall outside of the spectral region of interest, limiting their impact on our signal.

Interferogram Chirp/Phase Correction. The derivation of eq 5 assumes that the phase difference between the two MZI arms has no wavelength dependence given by $\hat{\phi}$. This yields a symmetric Fourier spectrum around the centerburst. However, a dispersive component in the phase delay, $\theta(k)$, can contribute an asymmetry or “chirp” (Figure 3, parts a and b), resulting in a change of the detection probability for a given k .²⁸

$$S^{\text{AntiCor}}(\delta') = \sum_i \dot{N}_i \cos(\delta k_i - \theta(k_i)) \quad (13)$$

Fourier transforming $S(\delta)$ yields a complex PL spectrum, $I(k)$:

$$I(k) = \int_{-\infty}^{\infty} S(\delta') e^{-ik\delta'} d\delta' = \text{Re}[I(k)] + i\text{Im}[I(k)] = |I(k)| e^{i\theta(k)} \quad (14)$$

To correct for this dispersive component, we employ the Mertz method from the FTIR literature, as described in the Supporting Information.²⁸ Briefly, we extract the slow moving phase, $\theta(k)$, from a subset of the data around the centerburst and use it to correct the overall DAS through the complex Euler identity. Figure 3d demonstrates the comparison between the Mertz phase corrected spectrum and the uncorrected spectrum.

Applications of DAFS. Energy transfer between two chromophores presents an ideal system to test this DAS method. FRET processes control the energy flow within many chemical or condensed phase systems,⁴ and FRET pairs are employed as implanted sensors and nanoscale rulers for studying dynamic distance fluctuations.^{29,30} First, we study a mixture of CdSe colloidal nanocrystals (NC) and pinacyanol chloride (PIC-Cl) dye. Our second sample shows the spectral breadth of the DAFS by probing emissions ranging from the visible to the SWIR with donor CdSe colloidal NCs and acceptor PbS colloidal NCs.

Visible Wavelength DAFS. To show the effectivity of the MZI DAFS in the conventional visible DAS regime, we prepared the mixed FRET solution of CdSe NC (donor) and PIC-Cl (acceptor) in dichloromethane. The linear PL spectra (Figure 4a) from a conventional grating spectrometer showed a depleted emission of the CdSe NC in the mixed solution at

2.15 eV relative to the isolated CdSe NC solution; this indicates an energy loss of the CdSe NC emissive state. Accordingly, we observe an enhanced emission in the FRET solution from the PIC-Cl at 1.95 eV in comparison to the isolated PIC-Cl solution in the mix, showing an energy transfer to the PIC-Cl. After a DAFS acquisition and analysis on the CdSe NC and PIC-Cl, we obtained the time-resolved anticorrelated signal displayed in Figure 4b. Applying the Mertz corrected Fourier transform to each time slice, we observe two spectral features in Figure 4c. The peak at 2.15 eV reflects the dynamics of the donor, CdSe NC, and the peak at 1.95 eV reflects the dynamics of the acceptor, PIC-Cl. By integrating across the spectral region for the CdSe NC (2–2.25 eV) and PIC-Cl (1.9–2.0 eV) we can resolve their respective TRPL lifetime traces. The bottom panel of Figure 4c shows similar lifetimes for both the CdSe NC and the PIC-Cl, which are consistent with a FRET process from a long-lived CdSe donor to a short-lived PIC-Cl acceptor.³¹ In comparison to the TCSPC traces taken from the isolated solutions of CdSe NC (Figure 4d) and PIC-Cl (Figure 4e), we observe diminished PL lifetimes in the CdSe NCs and increased PIC-Cl lifetimes (details of the fitting time constants can be found in the Supporting Information in Table S1). This is consistent with a FRET process, in which the CdSe NC more rapidly transfer their excited state energy to the PIC-Cl, resulting in longer overall lifetimes.^{11,31}

DAFS Spanning Visible to SWIR. To demonstrate the octave-spanning capabilities of DAFS, we show another donor–acceptor system, which requires resolving emission from 0.8 to 2.2 eV (560–1600 nm). Again, the CdSe NCs act as donors and are excited at 2.23 eV. The acceptors are PbS colloidal NCs, which emit between 0.8 and 1.1 eV. We concurrently acquire anticorrelated visible and SWIR photon streams using SPADs and SNSPDs from each output.

After processing, the 2D photon energy/lifetime histogram is shown in Figure 5. The spectrum shows features corresponding to both the CdSe NCs at 2.1 eV and PbS NCs at 1.1 eV. By integrating across the spectral region for the CdSe NC (2–2.25 eV) and PIC-Cl (1.9–2.0 eV), we can resolve their respective TRPL unique lifetime traces in the bottom panel of Figure 5. In comparison to the TCSPC traces taken from the isolated solutions of CdSe NC (Figure 4d) and PbS NC (Supporting Information, Figure S7), we observe somewhat unchanged PL lifetimes for the CdSe NC and a reduction in the PbS lifetimes (multiexponential fitting details found in the Supporting Information). This may be consistent with a FRET process, in which the CdSe NC more readily transfer their excited state energy to the PbS, resulting in a high transient excited state population, which causes faster emission.³¹ Further experiments and modeling are required to confirm the details of any possible FRET. However, this is beyond the scope of this paper, as we have successfully shown that using DAFS with SNSPDs and Si APDs allows us to measure spectrally resolved photoluminescence lifetimes from the SWIR through visible wavelengths.

DISCUSSION

We compare DAFS to conventional photon-resolved DA spectra, obtained by scanning a grating monochromator with a single pixel SPAD. In this grating-based implementation, the grating lines/mm, slit width, and path length of the spectrometer lead to a trade-off between resolution and throughput.²⁸ In most implementations, the monochromator

Figure 5. Corrected DAFS spectrum of the CdSe NC and PbS NC FRET solution. The left panel shows the time averaged spectrum. The bottom panel shows the time traces corresponding to the spectral components PbS NCs and CdSe NCs respectively taken by summing the spectral slices in the appropriately labeled ranges.

disrupts the optical mode, limiting its applicability for use with small area detectors, such as SNSPDs. Furthermore, in a grating-based measurement, fluctuations in the count rate cannot be separated from changes in the spectral content of the signal. This makes it challenging to acquire spectra from emitters with fluctuating brightness. DAFS overcomes the trade-off between resolution and throughput by collecting DA spectra interferometrically, thus avoiding use of a slit or grating (i.e., Jaquinot's advantage). Our theoretical spectral resolution is 12.4 μeV , depending only on the path length that our stage can sample.²⁸ Our approach retains the optical mode and polarization of the emitted photon stream allowing us to couple the light into cryogenically cooled SNSPDs and extend our method into the SWIR. By encoding spectral information in the anticorrelated photon signal from two single photon detectors positioned at each output of the interferometer DAFS acquisitions are insensitive to signal drift/fluctuation through spectrally balanced detection, as shown in Figure 3c.

Streak cameras provide an alternative method to measure TRPL spectra. Similar to an interferometric approach, streak cameras collect multiplexed spectra.³² Furthermore, the streak cameras have high time resolution of 0.2 ps, superior to that of APDs and SNSPDs; though SNSPDs are approaching picosecond resolution. However, streak cameras are prohibitively costly, even more so for SWIR detection using InGaAs technology in comparison to the components of our MZI interferometric setup. The cameras have a limited temporal range, making long lifetime measurements difficult, and are still subject to signal drift/fluctuation, which DAFS overcomes.

Interferometric detection methods are commonly used for mid-infrared absorption measurements,²⁸ e.g. FTIR, and have yet to be extensively implemented in the visible. Recently, Perri

et al. demonstrated similar single-path interferometric TRPL measurements.³³ Here, they adapt their translating-wedge-based identical pulses encoding system (TWINS) to provide a phase delay between “transmitted” and “reflected” paths. Our approach complements the TWINS interferometric method adding all-reflective epifluorescence collection, a Mach–Zehnder interferometer, and the use of SNSPDs. We thus obtain balanced spectral detection, increased photoluminescence collection, and a broad spectral range—well suited for samples with unknown or weak emission that require long acquisition times.

CONCLUSIONS

We implement and use decay-associated Fourier spectroscopy to attain energy resolved—and thus state specific—photoluminescence decay spectra across the visible and shortwave infrared regions. After processing the photon stream acquired along both output ports of a Mach–Zehnder interferometer, we acquire two-dimensional photon energy-lifetime histograms. Our implementation enables us to probe weak signals of visible and SWIR photons simultaneously, allowing us to interrogate the electronic states in organic and inorganic materials. In general, combining path length interferometry with single photon detection can provide new contrast in exploring how complex energy transfer manifests multichromophore systems. In the limit of detector noise dominating the signal from a given state, interferometric measurements are intrinsically multiplexed, and thus the signal is improved with higher count rates (i.e., Fellgett’s advantage). DAFS will therefore excel at measuring samples with very low photon count rates for a given state, especially in the background of a large signal. For example, material experiments on systems with low quantum yields (e.g., triplet phosphorescence), and low excitation fluxes used (e.g., exciton annihilation experiments) or low number density of emitters (e.g., in a microscope) would all be enhanced using DAFS. Utilizing SNSPDs as SWIR photon detectors, instead of InGaAs technology, also leverages faster reset times, lower dark count rates, and improved timing resolution for sensitive detection of weak signals in the SWIR. Finally, in using an all-reflective excitation/collection scheme allows for highly multiplexed detection from the visible (~ 390 nm) to the SWIR (~ 2 μ m). As demonstrated in Figure 5, we access octave spanning dynamics using SPADs and SNSPDs concurrently, without the need for filters to block out second order diffraction from a grating. This is ideal for studying new systems with unknown emission energies. In the future, we will apply DAFS techniques to second order correlation measurements, single molecule spectral dynamics, photon correlation Fourier spectroscopy, and the detection of entangled photons through antibunching.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b04924.

Details on the experimental setup, data acquisition, 2D histogramming, and data post processing, NC synthesis and solution preparation, optical characterization, and PL lifetime multiexponential time constants (PDF)

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Author Contributions

T.L.A. and J.R.C. designed the apparatus. All authors contributed to building, analysis, sample preparation and manuscript writing and revision.

Notes

The authors declare no competing financial interest.

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