

Picosecond Time-Resolved Fluorescence Spectra of Individual Graphene Nanoribbons by Single-Molecule Fourier Transform Spectroscopy

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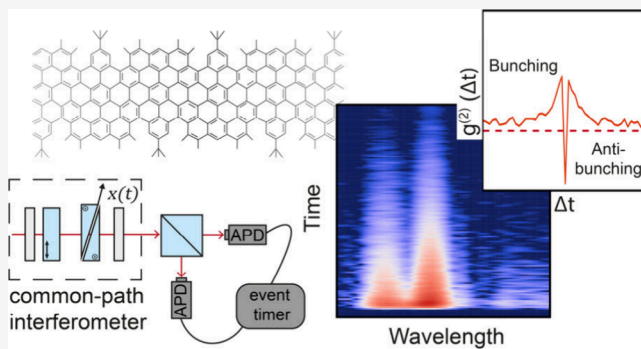
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ABSTRACT: We demonstrate the simultaneous acquisition of spectral and temporal information in single-molecule fluorescence by means of interferometric autocorrelation at room temperature. Time-correlated single-photon counting is used to assess the spectral dynamics on the picosecond time scale in the search for signatures of intramolecular energy transfer between different emitting sites within single cove–zigzag-edged graphene nanoribbons (GNRs). These GNRs show near-perfect photon antibunching, i.e., single-photon emission, along with sufficient photon count rates and long-term photostability to perform Fourier transform spectroscopy on the luminescence signal. Temporal gating of the fluorescence photons provides insight into intramolecular excited-state dynamics. In some GNRs, we observe that, as excitons diffuse within the nanoribbon, they annihilate with one another, increasing the degree of antibunching for photons with later arrival times. The existence of dark excited states within the GNR gives rise to the opposite effect, with photon bunching increasing as excitons are annihilated by these dark states, while they diffuse through the molecule, even when no perfect antibunching is observed. We conclude that short-lived bright and long-lived dark states exist in analogy to singlet and triplet excitations in multichromophoric molecular aggregates. The pronounced temporal dynamics in the photon statistics are not matched by the time-resolved fluorescence spectra, demonstrating the importance of studying both first- and second-order optical coherence in fluorescence in uncovering the electronic heterogeneity of GNRs, which remains masked in the ensemble.



Fluorescence autocorrelation constitutes a classic illustration of the wave–particle duality of light. The first-order coherence in an optical signal measures the interference of the electromagnetic wave with itself, which relates directly to the distribution of frequencies within the wave, i.e., the spectral breadth of an optical signal. The second-order coherence, the intensity autocorrelation, results in information on the particulate nature of light: a single photon traversing a beam splitter can be recorded in only one of the two beam paths, in transmission or reflection. While first-order coherence measurements have been employed to track how the emission of a single quantum emitter changes over time due to spectral diffusion,¹ these measurements have only rarely been combined with time-resolved excitation and detection of the emitter.^{2,3} It is desirable to perform both measurements at once on the same luminescence signal to extract spectral and temporal information on the emitting species simultaneously. This information is particularly important in complex fluorophore structures, where it is not immediately obvious what part of the molecule constitutes the emitting species and how many emitting sites are present within a single entity. Graphene nanoribbons (GNRs) have recently emerged as a

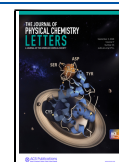
somewhat surprising nanoscale source of light,^{4–11} given that graphene itself is usually non-emissive. Whereas excitonic transitions were predicted early on^{12–15} and have shown interesting topological localization features,¹⁶ one would expect non-radiative decay to prevail so that no light emission should occur. Nevertheless, GNRs have been shown to exhibit bright fluorescence, even down to the level of single molecules.^{6,11} In analogy to π -conjugated polymers,^{17,18} the question arises whether individual GNRs contain only one or multiple emitting chromophores and how these units may interact with one another. How heterogeneous are different single GNRs in terms of their optical properties? To address these questions, we employ a single-photon Fourier transform spectrometer. To the best of our knowledge, this work reports the first direct measurement of photon antibunching from

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individual GNRs, providing new insight into the excited-state dynamics of these complex molecular systems. These measurements are complemented by the simultaneous acquisition of time-resolved fluorescence spectra from the same individual GNRs. While early GNRs were synthesized on a surface,^{19,20} allowing ribbons with well-defined width and non-trivial edge topologies that control the optoelectronic properties to be fabricated,¹⁶ it is now possible to synthesize such complex molecules in solution,^{21,22} enabling them to be processed for single-molecule microscopy just like, e.g., conjugated polymers.¹⁷ We investigate GNRs with a cove–zigzag-edged structure, the chemical structure of which is shown in Figure 1a (details regarding the synthesis of this specific GNR will be published elsewhere), as this kind of structure has been shown to be photophysically active and highly photostable while retaining the interesting electronic correlations inherent to GNRs.^{11,24–26} Dependent on the length and periodicity of the cove structure, these GNRs are expected to change the localization of edge states, which may conceivably have an interesting impact on the optoelectronic properties.²³

Figure 1b shows an ensemble photoluminescence (PL) spectrum of the GNRs with an average length of 13 nm, dissolved in toluene and recorded by a dispersive spectrometer at room temperature. The ensemble displays a broad spectrum with a PL peak at 792 nm and a shoulder close to 735 nm. Single GNRs were studied by embedding them in a non-fluorescent poly(methyl methacrylate) (PMMA) matrix. The samples were prepared on thin glass coverslips by spin-casting from a highly diluted GNR/PMMA/toluene solution, leading to well-separated single molecules with a random orientation in a ~ 150 nm thick film. Single GNRs can be addressed and excited individually in a confocal fluorescence microscope. All experiments were performed at room temperature, with the samples under a constant flow of nitrogen to exclude atmospheric oxygen, which impacts photostability (see section 3 of the Supporting Information for details). The sample was excited at 705 nm near the absorption maximum (spectrum shown in Figure S3 of the Supporting Information) using a laser diode emitting ~ 70 ps long pulses with a repetition rate of 20 MHz. Details of the experiment are given in section 1 of the Supporting Information. We examined 300 single GNRs and identified three types of characteristic behavior. Three examples of different spectra from individual GNR molecules are shown in Figure 1c–e, along with the PL decay determined by conventional time-correlated single-photon counting (TCSPC). Both the spectra and the decay transients differ significantly between these three examples, highlighting the importance of considering single GNRs. Whereas the first molecule in Figure 1c exhibits a single narrow peak at 807 nm, the second molecule in panel d has two overlapping spectral features, with peaks at 821 and 805 nm and a distinct peak with lower intensity at 765 nm. The third molecule in panel e has a narrow peak at 791 nm besides a comparatively broad feature at longer wavelengths with lower intensity. Differences are also apparent in the time-resolved PL. Whereas the molecule with a single-peak spectrum in panel c shows single-exponential decay, the example in panel d displays a superposition of a fast and slow exponential decay. Most single GNRs (approximately 70%) display more complex multi-exponential decay dynamics, such as the example in Figure 1e.

The heterogeneity of the single GNR spectra is reminiscent of that of single conjugated polymer molecules¹⁷ and other single-molecule emitters.²⁷ While the finite molecular-weight

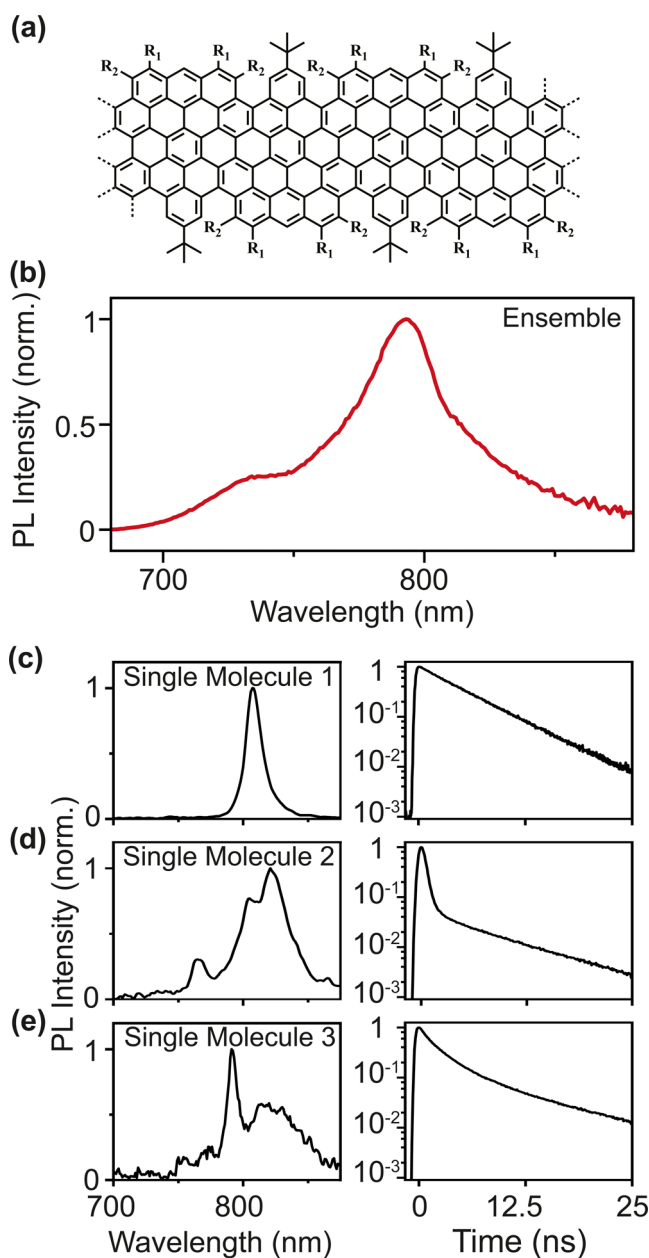


Figure 1. (a) Chemical structure of the cove–zigzag-edged GNRs. R₁ denotes a trimethylphenyl group, and R₂ denotes a *tert*-butylphenyl group. (b) Ensemble PL spectrum of the cove–zigzag GNRs dissolved in toluene. (c–e) Single-molecule spectra of three different nanoribbons excited by a 705 nm pulsed laser along with the corresponding time-resolved PL decay. The spectral properties differ significantly between single molecules. The presence of multiple bands in one spectrum appears to correlate with multi-exponential decay dynamics.

dispersity of the investigated GNR batch ($\mathcal{D} = 1.788$) may contribute to the observed spectral variations, it is conceivable that one single GNR may contain multiple emitting species, in analogy to multiple chromophores on a single polymer chain. These chromophores can interact through fluorescence resonance energy transfer (FRET), by transferring energy from a higher energy to a lower energy chromophore.¹⁷ However, if two identical chromophores are present, they may also interact by excited-state absorption: one excited chromophore absorbs the energy of the second chromophore,

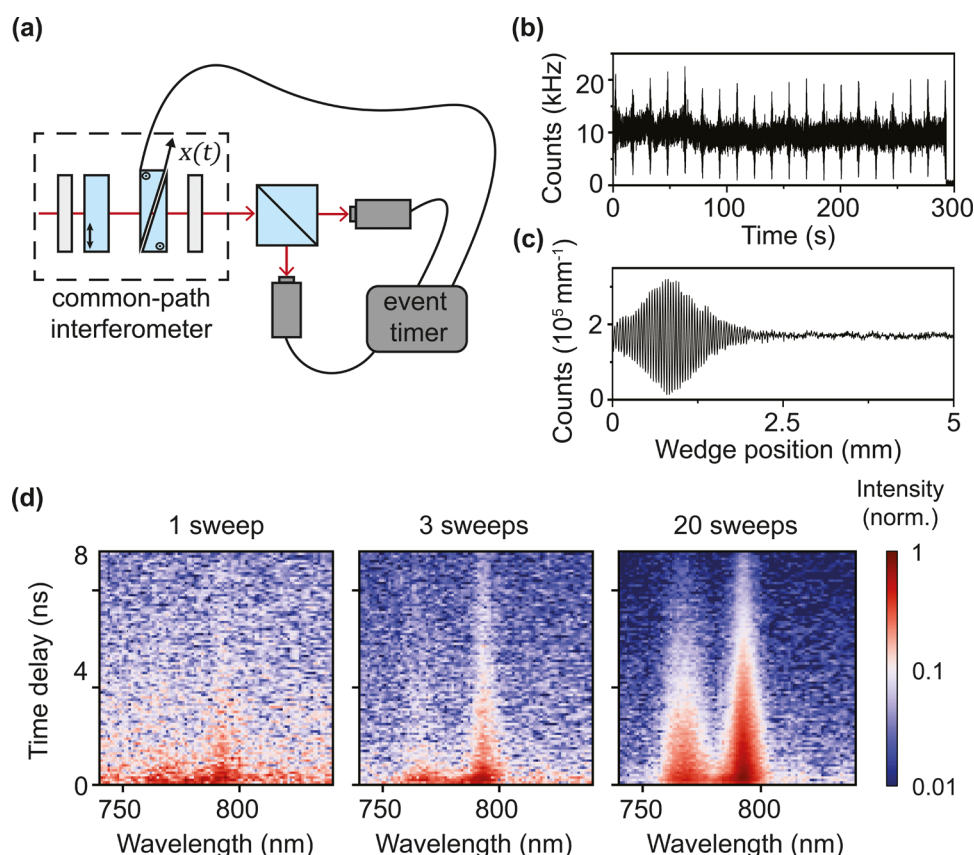


Figure 2. (a) Schematic of the common-path interferometer. A piezoelectric linear motion stage controls the interferometer path length by regulating the wedge thickness of the birefringent crystal, which is swept forward and backward repeatedly. (b) PL intensity trace of a single molecule with the interferometer in operation. The spikes correspond to interference minima and maxima. (c) The same data set can be plotted as a function of the wedge position, resulting in an interferogram that contains the spectral information. (d) Time-resolved PL spectra obtained by FT of single-molecule interferograms, as a function of the time delay between excitation pulse and photon arrival, and evaluated after 1, 3, or 20 sweeps of the interferometer path length.

leading to singlet–singlet or singlet–triplet annihilation, depending on the spin multiplicity of the excited state.²⁸

While it is straightforward to extract spectral information and temporal dynamics simultaneously by simply splitting the PL beam onto two detectors, a spectrometer and a photon counter, the presence of multiple emitting species on a single GNR along with a PL decay that is not single-exponential suggests that intramolecular FRET may occur within one single molecule.²⁹ The PL spectra should therefore change as a function of time after the excitation pulse. Single-molecule FRET dynamics can be spectrally resolved by means of fluorescence filters and recorded using TCSPC or image intensifiers,³⁰ but there are only very few reports of direct measurements of time-resolved PL spectra of single emitters.³¹ Such a time-resolved PL spectrum would be similar to an ensemble spectrum recorded, e.g., by a streak camera. To approach this problem, we employ Fourier transform (FT) spectroscopy, where spectral information is acquired simultaneously with the intensity autocorrelation $g^{(2)}(\Delta t)$, which, in turn, reports directly on the number of photons emitted from the single molecule. This combination is achieved by introducing an interferometer into the optical detection beam path before the beam splitter in the photon-correlation setup.

We use a birefringent common-path interferometer that provides high spatiotemporal stability to enable visible-light interferometry.^{32–34} The device consists of a Soleil–Babinet

compensator, with entrance and exit polarizers, as sketched in Figure 2a. Instead of separating the two replicas of the light beam spatially, the system projects them onto two orthogonal polarization states using the first polarizer. These two orthogonally polarized light fields are then delayed with respect to each other by introducing a fixed time delay for one polarization using a birefringent crystal. The time delay for the orthogonal polarization is controlled by a second crystal with the optical axis rotated by 90° that consists of two wedges, one of which can be translated in a direction perpendicular to the optical axis to vary the effective crystal thickness. The two polarization components are then projected back onto a common polarization state by the second polarizer, allowing them to interfere on the detector, which itself is an intensity autocorrelator, i.e., a beam splitter with two single-photon counters.³⁵

Combining this technique with TCSPC event timing to generate time-resolved PL spectra potentially allows spectrally overlapping features in the single-molecule luminescence to be disentangled while simultaneously providing sub-nanosecond temporal resolution. While related strategies have recently been applied to emitters with high photostability at room temperature, such as DNA-stabilized silver nanoclusters³⁶ or nitrogen-vacancy (NV) centers in diamond,³⁷ as well as single divacancies in 4H-SiC at cryogenic temperatures,³⁷ the approach has not been employed on the level of single molecules. Most organic fluorophores are prone to photo-

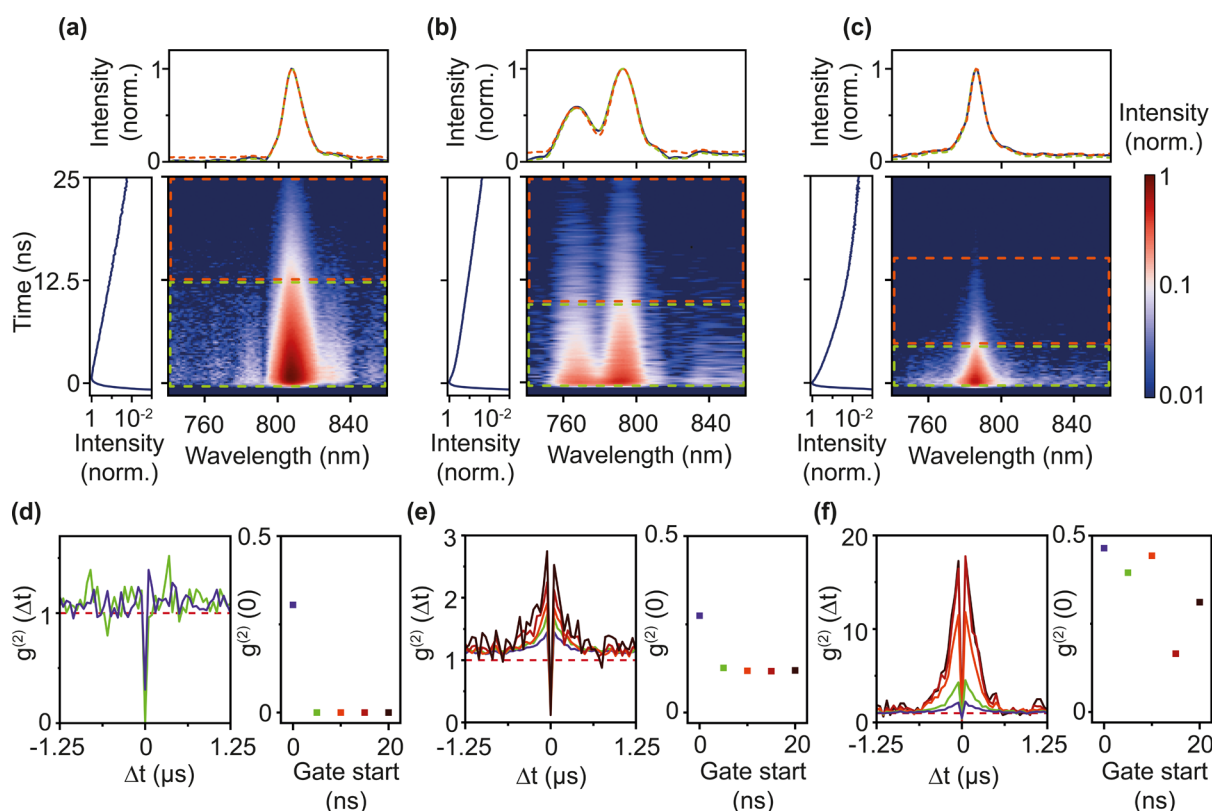


Figure 3. Time-resolved photoluminescence and photon-correlation measurements of three individual GNRs. (a–c) Time-resolved PL spectra together with the spectrally integrated fluorescence decay traces. The colored dashed boxes indicate the photon arrival time intervals used to obtain the correspondingly colored normalized spectra shown above the maps. (d–f) Time-gated second-order intensity autocorrelation functions, $g^{(2)}(\Delta t)$, for the corresponding molecules shown in panels a–c, obtained for photons arriving after gate start times of 0, 5, 10, and 20 ns following excitation. The corresponding values of $g^{(2)}(0)$ are plotted as a function of the gate start time in the panels on the right. The correlation measurements reveal molecule-dependent changes in photon antibunching and bunching with increasing photon arrival time.

bleaching at room temperature, limiting the number of detectable photons and preventing the acquisition of complete interferograms as a function of the difference in the optical path length. To address this limitation, we employ a protocol in which the wedge thickness is swept continuously in repeated cycles until photobleaching occurs while recording its movement as timing events together with the photodetection events. Prior to spectral and photon-correlation analysis, the fluorescence time traces were divided into intervals, and only sections with stable fluorescence decay were included in the analysis. Details of the selection criterion and timing procedure are provided in the [Supporting Information](#). Figure 2b shows the single-molecule PL intensity as a function of time as the wedge position is cycled 20 times over a period of 15 s per cycle. As the interferometer is swept, spikes and dips in the intensity occur, corresponding to constructive and destructive interference. The same data set can be translated into the coordinates of the interferometer, i.e., the position of the birefringent crystal wedge, resulting in the interferogram plotted in panel c. We sort photodetection events into individual time bins according to their arrival time after the corresponding photoexcitation pulse and Fourier transform the binned interferograms to acquire the time-resolved PL spectrum. Applying this procedure to an individual GNR yields the time-resolved PL maps shown in panel d for 1, 3, and 20 sweeps of the interferometer. Even one single sweep is sufficient to obtain spectral information from the interfero-

gram. The signal-to-noise ratio improves steadily as the size of the data set increases.

The fact that multiple peaks are seen in the single-GNR PL spectra raises the question of whether energy transfer occurs between different emissive sites within a single molecule. In addition to the spectral dynamics, for example, the faster decay of a higher energy emission feature by energy transfer to a lower energy band, FRET may also impact the PL photon statistics.²⁸ It is instructive to compute the intensity autocorrelation $g^{(2)}(\Delta t)$ as a function of the photon arrival time, i.e., to perform time-gated detection, where only photons arriving after a certain delay time after photoexcitation are considered in the autocorrelation.^{38,39} The example in Figure 3a shows a dominant PL peak at 805 nm with weak features at longer and shorter wavelengths, with the spectrally integrated PL exhibiting single-exponential decay. Three PL spectra recorded in different time windows indicated by the dashed boxes are plotted above on a normalized scale. From the time-resolved PL spectra, no obvious dynamics are apparent. However, the autocorrelation drops from $g^{(2)}(0) = 0.3$ when considering all photons (purple point in the right panel of Figure 3d) to $g^{(2)}(0) = 0.0$ when considering photons arriving after a delay time of 5 ns (green point in the right panel of Figure 3d). The $g^{(2)}(0)$ value for the prompt photons therefore indicates more than one effective chromophore emitting, whereas the later photons emanate from only one chromophore. Such dynamics only arise if there are multiple emitting species present on the GNR, and these emitting sites

can interact with each other by a mechanism analogous to singlet–singlet annihilation in multichromophoric aggregates.²⁸ As discussed in the [Supporting Information](#), analysis of the temporal evolution of the photon statistics yields an exciton annihilation rate of $(1.7 \pm 2) \times 10^9 \text{ s}^{-1}$, comparable to that found in aggregates of conjugated polymers.³⁸ However, since there is only one PL lifetime discernible and there are no dynamics in the PL spectrum, we conclude that the emitting species must be almost degenerate, implying the occurrence of homo-FRET.^{40,41} Such exciton–exciton annihilation in GNRs has previously only been discernible in transient absorption experiments in the ensemble.⁴² The situation appears different in panel b, where the PL spectrum is dominated by two distinct peaks. The initial spectrally integrated PL shows a shorter lived decay feature followed by an exponential decay. Nevertheless, the normalized time-resolved spectra do not change with time. Even though two spectral peaks are resolved, the single molecule again shows near-perfect photon antibunching, with the dip in the correlation dropping from 0.27 for all photons detected after excitation to 0.13 for photons detected 5 ns after excitation, as plotted in the right panel of [Figure 3e](#). This drop in $g^{(2)}(0)$ with photon gate time again implies the presence of multiple emissive species within the GNR and an interaction between them, i.e., exciton–exciton annihilation, even though the shape of the PL spectrum does not change discernibly with time. One possible interpretation for this observation is that the different spectral bands belong to different but degenerate electronic species, i.e., that the lower energy band is associated with a vibronic mode.

The single GNR also displays strong photon bunching, with $g^{(2)}(\Delta t)$ exceeding a value of unity (the Poisson limit) at Δt values of at least one laser repetition period. This effect also becomes more pronounced for photons detected later after excitation. Such photon bunching or fluorescence blinking is a signature of a long-lived dark molecular excited state, for example, a molecular triplet excitation.²⁸ The increase in $g^{(2)}(\Delta t)$ with gate time implies that excitations move within the GNR to be quenched by this dark state by a mechanism analogous to singlet–triplet annihilation in molecular multichromophoric aggregates.²⁸ The longer the excitons can diffuse within the GNR, the greater the effect of quenching and, hence, the greater the degree of photon bunching.

This quenching effect is amplified further in the third example in panel c, where the molecule shows single-peak emission with a non-exponential decay of the PL intensity. The zero-delay ($\Delta t = 0$) photon antibunching does not change systematically with the photon gate time and is comparatively high at $g^{(2)}(0) = 0.46$, dropping to 0.31 for a detection gate after 20 ns delay, implying the presence of at least two emitting sites that effectively do not couple to each other.³⁸ Nevertheless, the photon bunching amplitude rises very strongly with time, increasing almost 20-fold as the start of the photon detection gate is raised from 0 to 20 ns after excitation. This increase implies that, when one of the chromophores enters a dark state, i.e., switches off, the entire GNR becomes non-emissive. In the language of molecular singlet and triplet excitations, one would assert that singlet–singlet annihilation, responsible for photon antibunching, is not very effective, whereas the chromophores do clearly interact by singlet–triplet annihilation, implying the occurrence of energy transfer within the molecule.⁴³ Such quenching of emissive species by long-lived dark states is then likely responsible for the non-exponential PL decay observed in this example. We note that

this pronounced quenching by a dark state in the single-molecule luminescence contrasts with the conclusions previously drawn from single-photon emission from graphene quantum dots.⁴⁴

Single GNR molecules show exceptionally stable and long-lived single-photon emission at room temperature. Our measurements reveal pronounced molecule-to-molecule heterogeneity in the fluorescence spectra and decay dynamics, which is masked in ensemble measurements. We specifically searched for correlations among the spectral features resolved, their decay dynamics, and the temporal evolution of the photon statistics but failed to identify any systematic relationship. The individual spectral bands therefore cannot be assigned unambiguously to distinct chromophoric units within the GNR, a vibronic progression of an individual electronic transition, or conformationally induced variations in the local electronic structure. Nevertheless, the time-gated photon-correlation measurements demonstrate that multiple excitations can form within a single GNR and interact through exciton–exciton annihilation. If distinct, effectively degenerate chromophoric units are involved in this interaction, the absence of a discernible temporal redistribution of the fluorescence spectrum would be consistent with homo-FRET; however, the present data do not conclusively support this interpretation. Future experiments should focus on correlating structural details of the GNR, the length and width along with the cove–zigzag edge topology, with the spectral information and the photon statistics to illuminate the microscopic origins of the pronounced heterogeneity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcclett.6c02176>.

Figures S1–S8 and Tables S1 and S2 with information on sample preparation and the experimental setup, ensemble spectra, illustration of the influence of atmospheric conditions, operation of the common path interferometer and data analysis, long-time-scale photophysical behavior of single GNRs, details on the statistics of the photophysics of single GNRs, details of the photon counts and coincidence statistics for all data sets shown, and information on the determination of the SSA rate (PDF)

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Notes

The authors declare no competing financial interest.

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