

**Picosecond time-resolved fluorescence spectra of individual graphene nanoribbons by
single-molecule Fourier-transform spectroscopy
-Supplementary Information-**

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1. Sample preparation and experimental setup

The samples were prepared by individually dissolving the molecules and poly(methyl-methacrylate) (PMMA) in toluene and combining them, resulting in a diluted solution of ~1 pM of **graphene nanoribbons** (GNRs) and 3 wt% PMMA. The analyte/PMMA mixture was spin coated (2 min @ 2000 rpm) onto cleaned borosilicate cover slips, leading to well separated

single molecules immobilized in a PMMA film of approximately 150 nm thickness. Prior to each measurement, GNR-free PMMA samples were checked for fluorescent contaminations.

The measurements were performed on an inverse microscope (Olympus IX71) in confocal detection geometry. Excitation was provided by a fiber-coupled diode laser emitting ~70-ps-long pulses at a repetition rate of 20 MHz and a wavelength of 705 nm (PicoQuant, LDH-C-705). After passing an excitation filter (Thorlabs, FB700-10) and expanding the beam diameter to ~1 cm using a lens system, the light was circularly polarized by a quarter-wave plate. A custom dichroic mirror (AHF Analysentechnik AG) was used to couple the beam into a high-numerical-aperture oil-immersion objective (Olympus UPLSAPO 60XO, NA = 1.35), which focused the laser into a diffraction-limited spot on the sample plane. Light from the sample plane passed the beam splitter and was confocally filtered by a 50 μm -diameter pinhole and a long-pass filter (Thorlabs FELH0750). Individual analyte molecules embedded in the PMMA host matrix were localized by first scanning the sample across areas of $20 \times 20 \mu\text{m}^2$ using a piezo scanner (Physik Instrumente). Each diffraction-limited emission spot was subsequently positioned in the laser focus to record its photoluminescence (PL) under a time-averaged irradiance of 1870 W cm^{-2} . Spectrally and spatially filtered PL passed the common-path interferometer (Nireos S.r.l., Gemini), after which the signal was split by a 50:50 beamsplitter and detected with two single-photon avalanche photodiodes (Laser Components, Count-T100). Photon arrival times were recorded using a time-correlated single-photon counting (TCSPC) module (PicoQuant, HydraHarp 400). A schematic of the setup is shown in Fig. S1.

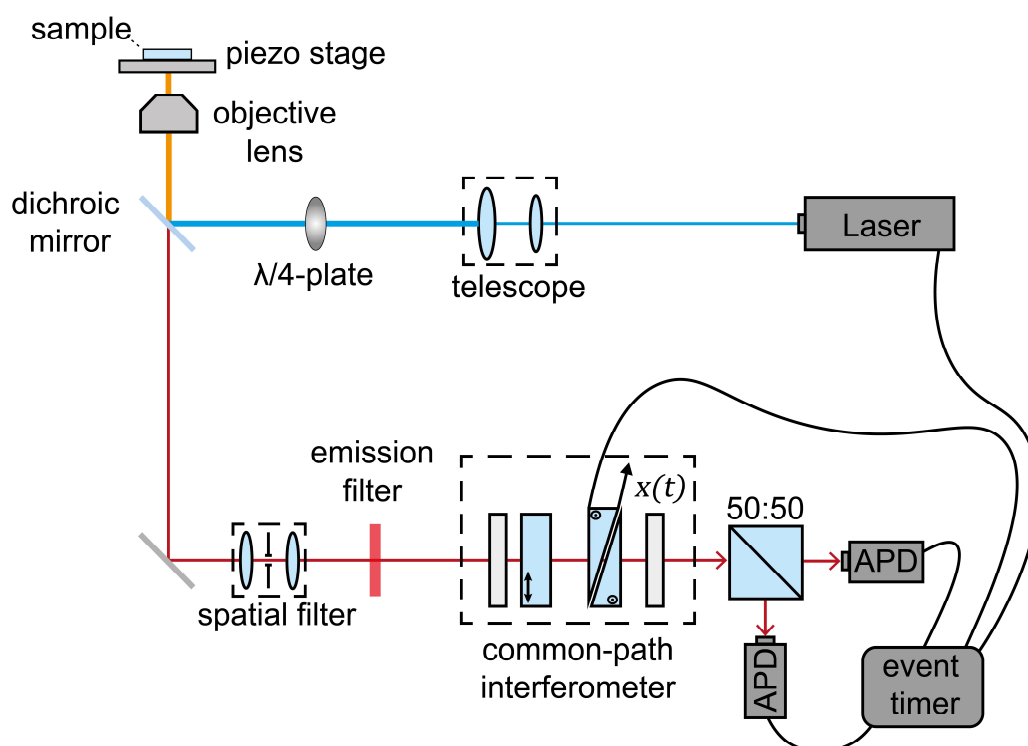


Figure S1. Schematic of the confocal microscope and detection path used for single-molecule PL measurements. The beam from a fiber-coupled pulsed diode laser (705 nm, 20 MHz) is expanded using a telescope, circularly polarized by a quarter-wave plate, and coupled into a high-NA objective via a dichroic mirror to excite the sample mounted on a piezo stage. The fluorescence is separated from the excitation light by the dichroic mirror and directed through a spatial filter (confocal pinhole) and a long-pass filter before entering the common-path interferometer. The output is split by a 50:50 beamsplitter and detected on two avalanche photodiodes (APDs) connected to an event timer that also records position-increment events from the interferometer and the timing of laser pulses.

To evaluate whether aggregation occurs, two samples were prepared from the same solution. For one sample, part of the solution was sonicated before spin coating, whereas for the second the solution was used without sonication. The location and brightness of luminescent spots was determined for both samples over an area of $40 \times 40 \mu\text{m}^2$, measured at 50 nm scan resolution

and 1 ms dwell time. No significant differences were observed between the two samples, as shown in Fig. S2.

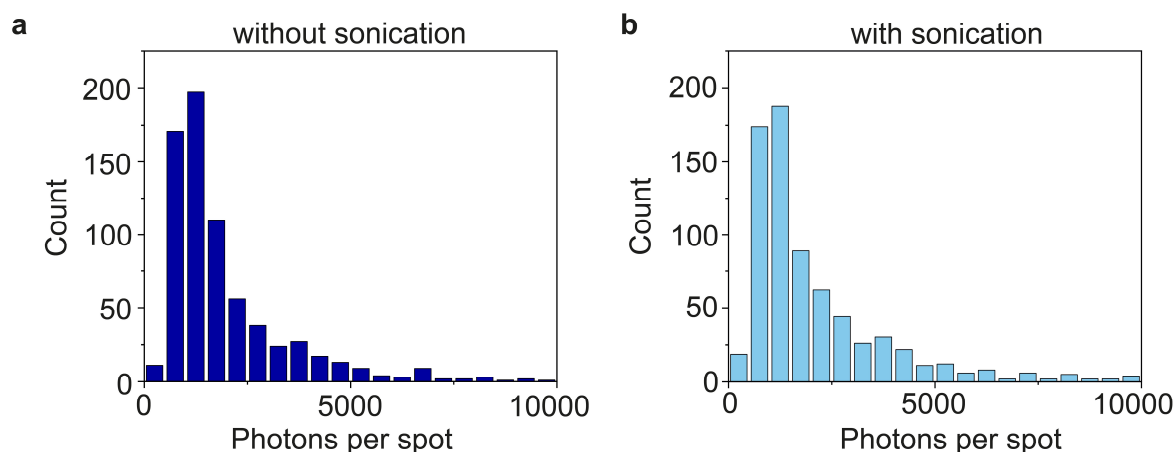


Figure S2. Histogram of the number of photons per diffraction-limited fluorescence spot observed inside $40 \times 40 \mu\text{m}^2$ sample regions. (a) Sample prepared without additional sonication of the solution. (b) Sample prepared by sonicating the solution prior to deposition.

2. Absorption and PL spectra of the ensemble

The absorption and PL spectra of an ensemble of GNRs dissolved in toluene were recorded using commercial UV-VIS absorption and fluorescence spectrometer instruments (Perkin-Elmer, Lambda 650 and Horiba, Fluoromax-4) and are shown in Fig. S3. The absorption spectrum shows characteristic peaks at 631 nm, 709 nm, and 790 nm. The emission spectrum shows a single peak at 791 nm and a shoulder at 734 nm.

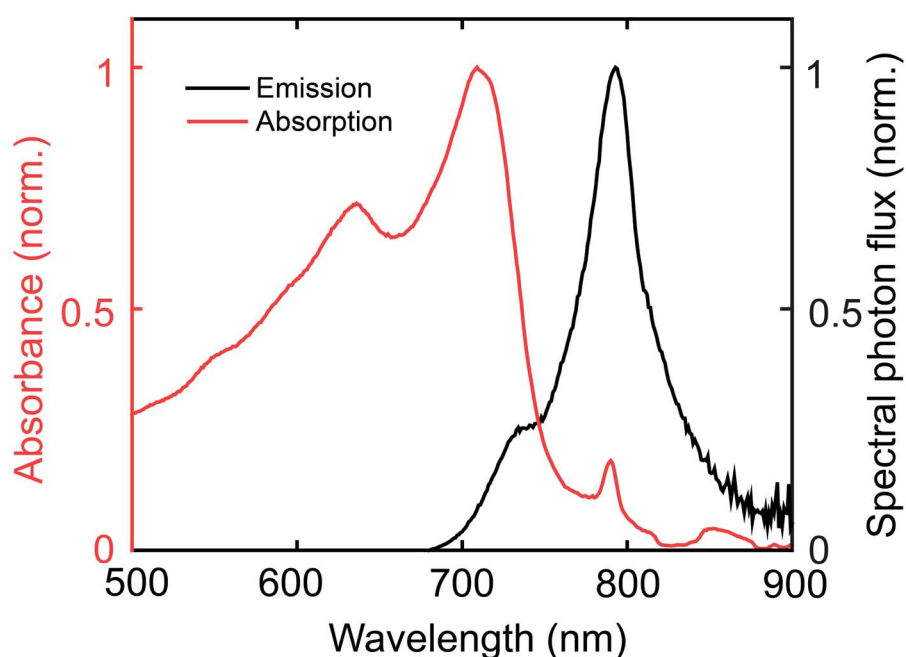


Figure S3. Normalized absorption (red) and PL (black) spectra of cove-zigzag edged GNRs dissolved in toluene. Emission was recorded under excitation at 470 nm. Both spectra were normalized to their respective maxima.

3. Influence of atmospheric conditions on photostability and dark-state lifetime

To compare the photostability of individual nanoribbons under ambient conditions and under a constant flow of nitrogen, a sample was prepared as described above and PL time traces of single GNRs were recorded for both environments. For every individual emissive spot, the time until photobleaching was determined. Only spots that exhibited a clear photon antibunching dip were included in the analysis. Two example traces and histograms of the photobleaching times are in Figure S4. Under a constant nitrogen flow, the exposure time until photobleaching is significantly increased, consistent with a suppression of photooxidative degradation. At the same time, the photon-correlation analysis reveals more pronounced long-lived dark-state shelving under nitrogen, whereas this contribution is reduced under ambient conditions. To quantify the dark-state dynamics, we fitted the prompt antibunching feature around zero delay,

with a single-exponential decay, as commonly used to describe intermittent bright-dark state dynamics in single emitters

$$g^{(2)}(\Delta\tau) = 1 + A \cdot \exp\left(-\frac{\Delta\tau}{\tau_{corr}}\right),$$

where A is the bunching amplitude relative to the long-delay baseline and τ_{corr} is the characteristic decay time of the correlation¹. Within a two-state bright-dark model, the mean residence time in the dark state is given by

$$\tau_{dark} = \tau_{corr}(1 + A).$$

For each environment, the median correlation curve of the corresponding single-molecule data set is plotted to visualize the ensemble-typical bunching behavior in panels e, f. The bunching amplitude and the resulting average dark-state lifetime are reduced under ambient conditions from $1.13 \pm 0.05 \mu\text{s}$ to $0.51 \pm 0.04 \mu\text{s}$, indicating that molecular oxygen suppresses long-lived dark-state shelving. This behavior is consistent with oxygen-induced quenching of molecular triplet states².

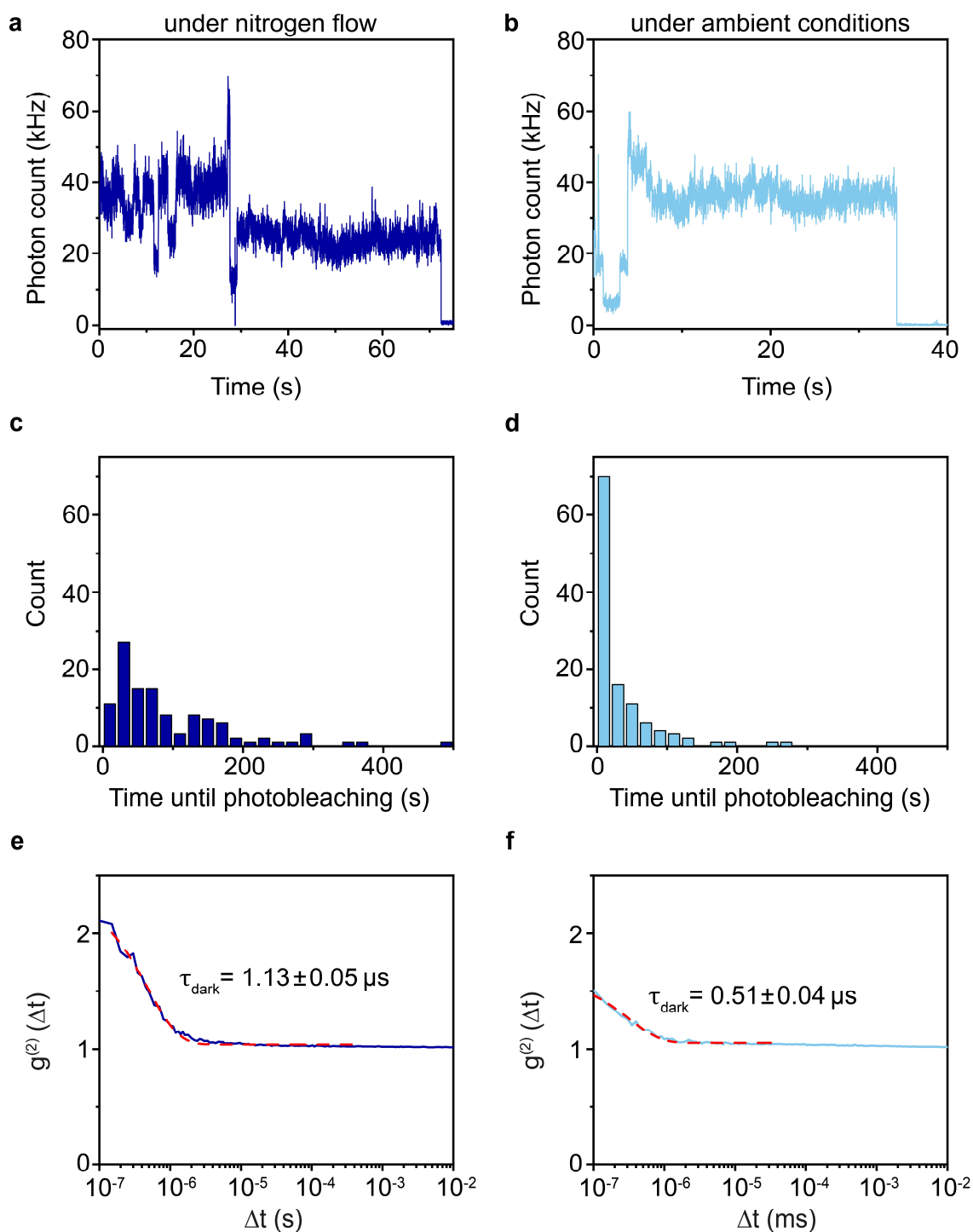


Figure S4. Influence of the atmosphere on PL intensity traces of single GNRs (a) under nitrogen flow and (b) under ambient conditions at an excitation intensity of 188 Wcm^{-2} . Photobleaching is evident from the abrupt drop of the signal to the background level. (c,d) Histograms of the time until photobleaching for individual immobilized nanoribbons that show photon antibunching. The mean values are 100 s and 36 s, respectively. (e,f) Median second-order

intensity autocorrelation curves $g^{(2)}(\Delta t)$ obtained from the corresponding single-molecule data sets. The red dashed lines show single-exponential fits to the photon-bunching contribution, from which the average dark time τ_{dark} is extracted. The median curves yield $\tau_{\text{dark}} = 1.13 \pm 0.05 \text{ } \mu\text{s}$ under nitrogen flow and $\tau_{\text{dark}} = 0.51 \pm 0.04 \text{ } \mu\text{s}$ under ambient conditions, indicating a reduced dark-state residence time in the presence of air.

4. Operation of the common-path interferometer

The commercial common-path interferometer was modified to allow fast delay scanning while still being able to precisely record the position of the wedge-shaped crystals. To this end, the original controller for the devices' piezo stage that sets the wedge position was replaced by a piezo controller that sends trigger signals at the start of a wedge-position sweep (event type “S”) and whenever the piezo stage has advanced by a preset distance of $5 \text{ } \mu\text{m}$ (event type “X”). We use a constant-speed forward sweep for data acquisition and a fast backward sweep that is not evaluated. The trigger signals are fed into the event timer in addition to the photodetection events D_1 and D_2 from the two APDs and the excitation-laser synchronization event L . After the measurements, the events are available as tabulated data of event types and the associated time with a precision of 2 ps as illustrated in Fig. S5.

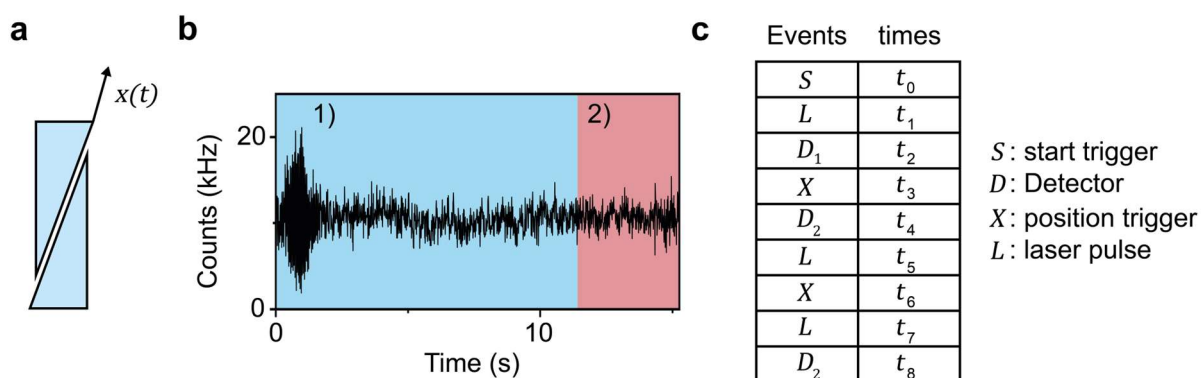


Figure S5. (a) The common-path interferometer controls the effective optical path length for one polarization direction by translating a wedge-shaped birefringent crystal by a distance $x(t)$ using a piezoelectrically-driven linear-motion stage. The crystal is translated at a constant

speed, with the piezo controller emitting trigger signals at 5 μm intervals. (b) The experiment consists of repeated slow forward scans, where x increases with time at a constant rate, and fast backward scans. A single forward and backward scan are shown, marked in blue (1) and red (2), respectively. Interference fringes are fully resolved on the forward sweep, while they are undersampled on the backward sweep. (c) The time of individual events (start of the experiment S , laser excitation pulse L , position advance trigger X , photodetection of either of the two photodetectors D_1 and D_2) is recorded by a fast event timer with a precision of 2 ps.

5. Analysis of TCSPC data

The wedge position x for each individual photon detection event can be inferred based on the time of the closest position trigger event X by assuming a locally constant speed of motion $\dot{x}(t)$ between subsequent trigger events as outlined in Fig. S5a. This approach makes the analysis much more robust towards minor variations in movement speed of the crystal wedge. Only photon events detected during the forward sweep (i.e. for increasing x) of the interferometer are used in the analysis. We histogram the photon detection events both with respect to the time difference to the preceding laser pulse, i.e. the photon arrival time, and with respect to the wedge position x . For each photon arrival time, the interferogram, i.e. the position-dependent photon counts, is corrected for motion-stage related variations in total acquisition time per position bin and then Fourier-transformed to the spatial frequency domain and then converted into an emission spectrum as function of wavelength following the procedure outlined by Perri *et al.*³

6. Photophysical behavior of individual molecules on longer timescales

Because individual GNRs can remain emissive for extended time periods, changes in their photophysical behavior may occur within a single measurement. Therefore, for all single-molecule analyses performed, we considered only time intervals during which the fluorescence lifetime remained stable. A representative example acquired under nitrogen flow with the

interferometer in the detection path is shown in Fig. S6. During the first interval (green), the photon count rate exhibits pronounced fluctuations, while the time-resolved PL decay remains unchanged. After the abrupt intensity decrease at 45 s, the molecule enters a second photophysical regime (red), characterized by a substantially faster PL decay. The corresponding time-resolved PL decays and linear fits on a semilogarithmic scale are shown in Fig. S6b,c. The extracted fluorescence lifetimes are 2.8 ns and 0.5 ns for the green and red intervals, respectively. Accordingly, only the green interval was included in the analysis.

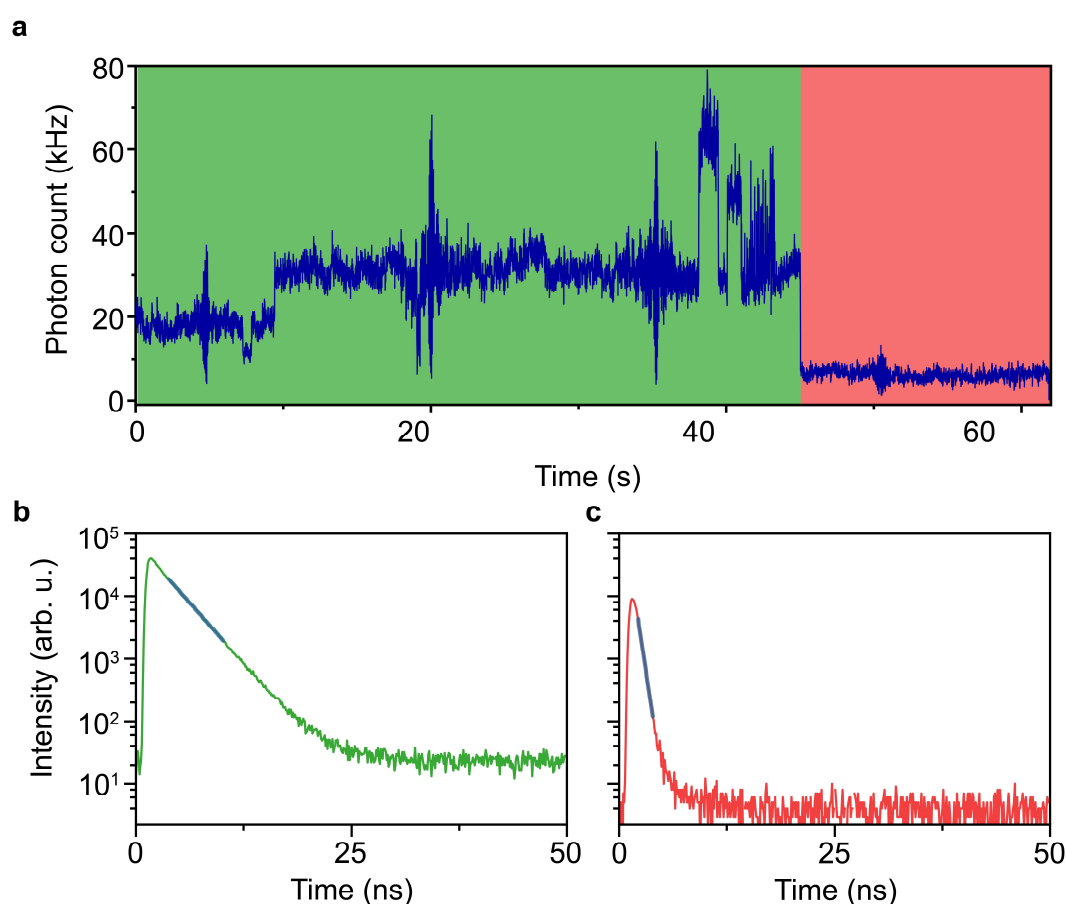


Figure S6. Representative photophysical behavior of an individual GNR over longer timescales. (a) Photon count-rate trace recorded under nitrogen flow with the interferometer in the detection path. The colored vertical markers delineate two time intervals exhibiting distinct photophysical behavior. During the first interval (green), the photon count rate fluctuates, whereas the time-resolved PL decay remains stable. Following an abrupt decrease in intensity at approximately 45 s, the molecule enters a second regime (red), characterized by

a faster PL decay. (b,c) Time-resolved PL decays integrated over the green and red intervals, respectively. The blue lines show linear fits to the decay curves on a semilogarithmic scale, yielding fluorescence lifetimes of 2.8 ns for the green interval and 0.5 ns for the red interval.

This behavior is also evident in the dataset shown in Fig. 2d of the main text. Because Fig. 2 is intended to illustrate the operating principle of the common-path interferometer and the reconstruction of time-resolved fluorescence spectra, the complete acquisition is shown without restricting the analysis to a single photophysically stable interval. Figure S7a compares normalized fluorescence decay traces obtained from three separate time intervals of the same dataset used in Fig. 2d, each comprising five consecutive interferometer sweeps. The corresponding acquisition time windows are indicated in the figure. The underlying fluorescence intensity trajectory (not shown) changes at an acquisition time of approximately 95 s, accompanied by a change in the fluorescence decay dynamics. The interval acquired before this transition exhibits a distinct fluorescence decay, whereas the two intervals selected after the transition show consistent decay behavior. In addition, Fig. S7b compares the wavelength-resolved fluorescence decay traces of the two spectral features centered at 769 and 793 nm, evaluated over all 20 sweeps. Within the experimental resolution, no systematic difference in decay dynamics is observed between the two spectral features.

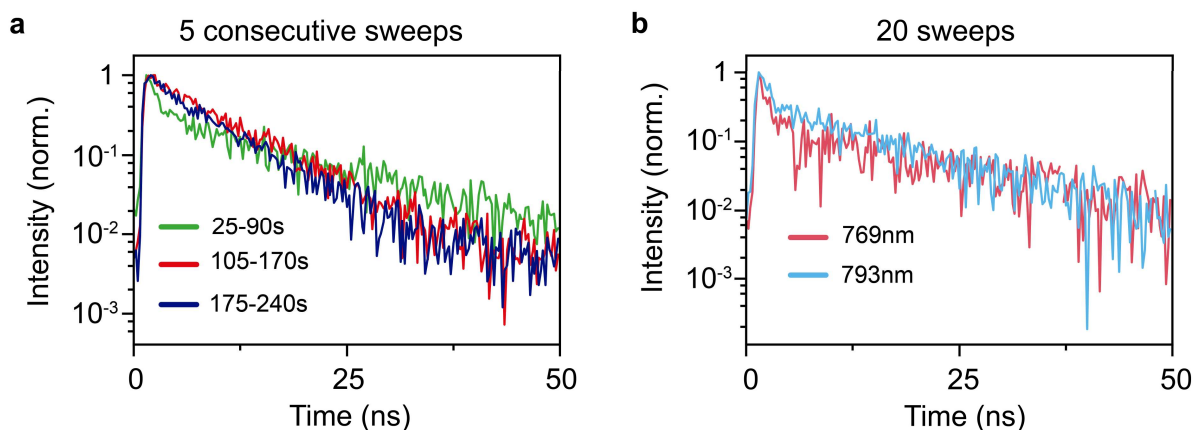


Figure S7. Fluorescence decay dynamics of the individual GNR shown in Fig. 2d of the main text. (a) Normalized fluorescence decay traces obtained from three separate acquisition time windows, each comprising five consecutive interferometer sweeps. The interval from 25 to 90 s was recorded before the slight change in fluorescence intensity at approximately 95 s and exhibits decay dynamics that differ from those of the intervals recorded between 105 and 170 s and between 175 and 240 s. The latter two traces exhibit consistent fluorescence decay behavior, indicating a photophysically stable regime following the intensity transition. (b) Wavelength-resolved PL decay of the spectral features centered at 769 and 793 nm, evaluated over all 20 interferometer sweeps. No systematic difference in the decay dynamics of the two spectral features is observed within the available photon statistics.

7. Statistics of single GNR photophysics

To provide a comprehensive overview of the photophysical heterogeneity within the sample investigated, all 300 individual GNRs were evaluated and classified according to their fluorescence decay behavior, the number of spectral peaks resolved, and the occurrence of photon bunching. The classification of the fluorescence decay dynamics follows the procedure described in Section 6. Photon bunching was identified by the presence of an enhanced correlation amplitude outside the central antibunching dip. The resulting distributions are summarized in Table S1.

PL decay behavior	Fraction of all GNRs	1 spectral peak	2 spectral peaks	3 spectral peaks	Bunching	No bunching
Monoexponential	70	66	4	0	55	15
Biexponential	20	5	15	0	20	0
Multiexponential	210	157	26	27	210	0
Total	300	228 (76%)	45 (15%)	27 (9%)	285 (95%)	15 (5.0%)

Table S1. Overview of the photophysical properties of the 300 single GNRs investigated. The GNRs were grouped according to their fluorescence decay behavior and further evaluated in terms of the number of spectral peaks resolved and the presence of photon bunching.

No systematic correlation was observed between the fluorescence decay behavior, the number or wavelength of the spectral peaks resolved, and the measured $g^{(2)}(0)$ values or photon bunching amplitudes. This likely reflects both the pronounced molecule-to-molecule heterogeneity and the influence of collective fluorescence blinking, which modifies the central photon correlation peak and thus the apparent $g^{(2)}(0)$ value, as previously demonstrated for fluorescent multichromophoric systems⁴.

To provide a quantitative measure of the photon statistics underlying the normalized correlation histograms shown in Fig. 3 of the main text, Table S2 lists the total number of photons, N_{ph} , recorded over the complete fluorescence trajectory of each molecule. For each correlation analysis, the table also provides the number of coincidence events in the central peak, N_0 , and the mean number of coincidence events across ten lateral peaks $\langle N_{lat} \rangle$, together with the corresponding standard deviation, σ_{lat} . The correlation bins correspond to integer multiples of the laser repetition period.

Main-text Panel	Gate start (ns)	Photon count N_{ph}	Central coincidences N_0	Lateral coincidences $\langle N_{lat} \rangle \pm \sigma_{lat}$
3a	0	27522869	1431	27640.1 $\pm$ 220.1
3a	5	-	51	7610.2 $\pm$ 89.0
3a	10	-	10	1101.2 $\pm$ 37.5
3a	15	-	5	161.0 $\pm$ 13.7
3a	20	-	0	26.4 $\pm$ 4.7
3b	0	12517120	1983	7928.8 $\pm$ 525.6
3b	5	-	234	2567.4 $\pm$ 284.9
3b	10	-	59	725.7 $\pm$ 112.7
3b	15	-	16	228.9 $\pm$ 42.3
3b	20	-	6	77.3 $\pm$ 19.7
3c	0	7152455	739	1595.0 $\pm$ 209.0
3c	5	-	58	341.9 $\pm$ 152.5
3c	10	-	13	149.6 $\pm$ 99.0
3c	15	-	2	85.2 $\pm$ 60.9
3c	20	-	2	48.2 $\pm$ 33.2

Table S2. Photon count and coincidence statistics underlying the normalized photon-correlation histograms shown in Fig. 3 of the main text. N_{ph} denotes the total number of photons contributing to each gated correlation analysis, N_0 is the number of coincidence events in the central peak, and $\langle N_{lat} \rangle \pm \sigma_{lat}$ gives the mean and standard deviation of the integrated coincidence counts in the lateral peaks. The standard deviation characterizes the variation among the normalization peaks and does not represent a formal uncertainty in $g^{(2)}(0)$.

8. Determination of the SSA rate

The absence of blinking behavior on any observable timescale in the nanoribbon leads to the conclusion that no dark-state dynamics are present⁵. Consequently, the second-order correlation function $g^{(2)}(\Delta t)$ shows a constant amplitude of unity for delay times $\Delta t \neq 0$, as observed in Figure 3d of the main text. Under these conditions, the number of independent emitters, N , can be extracted from the antibunching behavior using

$$N = \frac{1}{1 - N_c/N_l},$$

where N_c and N_l denote the central and lateral peak intensities of the correlation histogram at $\Delta\tau = 0$ and $\Delta\tau \neq 0$, respectively⁶.

It has previously been demonstrated by Hedley *et al.*⁷ that analyzing the time delay between the excitation pulse and the detection of a fluorescence photon allows exciton-exciton annihilation to be resolved under the assumptions outlined above. Since the probability for exciton-exciton annihilation increases for photons emitted at later times, the ratio of N_c/N_l decreases accordingly. This effect can be probed by introducing a temporal gate, where only photons arriving after a defined delay following excitation are considered in the correlation analysis. Following the procedure described by Hedley *et al.*⁷, a time-dependent expression for the number of independent emitters in the multichromophoric molecule can be obtained, which is related to the singlet-singlet annihilation (SSA) rate constant k_{SSA} :

$$N(t) = \{y_0 - [A \times \exp(-k_{SSA}t)]\}^{-1}$$

Here, $1/(y_0 - A)$ corresponds to the number of independent emitters at $t = 0$, while $1/y_0$ represents the asymptotic number of emitters at long delay times.

Figure S6a shows N_c and N_l extracted for discrete time intervals of 250 ps. Panel b displays the corresponding number of independent emitters, $N(t)$, derived from these values. This data is fitted with the above expression (red line) to extract the experimental SSA rate constant k_{SSA} .

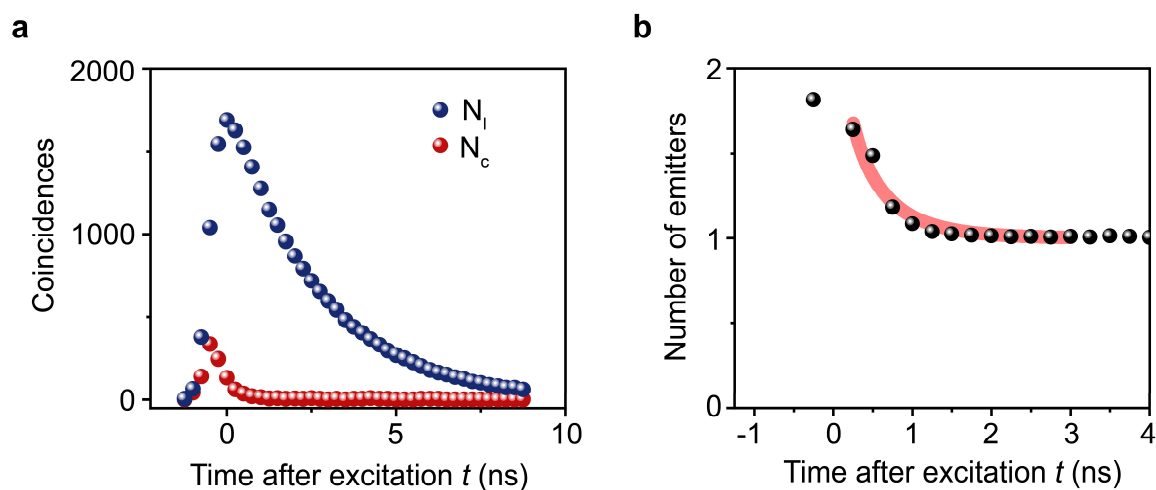


Figure S8. (a) Number of lateral (N_l) and central (N_c) detector coincidences as a function of time after laser excitation, evaluated using correlation windows of 250 ps width. (b) Corresponding time-dependent number of emitters, derived from N_c/N_l and fitted with the expression of $N(t)$ above (red line) to extract the experimental SSA rate constant k_{SSA} . Time zero corresponds to the maximum of the detector instrument response function (IRF) in both panels.

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