Supporting Information

Coverage Dependent Luminescence from Two-Dimensional Systems of Covalently Attached Perylene Fluorphores on Silica

Joseph M. McCrate and John G. Ekerdt*

Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, USA, *E-mail: ekerdt@che.utexas.edu, Tel.: +1 512-471-4689

Experimental Methods

A complete description of the technique and system used to covalently attach perylene fluorophores to fused silica surfaces in a UHV environment is given elsewhere.[1] Briefly, cleaned 1.6 cm × 1.6 cm fused silica wafers are attached to a Mo sample holder and loaded into a multi-chamber UHV system with a base pressure of ~10^{-9} torr. Samples are transferred to a quartz tube furnace and pretreated by heating to the desired temperature for 30 min. After cooling to below 100 °C, samples were moved to an exposure chamber. Samples were heated to ~60 °C and positioned ~2 cm from an evaporator containing the perylene-3-methanol (P3M) precursor, along with a small amount of perylene-3-methanamine (P3A) catalyst, which is necessary to obtain high bound fluorophore densities.[1] The evaporator was heated to from ~60 – 100 °C, depending on the desired fluorophore coverage. Exposure times of 30 – 90 min were used, again depending on the desired fluorophore coverage. The highest evaporator temperatures and longest exposure times were used to achieve nearly complete titration of free hydroxyl sites using the P3M precursor. At the end of the exposure time, the evaporator was turned off and the sample temperature was increased to ~100 °C for ~15 min, in an attempt to remove some of the physisorbed material and reduce contamination in the rest of the vacuum system.

After the exposure step, samples were moved in front of the photoluminescence (PL) assembly for in situ emission measurements. Samples were then moved into the tube furnace and annealed at 300 °C for 30 min to remove any residual physisorbed molecules. After cooling, a second emission measurement was collected.

The *in situ* PL assembly consists of a 405 nm continuous wave diode laser with an output power of 20mW (CrystalLaser) and a spectrometer (Ocean Optics QE6500) attached to separate lenses using fiber optics. The lenses are mounted in front of a viewport and are focused on the sample inside the UHV system with a spot size of ~1 mm^2. Spectra were collected with a 0.25 s integration time and averaged over three scans.

Although only very low densities of fluorophores are attached to the backside of the samples,[1] these low densities can still produce fluorescent emission that contributes to the signal. In order to eliminate the signal from the back of the sample, samples were moved to a separate chamber

in which a tungsten filament was positioned ~2 cm from the back of the sample. Atomic deuterium was generated by introducing 1×10^{-6} torr deuterium into the chamber and heating the tungsten filament to ~1500 K for 15 min.[2] Sample temperatures were estimated to reach ~150 °C during this process. After the atomic deuterium exposure, an additional *in situ* emission measurement was collected. This final *in situ* measurement is used for the spectra presented herein.

Ex situ fluorescence emission, excitation, and lifetime measurements were performed using a Fluorolog3 Fluorimeter (Horiba Jobin Yvon). The vacuum vessel was placed inside the instrument so that viewports were facing the excitation source (Xenon lamp) and the detector (photomultiplier tube), at a right angle from each other. The sample inside the vessel was positioned ~30° from the detector normal. All measurements were performed using a 5 nm spectral bandwidth and an integration time of 0.5 s. Corrected spectra were recorded by dividing the photomultiplier tube signal by the excitation reference signal and applying the correction factors supplied by the manufacturer. Time-correlated single photon counting was used to measure the decay profiles and record time-resolved emission spectra. A 405 nm pulsed light-emitting diode (LED) with a 1 MHz repetition rate and pulse width < 250 ps was used as the excitation source. After all fluorescence measurements were complete, the sample was removed from the vacuum vessel. An absorption spectrum was collected using a Cary 5000 UV-Vis Spectrometer with the beam normal to the sample surface. A 2 nm spectral bandwidth and 0.5 s dwell time were used during the collection and baseline subtraction was performed using a clean fused silica wafer.

Both steady-state and fluorescence decay measurements collected using a magic angle polarizer configuration were nearly identical to unpolarized measurements, as shown in Figure S1. The use of polarizers greatly reduces the intensity of light reaching the detector, requiring significantly longer measurement times, which introduces greater noise levels in the measurements. As no differences were observed between the magic angle polarized and unpolarized measurements, only unpolarized measurements are presented herein.

Results

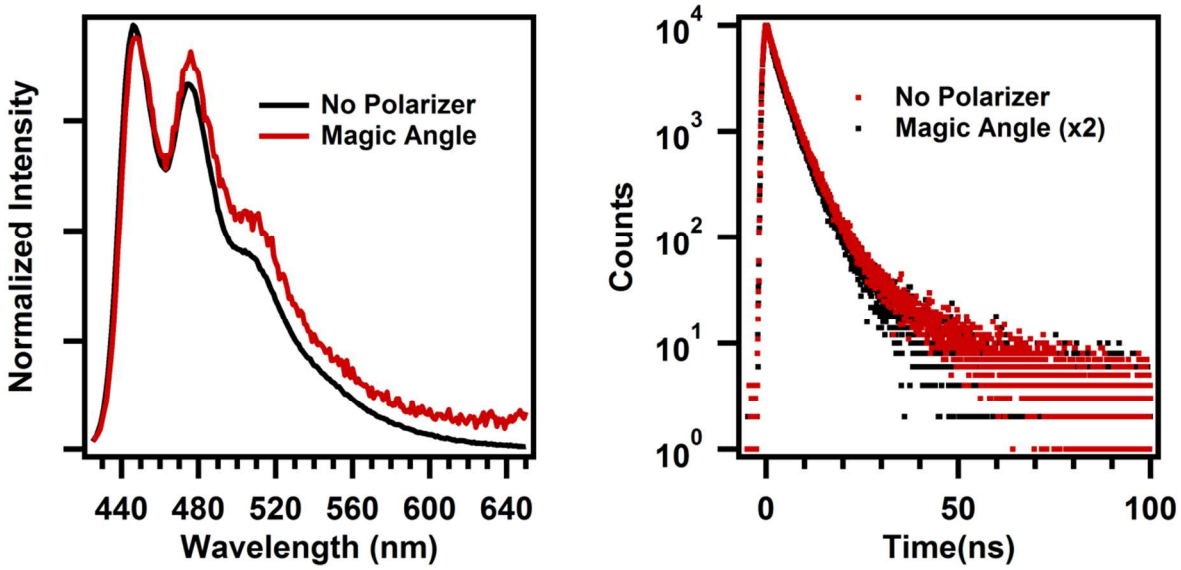

Figure S1. *Ex situ* emission spectra (Left) and fluorescence decay curves (Right) from 0.08 P3M / nm^2 sample collected using either no polarization (Unpolarized) or with a polarizer set at 0° between excitation monochromator and sample and a polarizer set at 55° between sample and detector monochromator (Magic Angle). Both the steady-state and time-resolved measurements appear nearly identical between the two settings. The decay curve collected using magic angle polarizer settings was scaled by a factor of two, due to the very low hit rate obtained with polarizers in place.

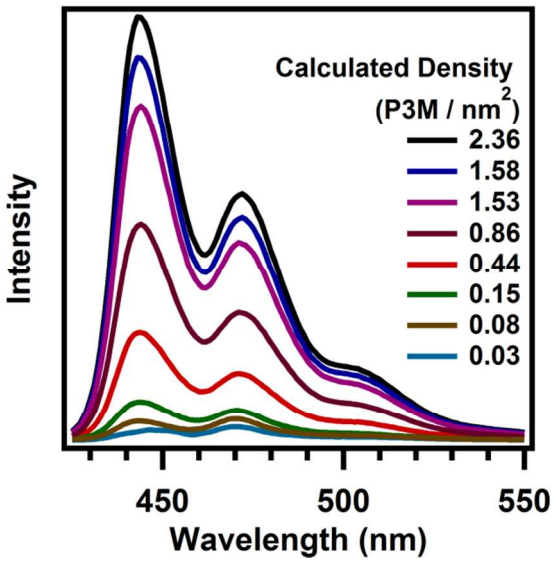

Figure S2. Fluorescence spectra from solutions prepared by removing P3M molecules from sample surfaces that had been cleaved from the center of the sample, to ensure molecules adsorbed on the edges did not contribute. The cleaved wafers were generally approximately 0.9 cm × 0.9 cm; however, the final dimensions of each sample were measured and used in the calculations. The error in the density measurements is estimated to be less than 10% of the calculated value.

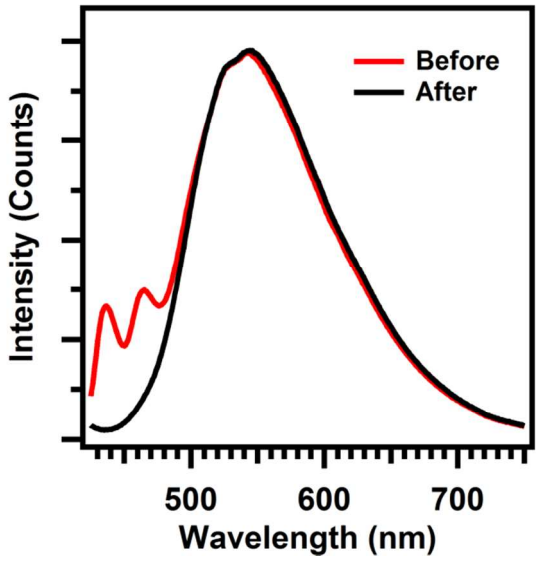

Figure S3. *In situ* emission spectra collected before and after the backside of the sample was exposed to atomic deuterium generated on a hot tungsten filament. The low wavelength features

are attributed to low densities of fluorophores (monomer emission) on the back of the sample, which are eliminated by the atomic deuterium exposure.

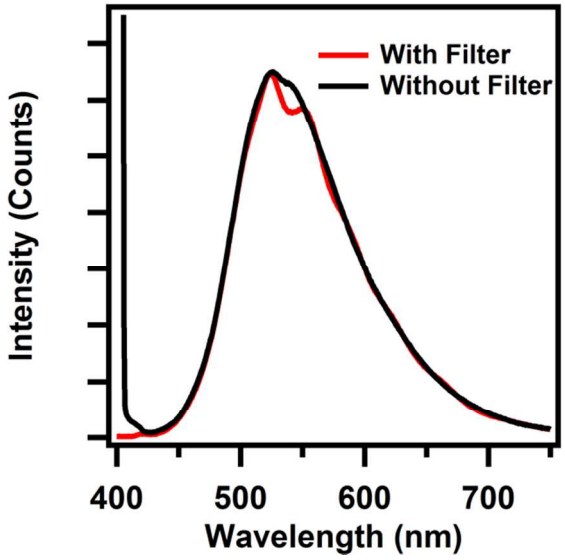

Figure S4. *In situ* emission spectra collected with our without 425 nm long-pass filter in place, showing the artifact around 550 nm due to the filter.

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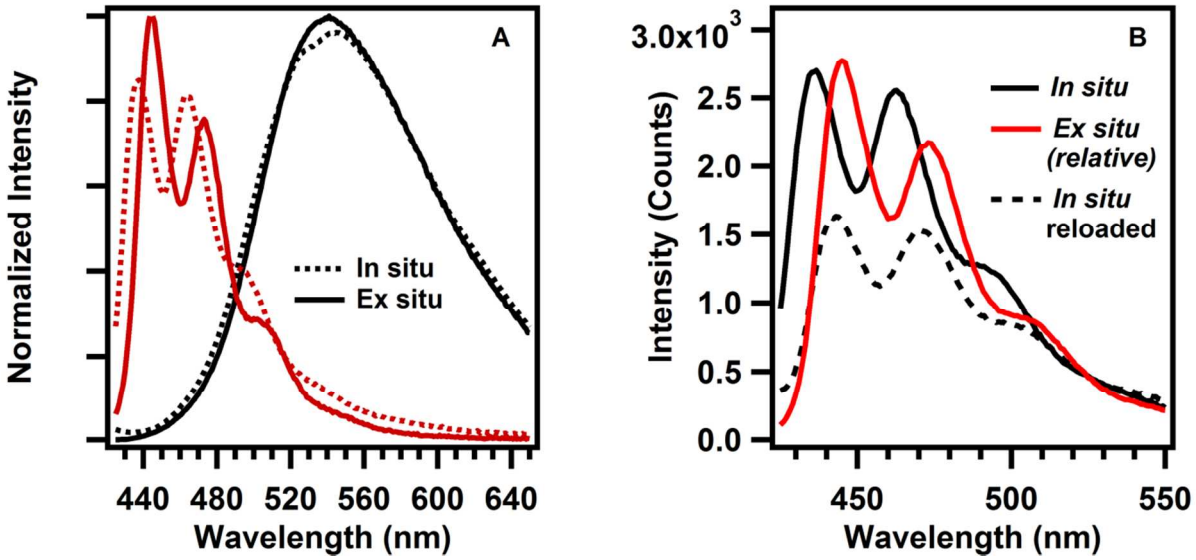


Figure S5. (A) Normalized *in situ* and *ex situ* emission spectra from low density (red line) and high density (black line) samples. **(B)** *In situ* emission spectra from sample collected after P3M exposure process (*In situ*) and after reloading sample back into vacuum system after *ex situ*

measurements (*In situ* reloaded). The relative *ex situ* emission spectrum is shown for comparison.

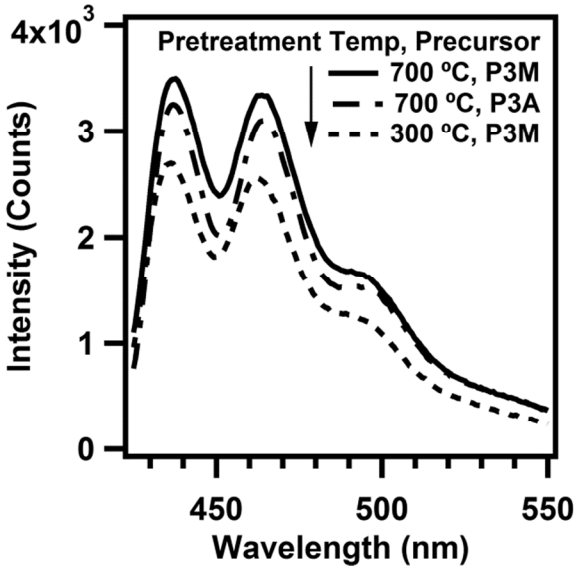


Figure S6. *In situ* emission spectra from samples pretreated at either 300 or 700 °C with low densities of bound P3M or P3A molecules. The 700 °C pretreated samples with P3M and P3A had densities of approximately 0.03 nm^{-2} and the 300 °C pretreated samples with P3M had a density of approximately 0.02 nm^{-2}. These results suggest that the density of hydroxyl sites does not significantly influence fluorescence emission. Both the ≡Si-O-R and ≡Si-NH-R species, where R is the remainder of the probe molecule, appear to yield similar emission spectra. This indicates the presence of the one-carbon tether effectively decouples the electronic properties of the perylene moiety from the functional group used to bind to the surface. A similar conclusion was reached for pyrene covalently attached to silica with a one-carbon tether.[3]

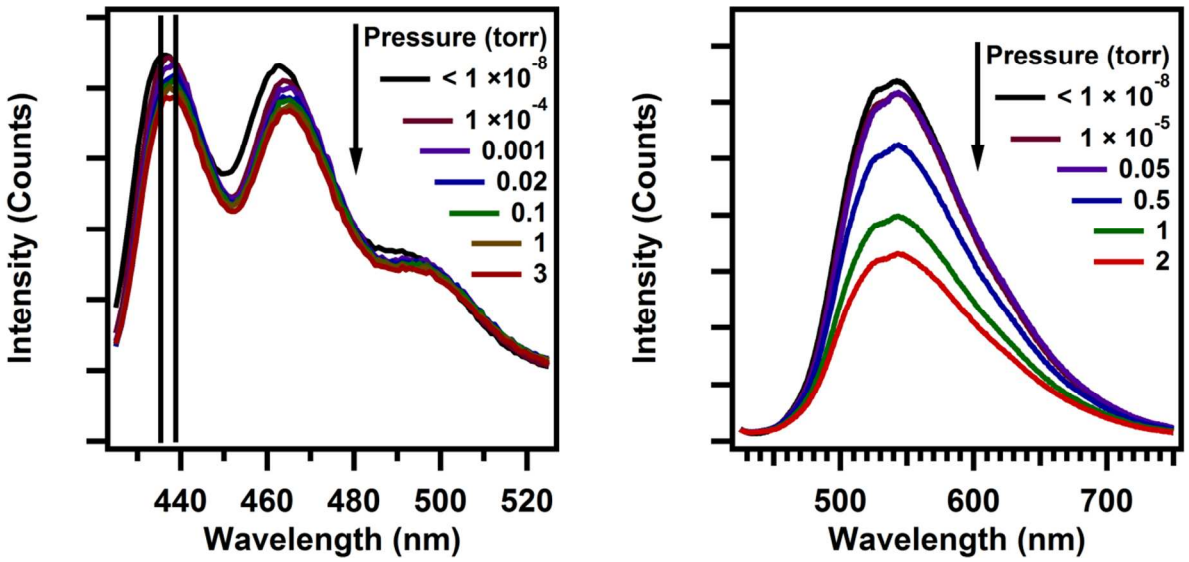


Figure S7. *In situ* emission spectra from samples displaying monomer (left) and excimer-like (right) emission collected at various chamber pressures. Pressures were increased by isolating pumps and leaking in air. Monomer emission displays a slight shift in the position of the vibronic peaks when the pressure is increased to 10^{-4} torr, and the intensity decreases only slightly with pressure up to 3 torr. The position of the excimer-like peak does not change with pressure, but the intensity decreases by approximately half between the $< 10^{-8}$ torr and 2 torr measurements. However, *ex situ* measurements were performed with pressures below 15 mtorr, so that little fluorescence quenching is expected for either sample at this pressure.

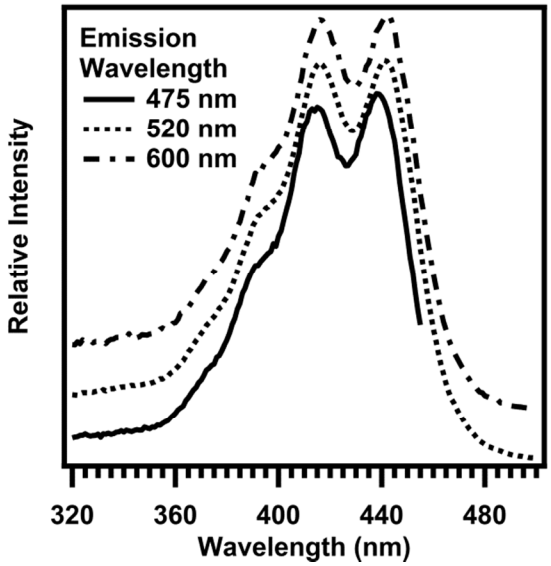


Figure S8. Excitation spectra at various emission wavelengths from sample with P3M density of 0.86 nm^{-2} showing that the feature shapes and positions are independent of emission wavelength. This indicates only one absorbing species is present in the system.

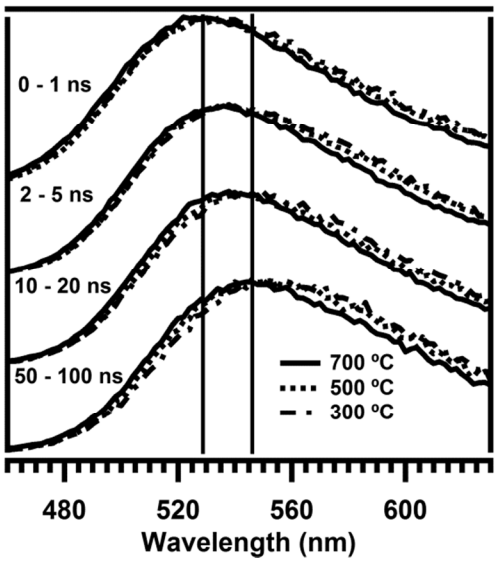


Figure S9. Normalized time-resolved emission spectra from samples pretreated to various temperatures and given high P3M exposures. The densities of the 300, 500, and 700 °C pretreated samples were found to be 1.58, 1.53, and 0.86 P3M / nm^2, respectively.

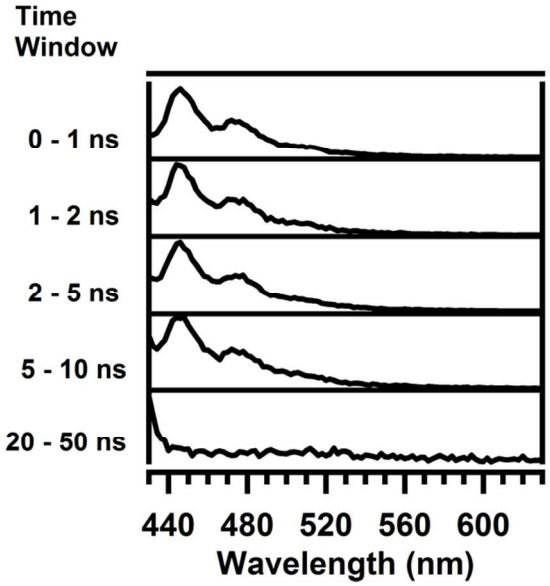
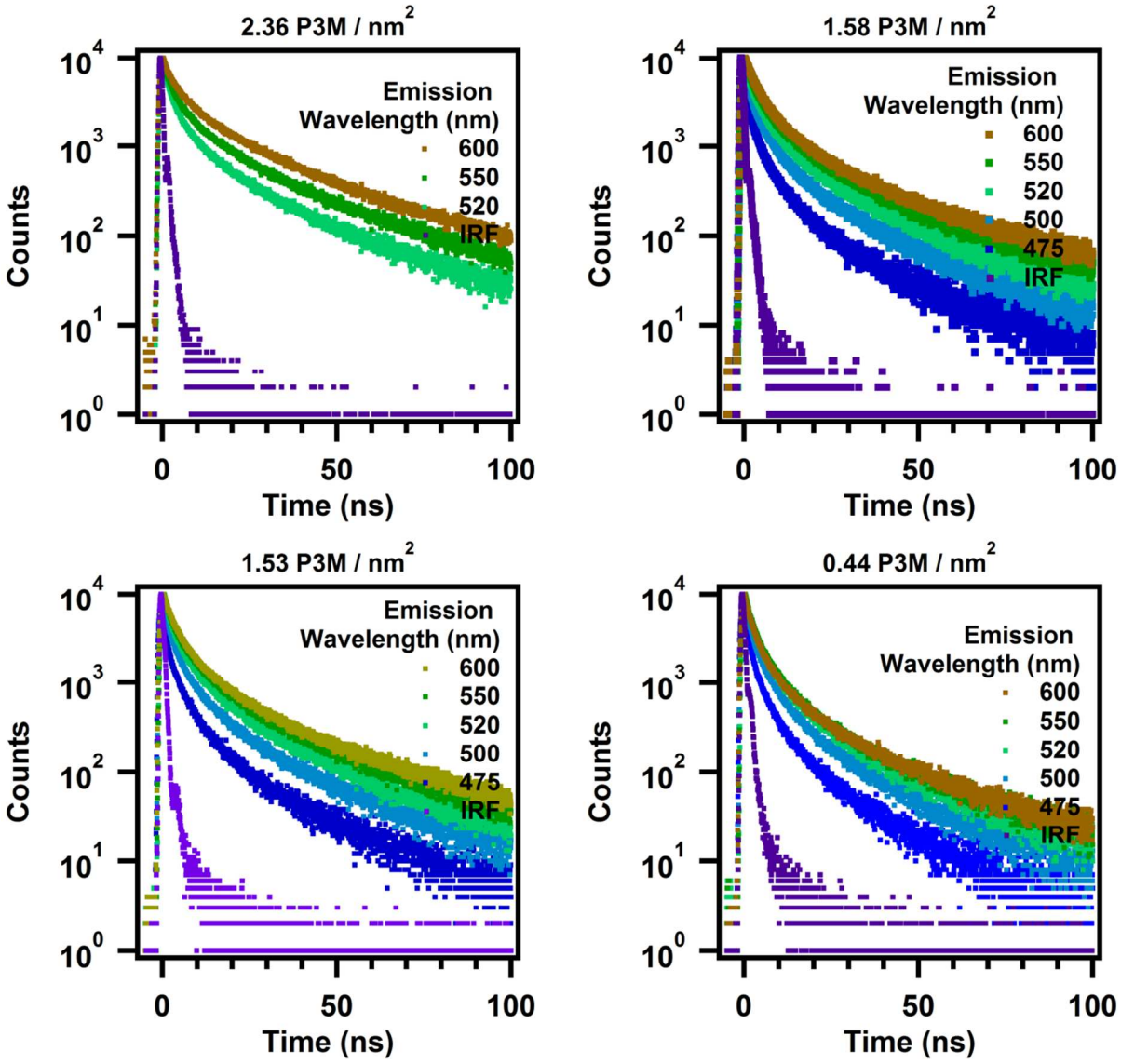


Figure S10. Time-resolved emission spectra from the sample with 0.03 P3A / nm^2 showing only monomer emission in all time windows. Essentially no signal is observed in the latest time window.


2.36 P3M / nm2
1.58 P3M / nm2
1.53 P3M / nm2
0.44 P3M / nm2
Emission
Wavelength (nm)
600
550
520
500
475
IRF
Counts
Time (ns)
0
50
100

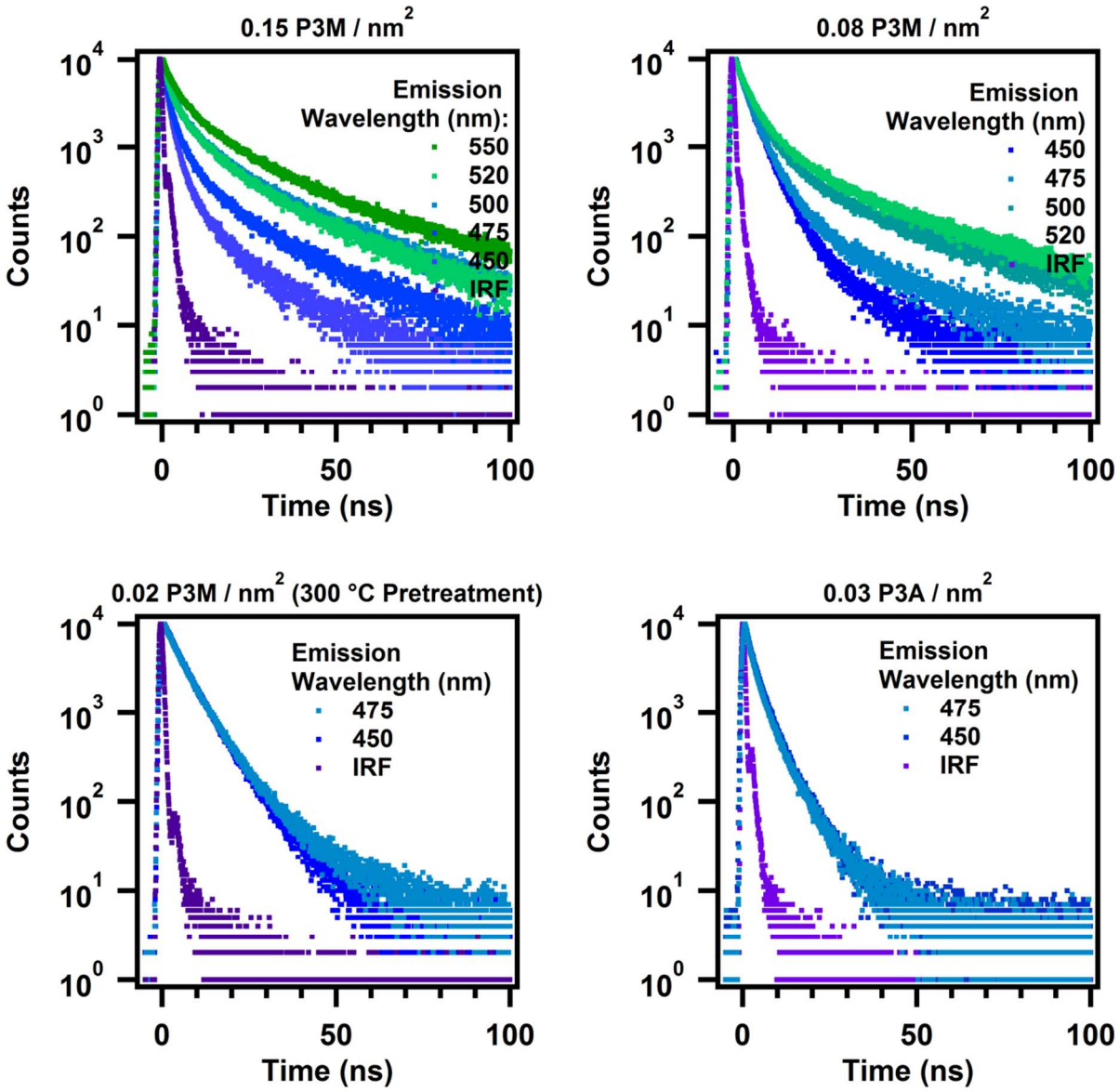


Figure S11. Fluorescence decay profiles from samples with various fluorophore densities.

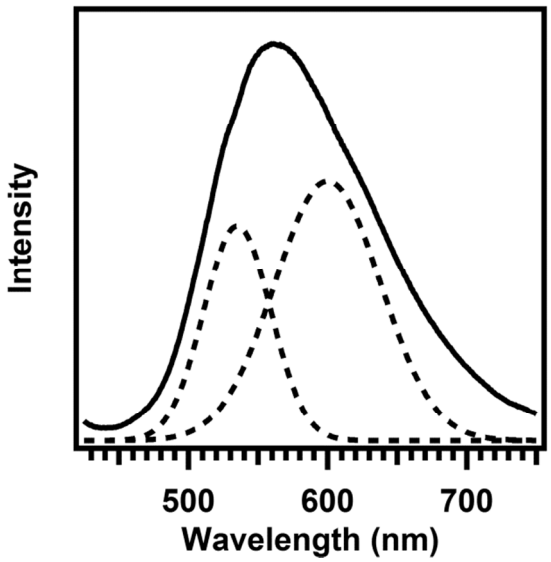


Figure S12. Deconvoluted emission spectrum from a sample with physisorbed material (2.36 P3M / nm^2) showing large contribution from a fully relaxed (600 nm centered) emission feature. The integrated intensity is approximately two-thirds attributed to fully relaxed emission and one-third attributed to emission from a partially relaxed species. The contribution from fully relaxed species is significantly larger than from samples with chemically bound P3M (maximum density of 1.56 nm^{-2}).

Relative quantum yields of excimer and monomer species:

The ratio of the excimer quantum yield to the monomer quantum yield can be estimated by comparing the intensities of samples exhibiting only monomer emission and only excimer-like emission. In the limit of low absorbance, the integrated fluorescence intensity, $I_F(\lambda_E)$, is given by:

$$I_F(\lambda_E) \cong 2.3k\Phi_F I_0(\lambda_E)A(\lambda_E) \quad (1)$$

where Φ_F is the quantum yield, $I_0(\lambda_E)$ is the intensity of the exciting light with wavelength λ_E, $A(\lambda_E)$ is the absorbance of the system at wavelength λ_E, and k is a factor accounting for the configuration of the detector.[4] The ratio of the excimer fluorescence quantum yield to the monomer fluorescence quantum yield can be obtained from Equation (3):

$$\frac{\Phi_F^{Ex}}{\Phi_F^{M}} = \frac{I_F^{Ex}(\lambda_E)}{I_F^{M}(\lambda_E)} \frac{A^{M}(\lambda_E)}{A^{Ex}(\lambda_E)} \quad (2).$$

In order to estimate this ratio, spectra from the 0.08 and 0.44 P3M / nm^2 samples were used. These samples were chosen because the former exhibited only monomeric emission and the latter only excimer emission. The *in situ* emission spectra from each sample were integrated, providing the relative integrated fluorescence intensities in Equation (2). The absorption ratio requires further consideration. Because the excitation source for the *in situ* emission spectra is a laser, only the ratio of the monomer and excimer absorbance at the laser wavelength (405 nm),

corresponding to the $S_0 \rightarrow S_1$ transition, is relevant for these calculations. As shown in Figure 4 in the text, samples exhibiting either monomer or excimer-like emission have very similar absorbance features. In principle, the relative absorbance term should be equal to the ratio of fluorophore densities for such a dilute system of absorbers; however, caution must be exercised in this analysis as the preferential alignment of molecules leads to a limiting value of absorbance in this system. Although the absorbance from the 0.08 P3M / nm^2 sample was too low to be detected, the absorbance of the weak feature from the 0.15 P3M / nm^2 sample, which exhibits a combination of monomer and excimer-like emission, can be compared with the absorbance of the 0.44 P3M / nm^2 sample to determine if a linear relationship between fluorophore density and absorbance is valid for the latter sample. The ratio of the absorbance features from the 0.15 and 0.44 P3M / nm^2 samples is close to the ratio of their densities, suggesting that the absorbance ratio in Equation (4) can be approximated by the ratio of fluorophore densities for the 0.08 and 0.44 P3M / nm^2 samples. Based on this analysis, the estimated ratio of the excimer fluorescence quantum yield to the monomer fluorescence quantum yield, Φ_F^{Ex}/Φ_F^M, is approximately 1/3, demonstrating that the excimer quantum yield is significantly lower than the monomer quantum yield, as anticipated. Because of the preferential alignment of fluorophores at higher densities, the ratio of absorbance features to density would not continue to be linear, complicating the analysis for these samples.

References

(1) McCrate, J.; Ekerdt, J. Titration of Free Hydroxyl and Strained Siloxane Sites on Silicon Dioxide with Fluorescent Probes. *Langmuir* **2013**, *29*, 11868–11875.

(2) Salivati, N.; Ekerdt, J. G. Temperature programmed desorption studies of deuterium passivated silicon nanocrystals. *Surf. Sci.* **2009**, *603*, 1121–1125.

(3) Mazur, M.; Blanchard, G. Probing intermolecular communication with surface-attached pyrene. *J. Phys. Chem. B* **2005**, *109*, 4076–4083.

(4) Valeur, B. *Molecular Fluorescence*; Wiley-VCH Verlag: Weinheim, 2002.