Supporting Information for:

Polymer Matrix Dependence of Conformational Dynamics within π-Stacked Perylenediimide Dimer and Trimer Revealed by Single Molecule Fluorescence Spectroscopy

Hyejin Yoo,[a] Hee Won Bahng,[a] Michael R. Wasielewski*[b] and Dongho Kim*[a]

a Spectroscopy Laboratory for Functional π-Electronic Systems

and Department of Chemistry

Yonsei University

134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, Korea

* E-mail : *dongho@yonsei.ac.kr*

b Department of Chemistry, Center for Nanofabrication and Molecular Self Assembly,

Materials Research Science and Engineering Center,

and Argonne-Northwestern Solar Energy Research (ANSER) Center,

Northwestern University, Evanston, Illinois 60208-3113, USA

* E-mail: *m-wasielewski@northwestern.edu*

Experimental Details for Time-Correlated Single Photon Counting System

A picosecond time-correlated single photon counting (TCSPC) system was used for time-resolved fluorescence decay measurements. As an excitation light source, we used a homemade cavity-dumped Ti:sapphire oscillator which provides a high repetition rate (200-400 kHz) of ultrashort pulses (100 fs at full width at half-maximum (fwhm)) pumped by a continuous wave (cw) Nd-YVO4 laser (Spectra Physics, Millennia). The second-harmonic of the fundamental beam was generated in a 1 mm thick BBO crystal and served as an excitation source. The residual beam was used as a trigger source detected by a fast photodiode. The excitation beam was focused onto a 10 mm thick cuvette containing the sample solution using a 5 cm focal length lens with s-polarization. The fluorescence from the sample was collected and focused onto a monochromator (Acton Research) by a 2″ plano-convex lens pair and detected using a microchannel plate photomultiplier tube (Hamamatsu). The full width at half-maximum (FWHM) of the instrument response function obtained by a dilute solution of coffee cream (diffuser) was typically ~70 ps in our TCSPC system. The decay fittings were determined using a least-squares deconvolution process (LIFETIME program with an iterative nonlinear least-squares deconvolution procedure developed at the University of Pennsylvania).[S1]

**Table S1.** Comparison of two polymer matrices.[S2]

	PMMA	PBMA
	poly (methyl methacrylate)	poly (n-butyl methacrylate)
structure	$-[CH_2-\underset{\underset{CH_3}{\overset{\overset{CH_3}{\|}}{\|}}{\overset{C=O}{\underset{O}{\|}}}]-$	$-[CH_2-C]-$
T_g	105 ℃	15 ℃

***Table S2.*** Fluorescence lifetimes and corresponding amplitudes of PDI **2** and **3** at each wavelength.

| | fluorescence decay times (ns) and relative amplitudes (%) of **2** | | | | | | | |
| | in PMMA | | | | in PBMA | | | |
λ_{em} (nm)	τ_1	τ_2	τ_3	X^2	τ_1	τ_2	τ_3	X^2
565	2.4 (13)	12.3(47)	30.0(40)	1.02	2.5 (36)	6.1(53)	28.6(11)	1.08
600	2.9(13)	13.0(44)	32.9(43)	1.12	4.0 (58)	9.5(23)	33.6(19)	1.01
650		12.0(40)	37.3(60)	1.06	3.8(44)	9.8(24)	39.6(32)	1.09
700		11.9(26)	39.4(74)	1.03	4.6 (34)	10.1(12)	41.6(54)	1.09
720		9.8(24)	39.5(76)	1.00	4.5 (27)	8.9(13)	41.9(60)	1.09

| | fluorescence decay times (ns) and relative amplitudes (%) of **3** | | | | | | | |
| | in PMMA | | | | in PBMA | | | |
λ_{em} (nm)	τ_1	τ_2	τ_3	X^2	τ_1	τ_2	τ_3	X^2
570	2.6 (16)	15.7(33)	38.5(51)	1.01	3.9(53)	8.4(38)	33.9(9)	1.05
600	1.3(10)	11.9(25)	39.3(65)	1.00	3.5(34)	7.1(53)	35.2(13)	1.13
650	1.6 (5)	11.4(21)	42.1(74)	1.00	3.8(40)	9.0(32)	39.8(28)	1.09
700		9.3(18)	44.6(82)	1.40	2.2(14)	9.7(19)	46.3(67)	1.04
720		7.6(16)	44.0(84)	1.49	2.3(16)	10.5(17)	46.0(67)	1.16
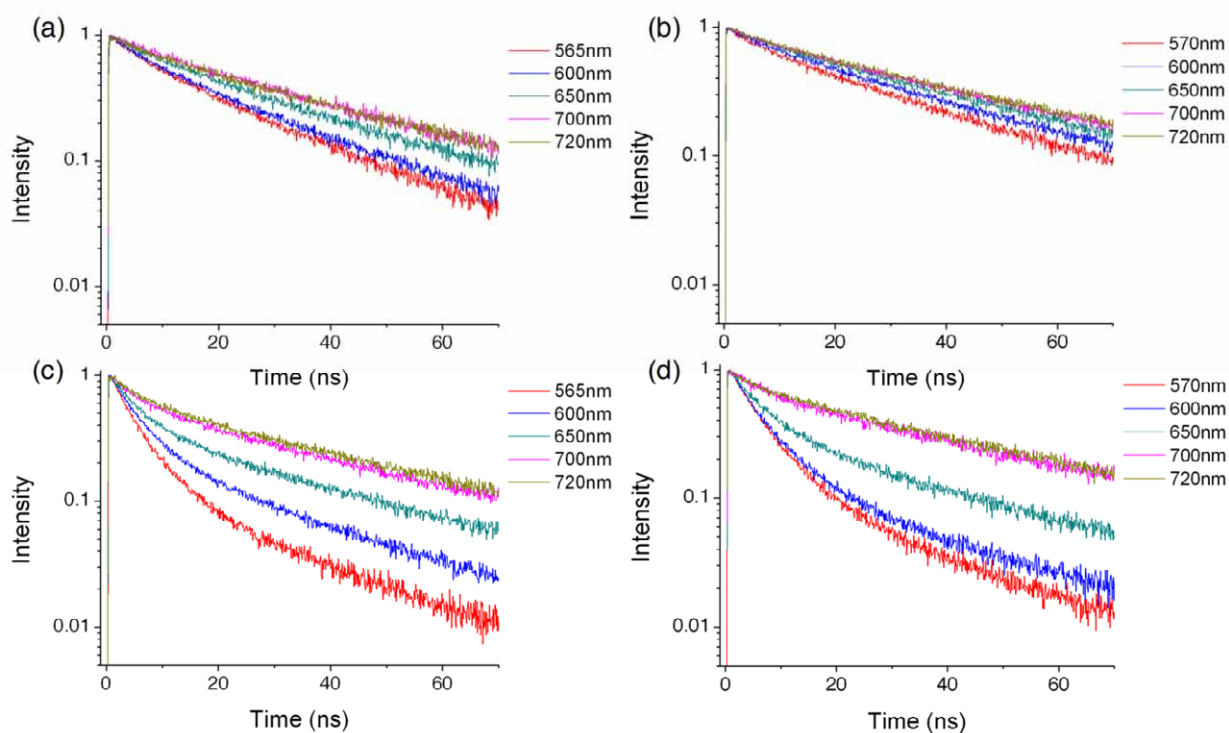
Figure S1. Fluorescence decay profiles of (a) **2** and (b) **3** in the PMMA and (c) **2** and (d) **3** in the PBMA matrices (λ_{ex} = 420 nm). The fitted fluorescence lifetimes and the portion of each component are presented in Table S2. Short fluorescence lifetimes (τ < 5 ns) mainly shown at short wavelength region correspond to the monomer state of **2** and **3**. When PDI units of **2** and **3** interact strongly, they show long excimer lifetimes (τ > 30 ns). Besides, the partially overlapped molecular structure leads to the excimer-like state that is energetically less stable than that having the optimal geometry, thus the fluorescence lifetime (τ ≈ 10 ns) from this state is shorter than the long excimer lifetime.[S3] Over all wavelength regions, the components for monomer fluorescence increase remarkably in the PBMA matrix than in the PMMA matrix. In addition, the dimer state of **3** was not resolved in the bulk measurements unlike the single molecule measurements.
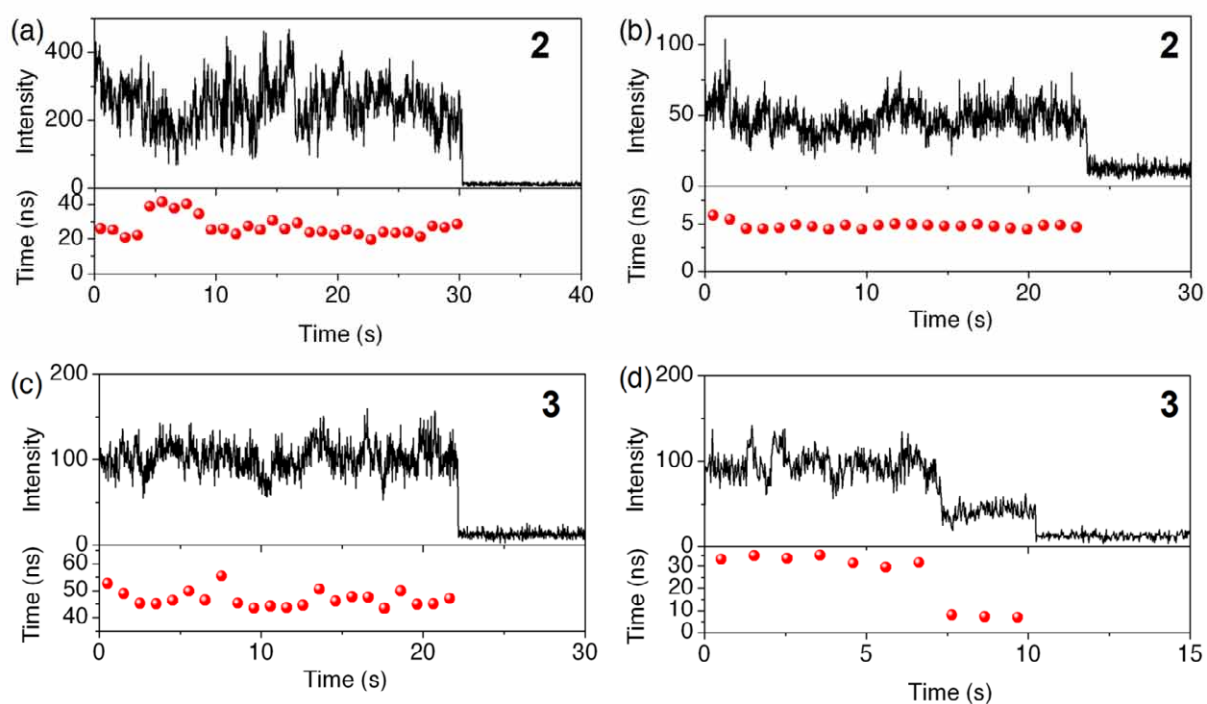
Figure S2. The representative fluorescence intensity and lifetime trajectories of **2** and **3** measured in the PBMA matrix. Both PDI **2** molecules as seen in (a) and (b) show one-step photobleaching processes, however, the molecular conformations are different: (a) one exhibits the fluorescence lifetime of excimer-like state and strongly fluctuated fluorescence intensity trace and (b) the other shows the fluorescence lifetime of monomer and relatively stable fluorescence intensity trace. PDI **3** molecule displayed in (c) shows one-step photobleaching behavior with fluorescence from the excimer-like state and PDI **3** in (d) shows stepwise photobleaching behavior with change of fluorescence lifetime from the excimer-like trimer to monomer state after photobleaching of two PDI units.
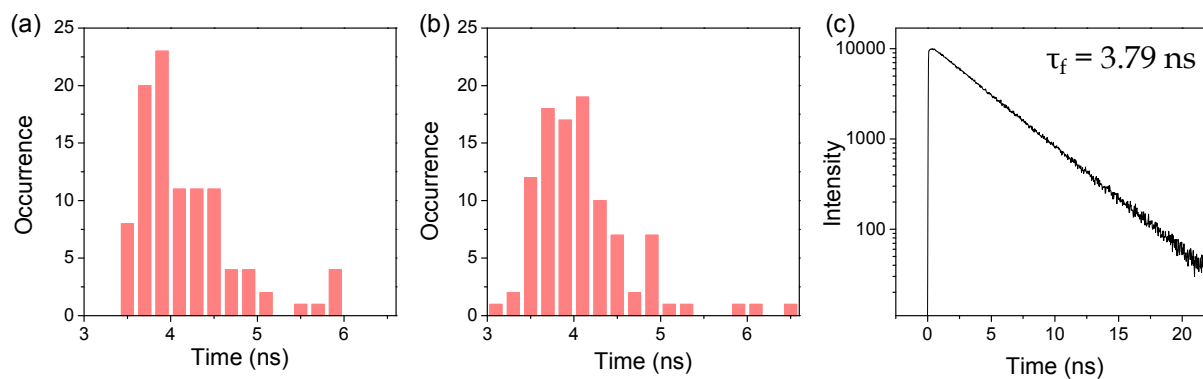
Figure S3. Initial fluorescence lifetime distributions of single molecules **1** in PMMA (a), PBMA (b) polymer matrices and bulk in toluene (c). The fluorescence lifetime fitting in each FIT for the first 1 s is regarded as an initial fluorescence lifetime of the molecule (a, b). The arithmetic mean values of individual initial fluorescence lifetime distributions for 100 single molecules are 4.17 and 4.09 ns in the PMMA and PBMA matrices, respectively.
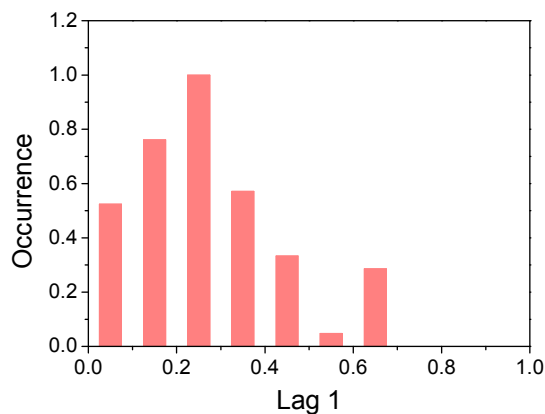
Figure S4. Normalized histogram of lag 1 values of monomer (PDI **1**) in the PBMA matrix. As most molecules of **1** show stable fluorescence intensity trajectories, they show small lag 1 values, like in the monomer state in 2.

References

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(S2)   R. A. L. Vallée, M. Cotlet, M. Van Der Auweraer, J. Hofkens, K. Müllen and F. C. De Schryver, *J. Am. Chem. Soc.* 2004, **126**, 2296.

(S3)   H. Yoo, J. Yang, A. Yousef, M. R. Wasielewski and D.Kim, *J. Am. Chem. Soc.* 2010, **132**, 3939.