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Excimer Formation Dynamics of Intramolecular π-Stacked Perylenediimides Probed by Single-Molecule Fluorescence Spectroscopy

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Abstract: π-Stacked perylenediimides (PDIs) have strong electronic communication between the individual molecules and show great promise as organic electronic materials for applications in field effect transistors, photovoltaics, and liquid crystal displays. To gain further insight into the relationship between conformational behaviors and electronic structures of π-stacked PDIs, we have investigated changes in the excimer-like state of cofacial PDI oligomers that result from π-stacking in real time by monitoring the single-molecule fluorescence intensity and lifetime trajectories in a PMMA polymer matrix. The fluorescence intensity and lifetime of π-stacked perylenediimides are sensitive to the degree of π-orbital interactions among PDI units, which is strongly associated with molecular conformations in the polymer matrix. Furthermore, our results can be applied to probe the conformational motions of biomolecules such as proteins.

Introduction

Multichromophoric arrays have recently received appreciable attention, owing to their utility as energy or charge transport materials for artificial light harvesting systems,[1−3] organic field effect transistors (OFETs),[4−7] and solar cells.[8] Accordingly, various molecular assemblies have been designed to construct effective electronic and photonic molecular devices, among which aromatic $\pi-\pi$ stacks are one of the most promising architectures to be implemented in electron transport materials such as n-type semiconductors.[9−12] In particular, perylenediimide (PDI) derivatives have proven to be good candidates for valuable π-stacked nanoobjects[13−15] because of their high photostability, electron affinity, and fluorescence emission.[16,17]

A recent example uses a xanthene group to align π-stacked PDIs in parallel to preserve the rigid cofacial structures (Chart 1). In these molecules, neighboring chromophores in close proximity give rise to strong electronic communication between them in both their ground and excited states. Upon photoexcitation of the PDIs in dimer **2** and trimer **3**, formation of an excimer-like state occurs. We use the term excimer-like because the PDIs in these molecules also interact in their ground states, unlike conventional excimers. The basic photophysical properties of these cofacial PDIs in solution have been investigated independently by Giaimo et al.[18] and Veldman et al.[19] These ensemble average measurements, however, conceal the unique behavior of each molecule: e.g., time traces and distributions of single molecules. In this work, the fluorescence dynamics of cofacial PDIs were probed in the solid state by single-molecule

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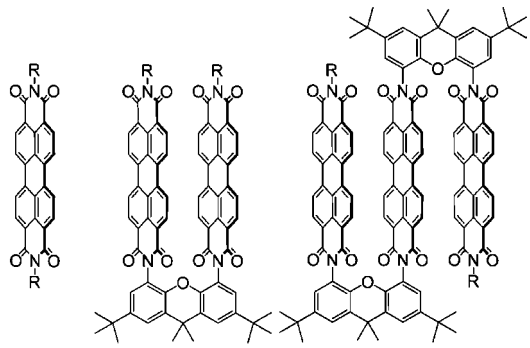
Chart 1. Molecular Structures of Cofacial PDIs



fluorescence microscopy which provides information on the complex processes of excimer-like state formation within individual molecules of dimer **2** and trimer **3**.

Experimental Section

Sample Preparation. A detailed description of the synthesis of **1**−**3** is reported in a previous paper.[18] Samples for single-molecule spectroscopic measurements were prepared by spin-coating (2000 rpm) a solution of cofacial PDI ($\sim 10^{-10}$ M) in chloroform containing 10 mg/mL poly(methyl methacrylate) (PMMA, Aldrich) onto thoroughly cleaned glass coverslips.

Single-Molecule Spectroscopy. A confocal microscope system based on the inverted-type microscope, coupled to a picosecond pulsed 470 nm diode laser (10 MHz repetition rate, pulse width <90 ps, PicoQuant), was employed for the detection of fluorescence of single molecules. The collimated, linearly polarized laser beam was sent to the input port of the confocal microscope after passing a beam expander to make the beam size large enough at the back focal plane. Then the laser beam was reflected by a dichroic mirror (Chroma Technology Corp., z470rdc) and focused onto the sample through an oil-immersion objective lens (100×, N.A. = 1.3, Nikon) at an average power of 0.5 μW. Fluorescence was collected by the same objective lens, passed through a dichroic mirror, cleaned with a notch filter (Kaiser Optical System, 470 nm) and long-pass filters (Chroma Technology Corp., HQ488LP), and focused through a 100 mm focal length lens into an active area of an avalanche photodiode (SPCM-AQR-16-FC, EG&G, Perkin-Elmer Optoelectronics) (APD). The sample positions were controlled using a piezoelectric tube scanner (XE-120, Park Systems). The signal from APD was delivered into a TCSPC card (SPC-830, Becker & Hickl GmbH, Germany) operated in FIFO (first-in-first-out) mode, which can construct the fluorescence intensity trajectory with a specific bin time and fluorescence decay profiles with an experimental instrument response of 500 ps. We have applied a binning time of 20 ms to acquire a sufficient signal-to-noise ratio in the FITs.

With a BIFL (burst-integrated fluorescence lifetime) data analyzer, we could extract a group of photons every 1 s. Because of the small number of emitted photon counts during short times, we bound up the photons from 16 channels of 4096 channels into one part and fitted by the maximum likelihood estimation (MLE) method, which provides a reasonable lifetime fit at low fluorescence intensity.[20,21] All the fluorescence lifetimes were fitted with single-exponential decay functions.

Ensemble Spectroscopy. Steady-state absorption spectra were taken in a UV−vis−near-IR spectrometer (Cary Model 5000, Varian), and steady-state fluorescence spectra were obtained in a fluorescence spectrometer (Model F-2500, Hitachi) at an excitation wavelength of 490 nm. All spectra were measured in toluene (Aldrich, anhydrous, ≥99.9%, spectrophotometric grade). A picosecond time-correlated single photon counting (TCSPC) system was used for time-resolved fluorescence decay measurements. The system consisted of a cavity-dumped Kerr lens mode-locked Ti:sapphire laser pumped by a continuous wave Nd:YVO_4 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 ($\sim 10^{-4}$ M) using a 50 mm focal length lens with s-polarization. The fluorescence from the sample was collected and focused onto a monochromator (Acton Research) by a 2 in. 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 ~50 ps in our TCSPC system.

Results and Discussion

The structures of PDI monomer **1**, cofacial dimer **2**, and trimer **3** with branched alkyl chain substituted imide groups are shown in Chart 1. H-type exciton coupling between the PDIs results in stronger absorption to the higher energy exciton state, as seen in the UV−vis spectra of **2** and **3**. Relaxation to the lower exciton state followed by formation of an excimer-like state red-shifts their fluorescence spectra and results in broad and structureless emission features (Figure S1 in the Supporting Information).[22,23] Furthermore, multiexponential fluorescence decay components (e.g., $\tau_1 = 0.87$ ns, $\tau_2 = 27.4$ ns at 700 nm emission for **2**), which are associated with dimer-like[24] and excimer-like states, respectively, have been extracted (Figure 1, Table 1, and Figures S2 and S3 in the Supporting Information). The contribution of τ_1 components in solution is larger than in the solid state at shorter wavelengths.

We have measured the fluorescence lifetimes of **2** and **3** embedded in a PMMA matrix using the TCSPC technique with an excitation wavelength of 420 nm. The highlight of the bulk lifetime measurements is the appearance of ~10 ns lifetime components in the solid state, which are not observed in solution. These components have already been reported in previous work on PDI dendrimers[24–26] and PDI foldamers,[27,28] in which neighboring PDIs interact by weak π-stacking and exhibit a fluorescence decay time of 8 ns due to the formation of an

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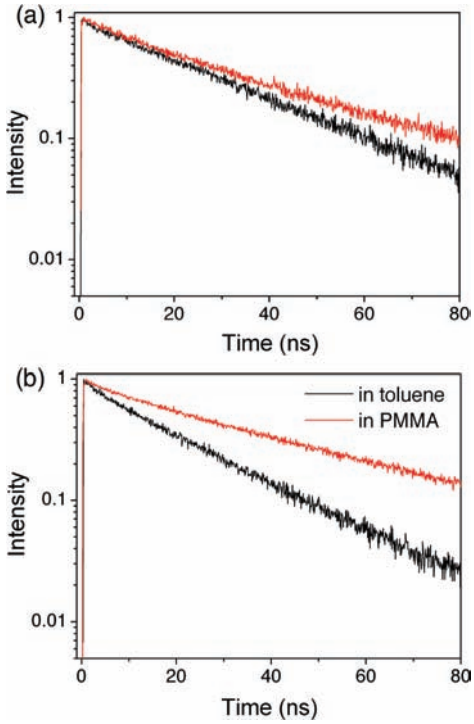

Figure 1. Fluorescence lifetime decay profiles of (a) **2** and (b) **3** in toluene and a PMMA matrix (λ_{ex} 420 nm, λ_{em} 700 nm). The fitted fluorescence lifetimes are presented in Table 1.

Table 1. Fitted Singlet Excited State Fluorescence Lifetimes of **2** and **3** in Each Environment[a]

		fluorescence lifetime (ns) and rel amplitude (%)					
		in soln[b]			in film[c]		
PDI	λ_{em} (nm)	τ_1	τ_m[d]	τ_2	τ_1	τ_2	τ_3
2	600	0.44 (43)	2.9 (17)	27.6 (40)	2.89 (13)	13 (44)	32.9 (43)
	700	0.87 (14)		27.4 (86)		11.9 (26)	39.4 (74)
3	600	1.75 (17)	19.9 (83)		1.62 (5)	11.4 (21)	42.1 (74)
	700			21.6		9.3 (18)	44.6 (82)

[a] λ_{ex} 420 nm. [b] Measured in toluene. [c] Bulk films were prepared by dropping the sample/PMMA solution (toluene) on the slide glass and drying at room temperature. [d] τ_m is added for proper fitting. It might be from a fluorescent monomer PDI impurity.

excimer-like state.[29] Because of structural distortions, the molecular orbitals cannot overlap optimally, and as a consequence, the two PDIs form a weakly coupled excimer-like complex. In the course of this process, the partially overlapped molecular structure leads to an excimer-like state that is energetically less stable than that having the optimal geometry, thus making the fluorescence lifetime from this state shorter than the ~28 ns lifetime of the more completely π-stacked excimer-like state. Indeed, when the molecule is embedded in the polymer matrix, its structure can be held by netlike polymer surroundings for a moment, and then it can change its conformation through tilting the dihedral angle between two or three PDIs.[30] Thus, unlike the case in solution, the decay components arising from weakly interacting chromophores can be revealed in the solid state.

Another interesting point is the comparison between solution- and solid-state lifetimes of the geometry-optimized excimer-like state that are longer than 20 ns. For dimer **2**, the long lifetimes of the strongly coupled excimer-like state in the solid state is 10 ns longer than in solution because the molecules possess a more stable excimer conformation in the polymer matrix. In comparison with that for trimer **3**, the lifetime in the solid state is 20 ns longer than that in solution. More nonradiative decay channels which are present in **3** lead the lifetime to be shorter than that of **2** in solution, as suggested in the previous study. In contrast, the fluorescence lifetime of **3** is longer in the solid state because the conformation of the adjacent three chromophores in **3** can be optimized for strong overlap between molecular orbitals, and then the molecule relaxes to a more stable excimer-like state.

To probe the excimer formation dynamics of cofacial PDIs, we have measured the fluorescence lifetimes and fluorescence intensity trajectories (FITs) of individual **2** and **3** molecules. The representative time traces of the fluorescence intensities and lifetimes of those molecules are shown in Figures 2 and Figure 3. Each fluorescence lifetime in the trace is obtained by fitting fluorescence decay profiles that are constructed from fluorescence photons per each integration time of 1 s.

All the fitted lifetimes in 220 FITs are assembled into a frequency histogram in Figure 2a. The complete lifetime distribution can be categorized into three Gaussian distributions with mean lifetimes of 22.9, 9.6, and 5.4 ns, respectively. The first distribution of lifetimes for the typical excimer-like emission covers the largest area (56%) of the whole histogram because most of the **2** molecules show fluorescence with the excimer-like lifetimes at the first parts of their FITs due to a rapid formation of the excimer-like state upon photoexcitation,[18] as seen in Figure 2b−d. Furthermore, the broad distribution ranging from 10 to 40 ns points out the inhomogeneities of excimers induced by various nanoenvironments in the polymer matrix. In other words, the energy level of the excimer-like state and the corresponding fluorescence lifetime are sensitive to molecular configuration and the degree of overlap between two PDIs. In fact, depending on the conformation determined by the dihedral angle, transverse and longitudinal displacements, and the substituent group in N-imide position of intermolecular PDI aggregates, absorption wavelengths of all local minimum states can vary.[31] In the same manner, emission wavelengths of those excimer-like states are diverse, as discussed in a previous work by Fink et al.[32] Therefore, the broad emission band of the excimer in ensemble measurements and the fluorescence lifetime variation of excimer-like states of single molecules can be attributed to the same reason. Lifetime fluctuations appear in the FITs of the excimer-like states as well: for example, Figure 2b, where a representative FIT with one-step (excimer-step) photobleaching reveals various lifetimes and fluorescence intensity fluctuations which indicate the changeable conformation of the excimer in real time.

The second distribution with a mean lifetime of 9.6 ns is from the excimer-like conformers with relatively poor orbital overlap. Although about half (48%) of the FITs show this behavior, the periods of holding the structure of the distorted conformer are

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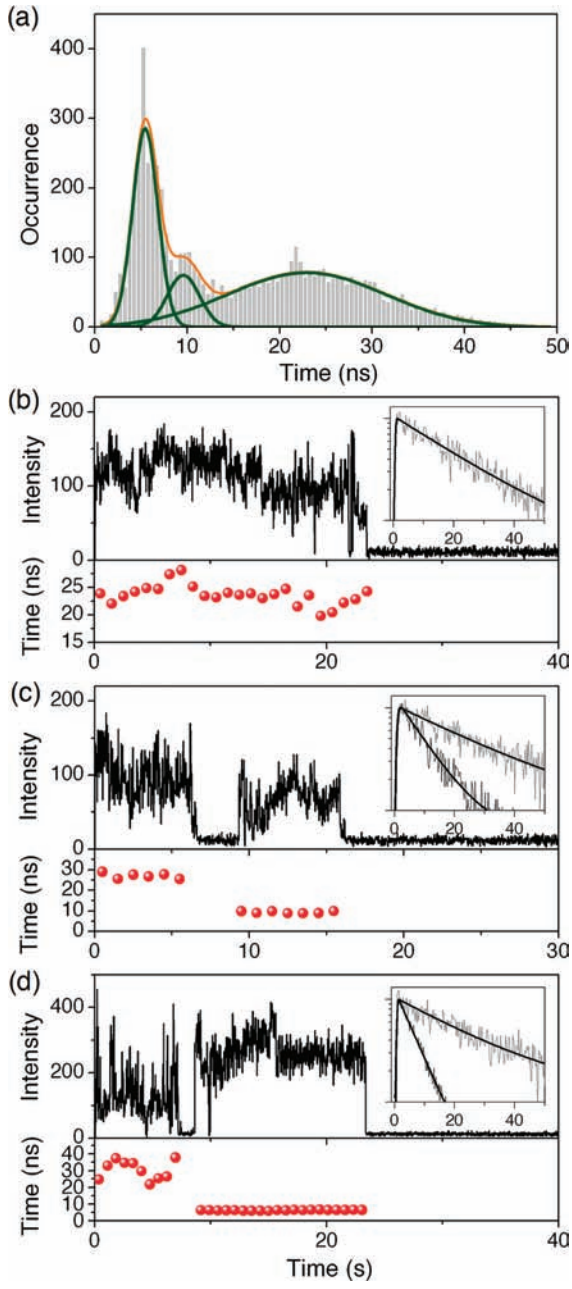


Figure 2. Single-molecule fluorescence behaviors of **2**. (a) Fluorescence lifetime distribution. The histogram consists of all the lifetimes fitted for every 1 s; individual Gaussian peaks are displayed as green curve lines. (b−d) Representative fluorescence intensity trajectories of **2** with their corresponding lifetime decay profiles. The *y* axis in the FIT indicates photon counts per 20 ms. The fluorescence decay profiles have been obtained from a group of photons for 1 s at each molecular state ((b) $\tau_F = 22.4$ ns, (c) $\tau_F = 28.7$, 9.4 ns, (d) $\tau_F = 24.9$, 6.4 ns), and the fitted values are represented as red points in the lifetime traces.

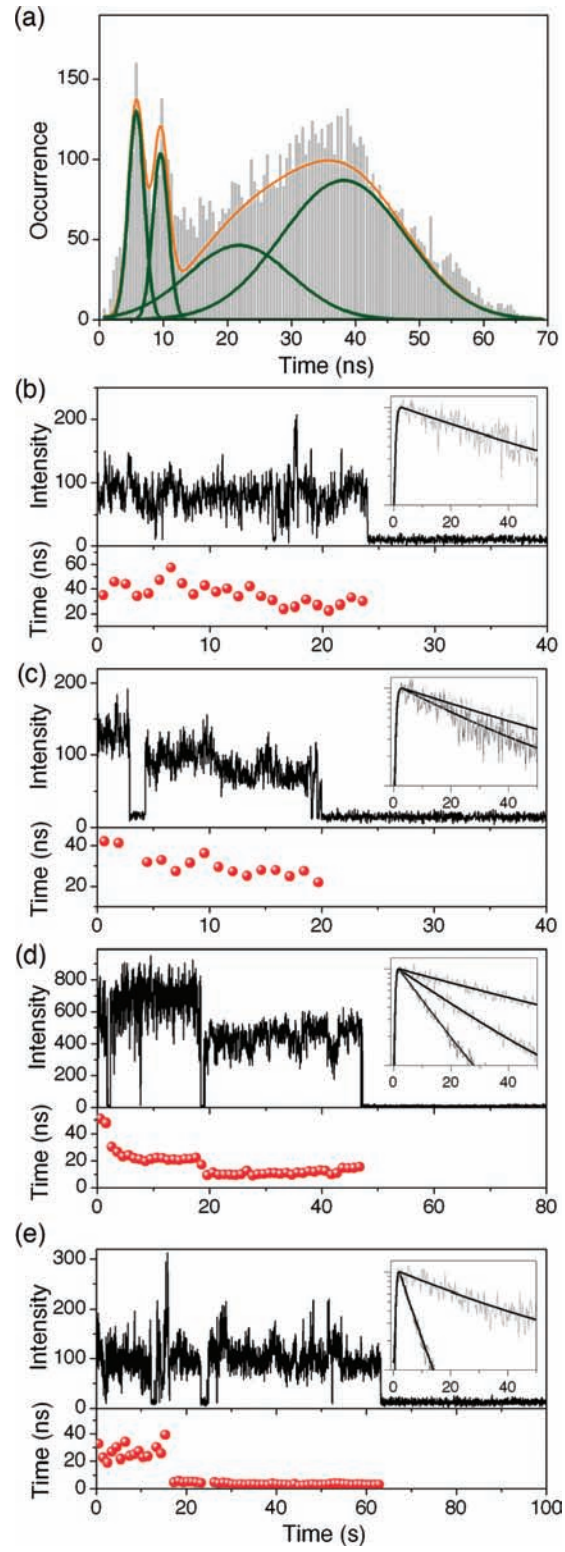


Figure 3. Single-molecule fluorescence behaviors of **3**. (a) Fluorescence lifetime distribution. (b−e) typical fluorescence intensity trajectories of single molecules of **3** with their corresponding lifetime decay profiles. The data analysis is same as that of Figure 2. The fitted fluorescence lifetimes are as follows: (b) $\tau_F = 38.7$ ns; (c) $\tau_F = 43.3$, 27.2 ns; (d) $\tau_F = 50.0$, 21.1, 10.8 ns; (e) $\tau_F = 33.1$, 4.9 ns.

fairly short; thus, the section corresponding to this distribution (11%) is rather small. As seen in the FIT in Figure 2c, which is the representative FIT showing a lifetime of about 9 ns, **2** emits fluorescence in the stable excimer-like state and re-emits for 7 s from the weakly interacting excimer-like state via the off state for 2 s.

Finally, the distribution with a mean lifetime of 5.4 ns corresponds to the lifetime distribution of monomer; after one of the PDI units in **2** is photobleached, the remaining one still fluoresces with the lifetime of the monomer. In contrast to the excimer lifetime distribution, the lifetime distribution of the monomeric fluorescence is narrow because the photobleached chromophore rarely influences the structural heterogeneity of the emitting monomer. Thus, the monomer can maintain its

homogeneity. Figure 2d exhibits an exemplary FIT showing monomeric fluorescence. The intensity decrease at the first intensity level compared to that of the linear PDI dimer[33−35] is the result of fluorescence emission from the excimer-like state.[22,23] However, at the second intensity level, the fluorescence intensity jumps to a slightly higher level due to the uncovered PDI monomer followed by photobleaching of another unit.[36] A remarkable change in the fluorescence lifetime from about 25 to 5 ns occurs simultaneously. It is of interest to observe a change in fluorescence lifetimes through off states as shown in Figure 2c,d, indicating that relatively large conformational changes or photobleaching may occur during off states.

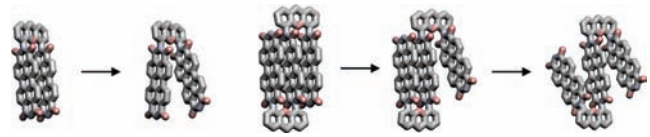
We have also carried out the same experiment for **3**. Figure 3a shows the fluorescence lifetime distribution of all the fitted lifetimes in 250 FITs of **3** with the photons collected during the integration time of 1 s. Like the distribution of **2**, that of **3** consists of three sections: strongly coupled excimer-like, weakly coupled excimer-like, and monomer emission lifetimes; however, the strongly coupled excimer-like state lifetime distribution clearly subdivides into two distributions.

One with a mean lifetime of 38.1 ns covers the largest area (57%) and corresponds to the spread of lifetimes for excimer-like states composed of three well-stacked PDIs. The broad histogram ranging from about 20 to 60 ns is ascribed to the inhomogeneities of this state in **3**. As mentioned above, when three PDI units form an ordered, closely packed array, the excimer-like state becomes more stable and energetically lower than that of **2** and, as a consequence, the fluorescence lifetime becomes longer. All four FITs in Figure 3 exhibit the lifetimes of the optimized π-stacked configuration of three PDIs in the first intensity region. Among them, Figure 3b shows the typical time trace of a one-step photobleaching event.

The asymmetric distribution of the excimer-like state lifetimes is attributed to the second distribution with a mean value of 21.9 ns, covering the second largest area (24%) of the total distribution histogram. Major contributions of these decay components are from the fluorescence of (1) two PDIs which can form the excimer-like state and emit the fluorescence with the lifetime of **2** after one of the PDI units in **3** is photobleached or (2) two PDIs strongly interact in **3** (dimer-like conformers), as suggested by the study in solution. Thus, the mean lifetime of this distribution is similar to that of the excimer-like state lifetime distribution of **2** and the full width at half-maximum of this distribution (22.5 ns) is also similar to that of **2** (23.5 ns). The FIT in Figure 3c is one of the examples containing the moment when the molecule experiences the conformational change from trimer to dimer or photobleaching of one dye via the off state with the fluorescence lifetime change.

In addition, the third and fourth distributions are also shown in the distribution of trimer lifetimes with mean lifetimes of 9.5 and 5.7 ns, respectively. One is caused by the conformers with partially overlapped $\pi-\pi$ interactions that exist only in the solid state, and the other corresponds to the fluorescence of the monomer subsequent to the photobleaching of two PDI units. Because **3** is most likely transformed into distorted conformers in the same way as **2** is, the proportion (8%) and fwhm (3.4 ns) of the third histogram with a mean lifetime of 9.5 ns are comparable to those in **2** (11% and 4.8 ns, respectively). The representative FIT in Figure 3d exhibits a step-by-step change of fluorescence intensity and lifetime from the excimer-like state with three PDIs, via that having two PDIs, to the partially overlapped excimer-like state having two PDIs.

Scheme 1. Hypothetical Change of Molecular Conformation: **2** from Strongly Coupled Excimer-Like to Weakly Coupled Excimer-Like Structure; **3** from Strongly Coupled Excimer-Like State to Dimer-Like Excimer State and Weakly Coupled Excimer-Like State



The typical time trace showing monomer fluorescence following excimer emission is presented in Figure 3e. Among all the FITs of **2** and **3**, 11% of those for **3** show monomeric fluorescence, while 39% of those for **2** do. This observation brings about an effect that the monomer lifetime histogram fills the small area (11%). In contrast, the sum of the dimer and trimer excimer-like state populations covers as much as 81% of the whole histogram. In other words, the majority of **3** molecules show sudden photobleaching of two or three dyes at the same time without additional monomeric fluorescence as seen in Figure 3e: that is, collective photobleaching behavior occurring in the strongly coupled case. Thus, it is likely to agree with the result that face-to-face PDI units interact more robustly in **3** than in **2**. As illustrated in Figure 3c−e, a change in fluorescence lifetimes in the FITs is accompanied by off states, indicating a large conformational change or photobleaching during the off states, similar to the case of **2**.

Finally, the individual fluorescence dynamics of the excimer-like state is unveiled with single-molecule results. The different widths of the lifetime distributions compared with that of the monomer imply different excimer structures and their heterogeneities. More importantly, the asymmetric distribution induced by the dimer-like excimer lifetime distribution (the second distribution) of Figure 3a as revealed by single-molecule detection implies that **3** may actually behave like both trimer and dimer, a unique feature which is hidden in ensemble-averaged measurements. Moreover, the FITs of each molecule allow us to probe the mechanism of fluorescence lifetime and intensity changes and, thus, the conformation of the excimer. A schematic illustration to show the possible change of molecular conformations of **2** and **3** is displayed in Scheme 1. Also, among the molecules showing stepwise photobleaching behavior, 83% of **2** and 71% of **3** experience off states when the molecules change their conformation with a change in fluorescence lifetimes. This feature indicates that most of molecules **2** and **3** are transformed into other conformers during the off states, which can be only observed by single-molecule fluorescence lifetime measurements in real time.

Conclusion

In conclusion, single-molecule space- and time-resolved spectroscopic detection reveals the dynamics of the excimer-

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(36) Most of the strongly coupled excimer-like PDIs emit slightly fewer photons than the monomer, as seen in Figure 2d,e; however, some PDIs fluoresce more brightly when they are in a strongly coupled excimer-like state than in a monomer state, because the monomer fluorescence may be disturbed by a neighboring PDI unit that is photobleached earlier, acting as a fluorescence quencher, in this case.

like states in **2** and **3** with a spread of fluorescence lifetimes corresponding to their inhomogeneous conformations. Our single-molecule studies show that the distributions of excimer-like state lifetimes depend on various torsional angles and distances between the intramolecular π-stacked PDIs. In addition, in real-time fluorescence lifetime and intensity measurements, we know that a single molecule experiences several energy states. The construction of excimer structures for **2** and **3**, which can be well-defined in the solid state, makes the fluorescence lifetime longer. This is especially the case for **3**, for which the lifetime in the solid state is even longer than that in solution because the polymer matrix restricts the molecular conformation to maintain optimized π-stacking. We suggest that, as more PDI molecules π-stack, the fluorescence lifetime of the assembly becomes longer through the effective formation of a delocalized excimer-like state in the solid. Thus, considerable intramolecular $\pi-\pi$ overlap in cofacial PDIs, with longer fluorescence lifetime, may favor the use of n-type organic semiconductors. Furthermore, this effect may have potential applications, where PDI molecules can be employed as a fluorescence probe in single-biomolecule detection by a change in the fluorescence lifetime of a PDI excimer depending on the distance and angle between the two PDI units attached to different sites. Such obvious changes in the lifetime of the dye label will alleviate the limitation of established methods by monitoring intensity changes through FRET processes.

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Supporting Information Available: Text, figures, and tables giving detailed information on (1) steady-state absorption and fluorescence spectra, (2) fluorescence decay profiles, and (3) single-molecule spectroscopic data with discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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