

# Direct Observation of Excimer-Mediated Intramolecular Electron Transfer in a Cofacially-Stacked Perylene Bisimide Pair

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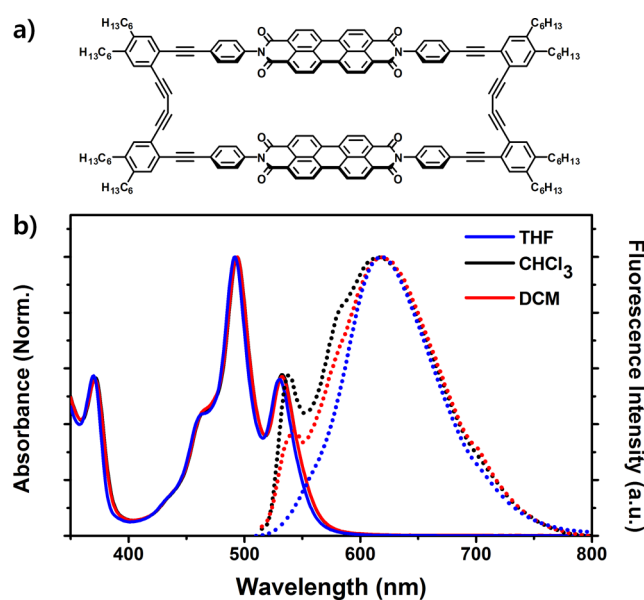
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**S** Supporting Information

**ABSTRACT:** We have elucidated excimer-mediated intramolecular electron transfer in cofacially stacked PBIs tethered by two phenylene-butadiynylene loops. The electron transfer between energetically equivalent PBIs is revealed by the simultaneous observation of the PBI radical anion and cation bands in the transient absorption spectra. The fluorescence decay time of the excimer states is in good agreement with the rise time of PBI radical bands in transient absorption spectra suggesting that the electron transfer dynamics proceed via the excimer state. We can conclude that the excimer state effectuates the efficient charge transfer in the cofacially stacked PBI dimer.

In natural light harvesting systems (LHS), a protein matrix compresses two bacteriochlorophyll (BChl) dyes into a closely  $\pi$ - $\pi$  stacked pair, called the special pair.<sup>1</sup> Excitation of this BChl dimer initiates the primary charge separation and hence is regarded as a key process of the reaction center.<sup>2</sup> However, the photoexcitation of cofacially stacked dimers in nonbiological systems leads typically to the excimer formation, resulting in dissipation of the excitation energy.<sup>3</sup> Thus, numerous studies have been devoted to develop molecular architectures tailored to prevent this detrimental process.<sup>4</sup> Interestingly, recent reports presented a new angle on the role of the excimer state that the excimer intermediate does not dissipate the excitation energy but facilitates the singlet fission.<sup>5</sup> It has raised doubts over whether the excimer surely acts as a trap site or the ideal artificial  $\pi$ - $\pi$  stacking system, effectuating charge transfer, is not yet realized.

Perylene bisimide (PBI) dyes have been considered as ideal building blocks for photofunctional supramolecular systems, owing to formation of stable radical cations and anions, and a flat molecular structure that facilitates intermolecular interactions with neighboring molecules.<sup>6</sup> In light of such features, we and others have designed various cofacially stacked PBI assemblies and investigated their photophysics.<sup>6,7</sup> It was found that the excited-state dynamics of self-assembled or other structurally flexible  $\pi$ -stacked PBIs are dominantly governed by efficient trapping to excimer states. Accordingly, it seems reasonable to draw the conclusion that cofacially stacked PBIs are in general inferior to the J-type counterparts in terms of charge and/or energy transport efficiency.<sup>8</sup> However, the foregoing question prompted us to design new types of PBI  $\pi$ -stacks where the dyes



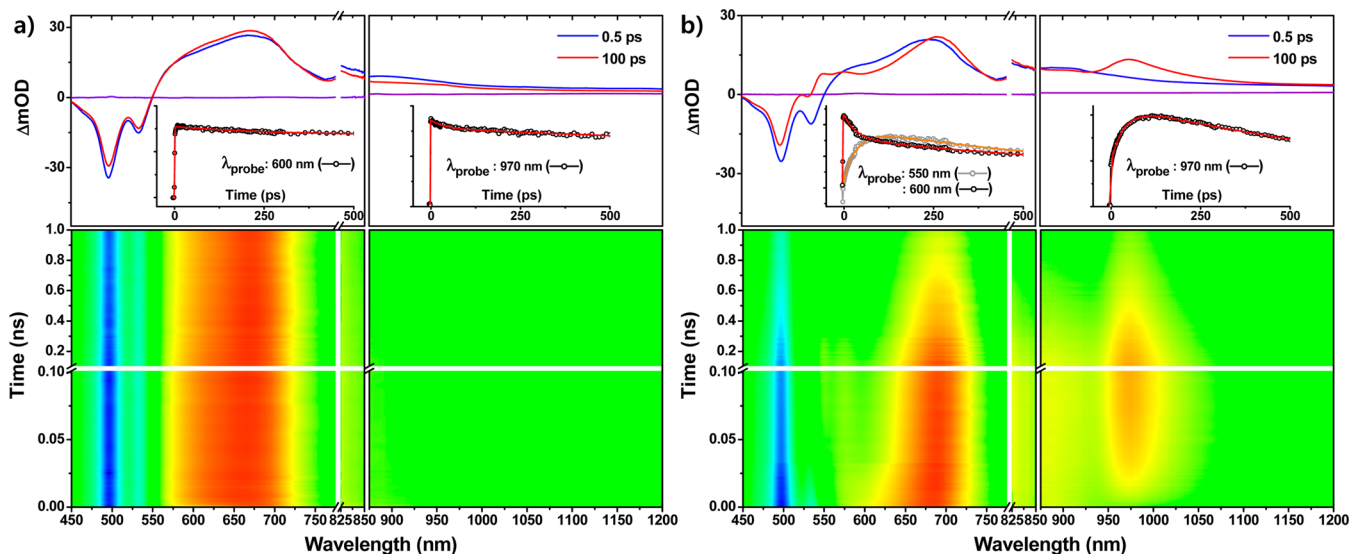
**Figure 1.** (a) Molecular structure of PBI-CP. (b) Steady-state absorption (solid lines) and fluorescence (dotted lines) spectra of PBI-CP.

are positioned in a more rigid geometry, similar as given in natural LHS enforced by the protein matrix, and to reexamine the role of the excimer in the excited-state dynamics of PBI  $\pi$ -stacks.

To this end, we have prepared the cyclophane-type cofacially stacked PBI dimer, PBI-CP, composed of two identical PBI units tethered by two phenylene-butadiynylene loops (Figure 1a). Because this cyclophane confines the spatial arrangement and the coupling of the constituent PBIs, we were able to elucidate the excited-state dynamics of  $\pi$ - $\pi$  stacked dimer in different solvents including those where PBI assemblies typically dissociate into well-solvated monomeric units. Interestingly, the unprecedented direct spectroscopic signatures of the electron transfer (ET) process in this PBI-CP particularly in good solvating solvents, i.e., chloroform (CHCl<sub>3</sub>) and dichloromethane (DCM), were obtained by performing femtosecond transient absorption (fs-TA) spectroscopy. The mechanism of ET via excimer state in this

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**Figure 2.** (top) Femtosecond transient absorption spectra and (bottom) two-dimensional TA contour maps of PBI-CP in (a) THF and (b)  $\text{CHCl}_3$ , respectively, after photoexcitation at 495 nm. Insets show the decay profiles.

tailored PBI “special” dimer is further suggested by the transient fluorescence (TF) spectra.<sup>9</sup>

The absorption spectrum of PBI-CP in THF exhibits bands at 493 and 532 nm, where a reversal of the band intensities is an evidence of the pronounced excitonic coupling. Since the transition to the lower Frenkel exciton is forbidden in cofacially stacked aggregates according to Kasha’s molecular exciton model, the diminished intensity of the corresponding bands indicates H-type stacking structure of PBI-CP.<sup>10</sup> As shown in Figure 1b, the absorption spectra of PBI-CP in chlorinated solvents are almost the same as that in THF, manifesting efficient  $\pi$ – $\pi$  interaction between the two PBI moieties independent of the given solvent. This result is different from earlier results for PBI dimers linked by more flexible tethers.<sup>11</sup> Our previous studies on the phenylene-butadiynylene-tethered PBI foldamers have revealed that the folded  $\pi$ -stacked conformation (i.e., aggregates) is favored in solvents with inferior solvation properties, i.e., THF, whereas the unfolded conformation (i.e., monomer-like uncoupled dyes) is favored in good solvating solvents, e.g.,  $\text{CHCl}_3$  and DCM, owing to the much stronger interactions between solute and solvent molecules in the latter media.<sup>11</sup> On the contrary, hardly different spectral features in the absorption spectra of PBI-CP in chlorinated solvents are virtually anticipated when considered the cyclophane-type structure of PBI-CP with a confined conformational flexibility. The structure optimization for PBI-CP performed by DFT calculations (B97D3/def2-SVP) revealed a tight face-to-face stacked geometry with a PBI–PBI distance of 3.24 Å and a rotational displacement of 28.6° (Figure S1). The latter is in accordance with the preferred rotational angle found by calculations and experiments for self-assembled PBI dimers in the ground state.<sup>12</sup> Furthermore, steady-state absorption spectra imply that PBI-CP retains in the ground state the intramolecular distance and the rotational displacement in all the studied solvents. This behavior can be attributed to the rigid linkers imposing a defined mutual arrangement of PBI units at closest possible van-der-Waals distance. Hence, the excitonic interactions are only slightly affected by the change of the medium. The intriguing features were observed in the fluorescence spectra of PBI-CP. While the fluorescence spectrum of PBI-CP shows exclusively broad and

red-shifted excimer band in THF, the monomer-like 0–0 and 0–1 bands are clearly visible superimposed onto excimer fluorescence band in  $\text{CHCl}_3$ . Based on the similarity in the absorption spectra and the dissimilarity in the fluorescence spectra of PBI-CP in THF and chlorinated solvents, we can infer that the excited-state dynamics are varied in concert with solvents. Moreover, approximately 10-fold low fluorescence quantum yields of PBI-CP in chlorinated solvents compared to that in THF (Table S1) suggest the presence of a very effective nonradiative decay channel that strongly quenches the fluorescence, particularly in good solvating solvents.

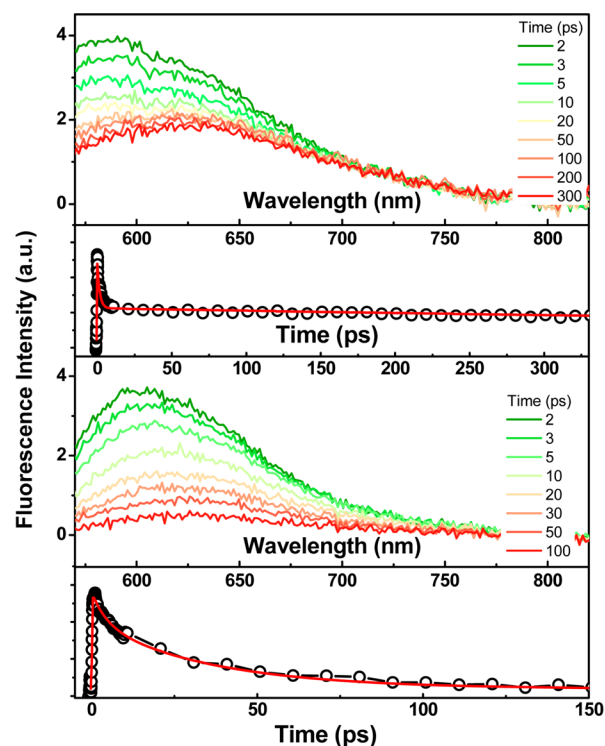
To acquire an in-depth understanding of the solvent-sensitive excited-state dynamics, we have performed fs-TA measurements for PBI-CP (Figures 2 and S2). In THF, the TA spectra of PBI-CP shows the ground-state bleaching (GSB) bands at 495 and 532 nm, and the strong excited-state absorption (ESA) bands in the range from 550 to 1200 nm without perceptible structures. The ESA species monitored at 600 nm decays with a time constant of 16 ns, indicative of the long-lived excimer state.<sup>13</sup> Even though PBI-CP represents a p–n heterojunction system, ET from the electron-rich loops to electron-poor PBIs seems to be efficiently suppressed upon the excimer formation, in excellent agreement with our previous findings on structurally more flexible PBI foldamers bearing similar phenylene-butadiynylene linkers.<sup>11</sup> However, the TA spectra of PBI-CP in chlorinated solvents exhibit conspicuous spectral changes in the ESA signals throughout ca. 530–1200 nm. In  $\text{CHCl}_3$ , initially broad and structureless ESA band in the visible region gradually sharpens and red-shifts to 690 nm within several hundreds of picoseconds. The decay profile of ESA species recorded at 600 nm was well-fitted to a double-exponential function with time constants of 36 ps and 1.1 ns (Table S2). In the NIR region, a new transient species appears at 970 nm with the rise time constant of 36 ps, then decays with a time constant of 1.1 ns. Since the formation of PBI radical anions gives typical rise to new bands at 710, 800, and 960 nm, the newly emerging bands at 690 and 970 nm serve as a direct measure of the ET processes in PBI-CP.<sup>14</sup> It is noteworthy that other positive bands in visible region at 548 and 575 nm rose with the time constant of 34 ps. Such distinct bands in the TA spectra can be assigned to the spectral

features of PBI radical cation.<sup>4b,15</sup> The coexistence of PBI radical anion and cation bands is a clear manifestation of the symmetry-breaking ET between the two PBI moieties appended to the phenylene-butadiynylene loops.

It is generally accepted that the excited-state relaxation pathways of PBI  $\pi$ -stacks is predominantly governed by the formation of excimer traps.<sup>3,16</sup> For instance, several PBI foldamers exhibited broad plateau-like ESA structures in the TA spectra with extremely long lifetime in their stacked states in THF, being fingerprints of the excimer state.<sup>11</sup> However, in good solvating solvents such as  $\text{CHCl}_3$  and DCM, where the PBI foldamers prefer to be in an unfolded conformation, the ET process from phenylene-ethylene substituents to PBI moieties occurred but not between PBI moieties.<sup>11</sup> A recent study by Wasielewski and co-workers on a tailored PBI triangle system revealed that the energetically degenerate symmetry-broken state is followed by the subsequent electron and hole transfer between PBI moieties.<sup>4b</sup> However, this PBI triangle system was specially designed to prevent  $\pi$ - $\pi$  stacking and concomitant excimer formation. Accordingly, the simultaneously emerging PBI radical anion and cation bands of PBI-CP in chlorinated solvents allow us to conjecture a quite special ET dynamics between identical PBI moieties in a rigid  $\pi$ - $\pi$  stacked arrangement. In our synthetic PBI-CP model system, the rigid cyclophane-enforced geometry imposes a certain degree of conformational constraint on the molecule so that it maintains a predefined rotational displacement and sufficiently close PBI-PBI distance even in good solvating solvents. Thus, it seems that the resultant electronic interaction between adjacent PBI moieties renders ET possible by prohibiting structural relaxation into the deep excimer trap state. To further examine the feasibility of the symmetry-breaking ET in PBI-CP, we have estimated the thermodynamical driving force of the ET process from electrochemical data by performing a Weller analysis (the detailed electrochemical studies are described in Supporting Information).<sup>17</sup> The estimated negative  $\Delta G^\circ$  value of  $-0.55$  eV indicates that the ET process between PBI moieties of PBI-CP is indeed an exergonic process and thermodynamically favored with respect to the alternative ET process from the phenylene-butadiynylene backbone to PBI.

Now, a critical question arises of whether ET and excimer formation in PBI-CP are competitive or consecutive processes. When comparing the spectral shapes of the ESA bands observed at 530–1200 nm, the broad and featureless spectra are prevalent at earlier times regardless of the solvents. From the ESA bands at nascent stage, we can surmise that the excimer formation is dominant immediately after photoexcitation even in good solvating solvents. It should be noted that the PBI radical bands appear much slower than the generally known excimer formation time (i.e.,  $\sim 36$  ps vs  $\sim 200$  fs).<sup>3c,16</sup> When the ET dynamics is in competition with faster excimer formation process, it rarely provides such intense radical bands in the TA spectra. Accordingly, we can conjecture that the ET dynamics of PBI-CP in a good solvating solvent proceed via an intermediate excimer state.

To delve deeper into ET dynamics in PBI-CP, the TF spectra were obtained by performing femtosecond broadband fluorescence upconversion measurements.<sup>9</sup> We applied photoexcitation at 495 nm so as to avoid spectral interference caused by the strong pump pulse. Unfortunately, due to the extremely low fluorescence quantum yields of PBI-CP, the early time TF spectra are hampered by the spectral interference caused by the spectrally broad and strong pump pulse. In addition, the blue edges of the TF spectra, where absorption and emission bands



**Figure 3.** Transient fluorescence spectra of PBI-CP in THF (top) and  $\text{CHCl}_3$  (third), respectively. The decay profiles of PBI-CP in THF (second) and  $\text{CHCl}_3$  (bottom), monitored at 650 nm.

overlap, are distorted by strong self-absorption effects. However, because the early time dynamics of Frenkel exciton is beyond the scope of this study, we have rather concentrated on the dynamics of readily generated excimer state. As shown in Figures 3 and S3, the initial TF spectra decay with time constants of 1.6 and 2.1 ps, respectively, representing the structural reorganization of the energetically higher-lying excimer species.<sup>16</sup> Interestingly, the time evolutions of the TF spectra in THF and  $\text{CHCl}_3$  exhibit markedly different features after several tens of picoseconds.<sup>11,16</sup> The decaying component in THF is too long-lived to determine an accurate time constant within the time window of our apparatus, which is in compliance with the conventionally known excimer lifetimes of self-assembled PBI stacks.<sup>16</sup> In sharp contrast, the temporal profiles in chlorinated solvents decay completely with the time constant of 33 ps. These unusually short evolution times of excimer fluorescence are consistent with the rise times of the PBI radical bands extracted from the TA kinetic traces, i.e., the ET time scales, implying the relaxation of photogenerated excimer state into the charge transfer state. Therefore, this observation further substantiates our proposed mechanism of intramolecular ET via the excimer intermediate state.

In order to understand such an excimer-mediated ET mechanism, it is necessary to evoke the role of solvent. Due to the enthalpy of solvation, PBI moieties prefer being surrounded by a  $\text{CHCl}_3$  solvation shell, while they prefer to be  $\pi$ - $\pi$  stacked in THF.<sup>11</sup> Accordingly, PBI-CP in THF favors the contacted geometry and hence behaves like self-assembled systems in a poor solvent. However, in spite of its spacer-enforced closely stacked geometry, PBI-CP in chlorinated solvents has the possibility of structural relaxation between two PBI moieties. This can be further supported by the fact that the excimer band peak position of PBI-CP in  $\text{CHCl}_3$  becomes red-shifted



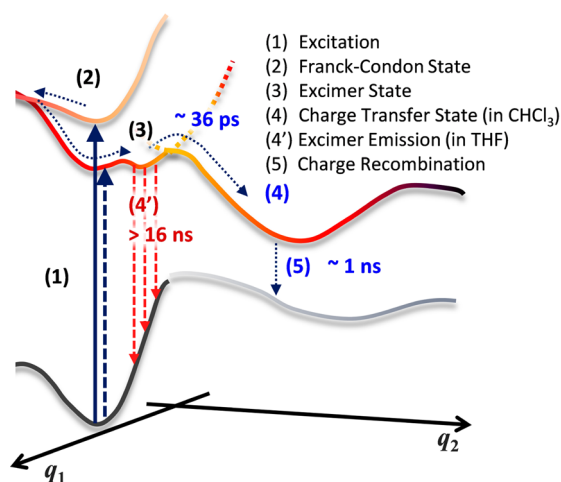


Figure 4. Schematic energy state diagram of PBI-CP.

significantly more than that in THF (Figure S5). Consequently, we can delineate the excimer-mediated ET process as depicted in Figure 4. Initially, the cyclophane-type structure of PBI-CP enables PBI moieties to relax to some extent toward the excimer state resulting in enhanced intermolecular interaction. Subsequently, under the influence of good solvating solvents, the molecular motion, e.g., rotational displacements, of the PBI  $\pi$ -faces takes place. Hereat, the symmetry-breaking ET process in  $\pi$ -stacks is facilitated by polar environment and a good electronic communication between two stacked moieties, stemming from excimer formation. Finally, the generated charge transfer state decays with the charge recombination time of 1.1 ns.

We have demonstrated the efficient excimer-mediated ET process of a rigidly tethered PBI-CP in chlorinated solvents. The coexistence of the PBI radical anion and cation bands in the TA spectra reveals an ET between two identical PBI moieties, i.e., symmetry-breaking ET similar as given in the special BChl pair in photosynthetic reaction centers.<sup>1,3b</sup> Thus, it appears to us that a rigid fixation of the dyes is a prerequisite for symmetry-breaking ET among  $\pi$ - $\pi$  stacked dyes that is provided in our system by rigid phenylene-butadiynylene tethers and by the protein environment in the natural reaction centers. Our findings not only cast a new perspective on the role of excimer states but also pave the way for ameliorating the charge transfer efficiency of molecular assemblies for future applications in the field of molecular optoelectronic materials.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04591.

Detailed experimental methods (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40.
- (2) (a) Cardona, T.; Sedoud, A.; Cox, N.; Rutherford, A. W. *Biochim. Biophys. Acta, Bioenerg.* **2012**, *1817*, 26. (b) Jia, Y.; Jonas, D. M.; Joo, T.; Nagasawa, Y.; Lang, M. J.; Fleming, G. R. *J. Phys. Chem.* **1995**, *99*, 6263.
- (3) (a) Schubert, A.; Settels, V.; Liu, W.; Würthner, F.; Meier, C.; Fink, R. F.; Schindlbeck, S.; Lochbrunner, S.; Engels, B.; Engel, V. *J. Phys. Chem. Lett.* **2013**, *4*, 792. (b) Vauthey, E. *ChemPhysChem* **2012**, *13*, 2001. (c) Sung, J.; Kim, P.; Fimmel, B.; Würthner, F.; Kim, D. *Nat. Commun.* **2015**, *6*, 8646.
- (4) (a) Keivanidis, P.; Howard, I. A.; Friend, R. H. *Adv. Funct. Mater.* **2008**, *18*, 3189. (b) Wu, Y.; Young, R. M.; Frascioni, M.; Schneebeli, S. T.; Spent, P.; Gardner, D. M.; Brown, K. E.; Würthner, F.; Stoddart, J. F.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2015**, *137*, 13236. (c) Bagnich, S. A.; Athanasopoulos, S.; Rudnick, A.; Schroegele, P.; Bauer, I.; Greenham, N. C.; Strohrriegel, P.; Köhler, A. *J. Phys. Chem. C* **2015**, *119*, 2380.
- (5) (a) Walker, B. J.; Musser, A. J.; Beljonne, D.; Friend, R. H. *Nat. Chem.* **2013**, *5*, 1019. (b) Feng, X.; Krylov, A. I. *Phys. Chem. Chem. Phys.* **2016**, *18*, 7751. (c) Korovina, N.; Das, S.; Nett, Z.; Feng, X.; Joy, J.; Haiges, R.; Krylov, A. I.; Bradforth, S. E.; Thompson, M. E. *J. Am. Chem. Soc.* **2016**, *138*, 617.
- (6) Würthner, F.; Saha-Möller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D. *Chem. Rev.* **2016**, *116*, 962.
- (7) (a) Wasielewski, M. R. *Acc. Chem. Res.* **2009**, *42*, 1910. (b) Schwartz, E.; Palermo, V.; Finlayson, C. E.; Huang, Y.; Otten, M. B.; Liscio, A.; Trapani, S.; González-Valls, I.; Brocorens, P.; Cornelissen, J. J. L. M.; Peneva, L.; Müllen, K.; Spano, F. C.; Yartsev, A.; Westenhoff, S.; Friend, R. H.; Beljonne, D.; Nolte, R. J. M.; Samorì, P.; Rowan, A. E. *Chem. - Eur. J.* **2009**, *15*, 2536.
- (8) (a) Kaiser, T. E.; Stepanenko, V.; Würthner, F. *J. Am. Chem. Soc.* **2009**, *131*, 6719. (b) Lindquist, R. J.; Lefler, K. M.; Brown, K. E.; Dyar, S. M.; Margulies, E. A.; Young, R. M.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2014**, *136*, 14912.
- (9) (a) Sajadi, M.; Quick, M.; Ernsting, N. P. *Appl. Phys. Lett.* **2013**, *103*, 173514. (b) Gerecke, M.; Bierhance, G.; Gutmann, M.; Ernsting, N. P.; Rosspeintner, A. *Rev. Sci. Instrum.* **2016**, *87*, 053115.
- (10) (a) Kasha, M.; Rawls, H. R.; Ashraf El-Bayoumi, M. *Pure Appl. Chem.* **1965**, *11*, 7599. (b) Spano, F. C. *Acc. Chem. Res.* **2010**, *43*, 429.
- (11) (a) Nowak-Król, A.; Fimmel, B.; Son, M.; Kim, D.; Würthner, F. *Faraday Discuss.* **2015**, *185*, 507. (b) Son, M.; Fimmel, B.; Dehm, V.; Würthner, F.; Kim, D. *ChemPhysChem* **2015**, *16*, 1757.
- (12) Fink, R. F.; Seibt, J.; Engel, V.; Renz, M.; Kaupp, M.; Lochbrunner, S.; Zhao, H.-M.; Pfister, J.; Würthner, F.; Engels, B. *J. Am. Chem. Soc.* **2008**, *130*, 12858.
- (13) (a) Ford, W. E.; Kamat, P. V. *J. Phys. Chem.* **1987**, *97*, 6373. (b) Son, M.; Park, K. H.; Shao, C.; Würthner, F.; Kim, D. *J. Phys. Chem. Lett.* **2014**, *5*, 3601.
- (14) Hippius, C.; van Stokkum, I. H. M.; Zangrando, E.; Williams, R. M.; Würthner, F. *J. Phys. Chem. C* **2007**, *111*, 13988.
- (15) Lukas, A. S.; Zhao, Y.; Miller, S. E.; Wasielewski, M. R. *J. Phys. Chem. B* **2002**, *106*, 1299.
- (16) (a) Lim, J. M.; Kim, P.; Yoon, M. - C.; Sung, J.; Dehm, V.; Chen, Z.; Würthner, F.; Kim, D. *Chem. Sci.* **2013**, *4*, 388. (b) Brown, K. E.; Salamant, W. A.; Shoer, L. E.; Young, R. M.; Wasielewski, M. R. *J. Phys. Chem. Lett.* **2014**, *5*, 2588.
- (17) Weller, A. Z. *Phys. Chem.* **1982**, *133*, 93.