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Electron Delocalization in One-Dimensional Perylenediimide Nanobelts through Photoinduced Electron Transfer

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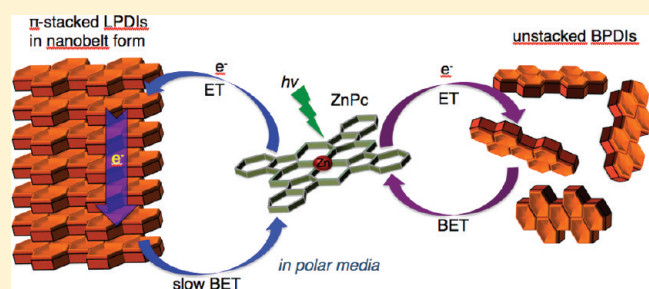
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 Supporting Information

ABSTRACT: Photoinduced electron transfer (PET) of a hybrid system comprising *N,N'*-dihexadecylperylene-3,4,9,10-tetracarboxylic diimide (LPDI), which forms nanobelt structures of the form (LPDI)_n, and soluble zinc (tetra-*tert*-butyl)phthalocyanine (ZnTBPC) has been investigated in polar benzonitrile. The PET of a mixture system comprising *N,N'*-diheptadecan-9-ylperylene-3,4,9,10-tetracarboxylic diimide (BPDI) dissolved thoroughly in benzonitrile and ZnTBPC was also examined for comparison. LPDI nanobelt structures were identified using steady-state absorption and emission spectroscopies, as well as dynamic light scattering (DLS), in suspension and detected using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in the solid state. The electron paramagnetic resonance (EPR) spectrum of the radical anion of LPDI nanobelts [(LPDI)_n•⁻] was quite different from that of BPDI (BPDI•⁻) because of enhanced electron delocalization within the one-dimensional LPDI aggregates. Polar benzonitrile enables intermolecular light-induced electron transfer from the low-lying triplet state of ZnTBPC to the LPDI nanobelts through its stabilization effect on the electron-transfer species, as indicated by free energy calculations. Nanosecond transient absorption spectra displayed marked broadening of the radical anion peak of LPDI nanobelts in the near-infrared (NIR) region upon excitation, confirming the delocalization of the transferred electron within the nanostructure. Whereas both the hybrid and mixture systems have nearly the same rate constants (*k*_{et}) of PET from the PDIs to ZnTBPC, the rate of back electron transfer (*k*_{bet}) of (LPDI)_n•⁻/ZnTBPC^{•+} is lower than that of BPDI•⁻/ZnTBPC^{•+}, which might result from the effect of electron delocalization within the nanobelt structure.



1. INTRODUCTION

Well-ordered assemblies formed by weak interactions at the nanoscale are indispensable components of advanced materials for photonics and electronics in which electron transfer and/or transport is of critical importance.¹ Perylenediimide (PDI) and its derivatives are common building blocks of many self-assembly models designed for various applications because of their large planar π -systems and their high photoemission and electron deficiency.² The large π -plane of PDIs is responsible for their intrinsic insolubility, however this aromatic core facilitates intermolecular π - π interactions. Substitution from nitrogen atoms of PDI brings about marked solubility variations and shapes the aggregation pattern³ although they have negligible effect on spectroscopic and electrochemical properties of PDIs due to the lack of electronic communication with the aromatic core.⁴ Linear side-chains generally introduce one-dimensional morphologies in aggregation, whereas branched substituents lead to zero-dimensional aggregates at the nanoscale or enhanced solubility due to steric hindrance in many solvents.^{3,5} One-dimensional

semiconducting nanostructures formed by the π - π stacking of PDIs (nanobelts) have the potential for high charge-carrier mobilities along the long axis through π -electron delocalization,⁶ which is an essential parameter to increase the performance of optoelectronic devices. Despite the fact that many photoinduced applications of PDI nanobelts are available, a fundamental study on π -electron delocalization within the nanobelt through the photoinitiated electron-transfer process is still needed to elucidate its mechanism.

In this study, we investigated the photoinduced electron-transfer (PET) mechanism of a hybrid system consisting of suspended electron-accepting PDI nanobelt structures and a soluble electron-donor molecule, for the first time. For this purpose, a polar environment was selected that provides pivotal assistance to the stabilization of the electron-transfer species by

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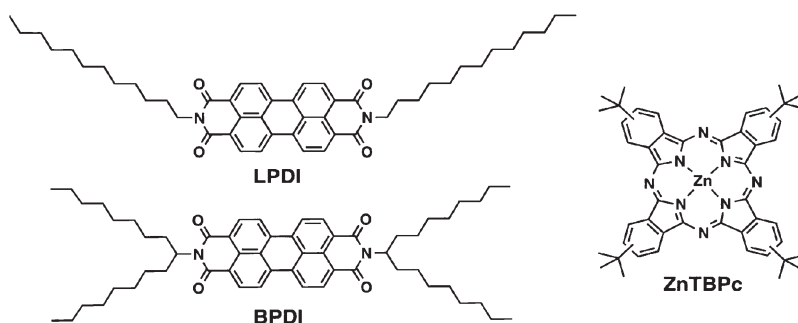


Figure 1. Molecular structures of the investigated compounds.

lowering the energy level of the charge-separated state so that even low-energy-level triplet excited states can supply an exothermic driving force for PET reactions.⁷ To appreciate the contribution of one-dimensional self-assembly to the charge stabilization by delocalization, we examined and compared the intermolecular PET processes existing (i) between zinc (tetra-*tert*-butyl)phthalocyanine (ZnTBPC) and *N,N'*-ditridecylperylene-3,9,10,16-tetracarboxylic diimide (LPDI), having linear alkyl chains and forming a one-dimensional nanobelt structure in polar benzonitrile (PhCN) and (ii) between ZnTBPC and *N,N'*-diheptadecan-9-ylperylene-3,9,10,16-tetracarboxylic diimide (BPDI), containing branched alkyl chains that are dissolved thoroughly in PhCN at room temperature (Figure 1). In these systems, the LPDI nanobelts and BPDI act as electron acceptors, and ZnTBPC is used as a photosensitizer as well as an electron-donor component in both cases.⁸ In most cases where PDIs are covalently linked to the phthalocyanines, intramolecular PET takes place through the singlet excited states to yield charge separation decayed to low-lying ³PDI* or ³ZnTBPC* states, and the lifetimes of the charge-separated state were found to be in the range of picoseconds to nanoseconds.⁹ However, only one study in the literature has investigated intermolecular photoinduced events of PDIs and phthalocyanines, in which electron transfer was achieved through the triplet excited state of the phthalocyanine moieties in PhCN.¹⁰ In this study, the bimolecular electron-transfer processes of the LPDI/ZnTBPC and BPDI/ZnTBPC systems were studied by employing nanosecond laser photolysis with visible/near-IR detectors.

2. EXPERIMENTAL SECTION

2.1. Materials. Zinc(tetra-*tert*-butyl)phthalocyanine (ZnTBPC)¹¹ and *N,N'*-diheptadecan-9-ylperylene-3,9,10,16-tetracarboxylic diimide (BPDI)¹² were synthesized according to the reported procedures. *N,N'*-Ditridecylperylene-3,9,10,16-tetracarboxylic diimide (LPDI) was purchased from commercial sources and used as received. Fabrication of LPDI nanobelts was achieved through solution-based self-assembly.³ The one-dimensional growth of the molecular assembly was achieved by slow crystallization at the interface between chloroform, in which PDI dissolves appreciably, and acetonitrile or methanol, in which PDI has very limited solubility. The polarity difference in the solvents provides separate phases for an extended period. A larger amount of the polar solvent (i.e., acetonitrile or methanol) was transferred to the top of a concentrated chloroform solution. Red crystals formed at the interface within minutes and then slowly diffused into the upper phase of the polar solvent. The nanobelts, transferred by pipetting, were cast onto a glass surface to dry.

2.2. Instruments. Steady-state absorption measurements were recorded on a Shimadzu UV-3100PC spectrometer or a

Hewlett-Packard 8453 diode-array spectrophotometer. Fluorescence measurements were carried out on a Shimadzu spectrofluorophotometer (RF-5300PC). Dynamic light scattering (DLS) measurements were carried out using a Zetasizer Nano S instrument (Malvern Instruments Ltd., Malvern, U.K.). The DLS instrument used in this work has a range between 0.6 and 6000 nm, and therefore, any structures over this limit could not be detected. Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL X-band spectrometer (JES-RE1XE) at room temperature and 77 K. EPR spectra of radical anions of BPDI and LPDI nanobelts in benzonitrile were measured right after the addition of hydrazine under an inert atmosphere. The *g* value was calibrated using an Mn²⁺ marker. Scanning electron microscopy (SEM) images of nanobelts were recorded on a JEOL FE-SEM JSM-6320F instrument operating at 5 kV. SEM samples were placed on a piece of aluminum foil that was attached to a bulk metal mount by double-sided carbon tape. Transmission electron microscopy (TEM) images were collected on a Hitachi model H-800 transmission emission microscope operating at an accelerating voltage of 200 kV. TEM samples were prepared by depositing a drop of dispersion on carbon-coated copper grids (250 mesh).

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV instrument. Incident X-ray radiation was produced by a Cu X-ray tube, operating at 40 kV and 40 mA with Cu K α radiation of 1.54-Å wavelength. The scanning rate was 4°/min from 10° to 70° in 2 θ . Density functional theory (DFT) calculations were performed on a COMPAQ DS20E computer. Geometry optimizations were carried out using the Becke3LYP functional and the 6-31G basis set,¹³ with the unrestricted Hartree–Fock (UHF) formalism as implemented in the Gaussian 03 program, revision C.02. Graphical outputs of the computational results were generated with the GaussView software program (version 3.09) developed by Semichem, Inc.

Electrochemical measurements were performed on an ALS630B electrochemical analyzer in deaerated PhCN containing 0.10 M TBAPF₆ as a supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode. The Pt working electrode was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to a Ag/AgNO₃ (0.01 M) reference electrode. All potentials (vs Ag/AgNO₃) were converted to values versus a saturated calomel electrode (SCE) by adding 0.29 V. All electrochemical measurements were carried out under an atmospheric pressure of argon. For nanosecond transient absorption measurements, deaerated solutions of the compounds

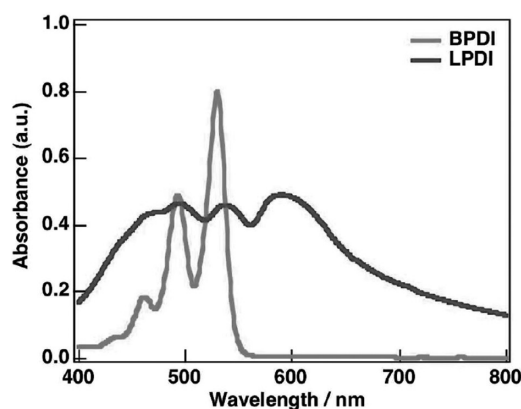


Figure 2. Steady-state absorption spectra of 0.01 mM BPDI and 0.19 mM LPDI in PhCN at room temperature.

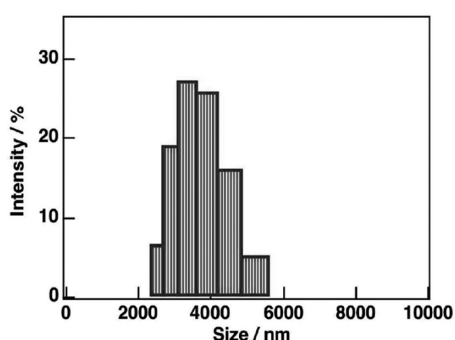


Figure 3. Size distribution diagram of LPDI nanobelts (2.5 mM) in PhCN at room temperature.

were excited with a Panther optical parametric oscillator (OPO) equipped with a Nd:YAG laser (Continuum, SLII-10, 4–6 ns fwhm) with a power of 10–15 mJ per pulse. The PET reactions were monitored by continuous exposure to a Xe lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. Solutions were deoxygenated by argon purging for 15 min prior to measurements.

3. RESULTS AND DISCUSSION

3.1. Spectral Characterization of LPDI Nanobelts in Solution. As shown in Figure 2, LPDI molecules undergo suspension as a result of their low solubility at room temperature in PhCN, whereas BPDI, thoroughly dissolved in PhCN, conserves its pronounced absorption peaks, with the maximum at 530 nm corresponding to the 0–0 transition. Aggregation of LPDI molecules can be recognized from enhanced 0–1, 0–2, and 0–3 transitions compared to the 0–0 transition. Aggregation also affords a bathochromic shift from 530 to 537 nm. In addition, the absorption spectrum of LPDI suspension displays the formation of new band at around 590 nm, resulting from cofacial stacking through π – π interactions of the PDI planes.^{4a,b,14} Such stacking of PDI planes generally leads to relatively long one-dimensional organizations with the help of the long linear alkyl chains attached to the nitrogen atoms of PDI.^{3,5} On the contrary, BPDI molecules do not show such aggregation behavior in PhCN because of the steric hindrance of their branched alkyl chains.^{3,5} The absorption spectra of LPDI

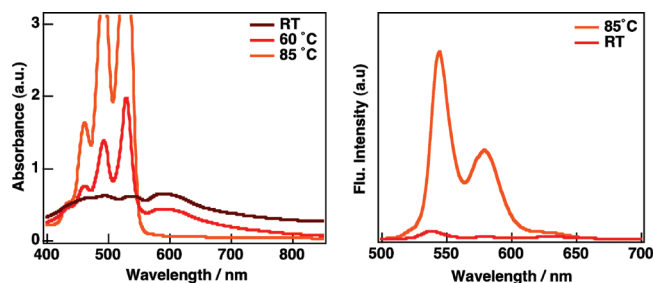


Figure 4. Steady-state absorption (left) and emission (right) spectra of LPDI in PhCN at the indicated temperatures.

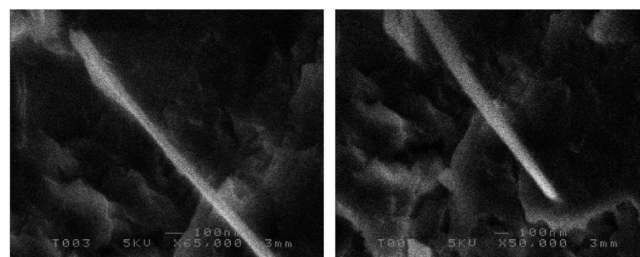


Figure 5. SEM images of LPDI nanobelts, fabricated by phase-transfer crystallization between excess methanol and a concentrated chloroform solution.

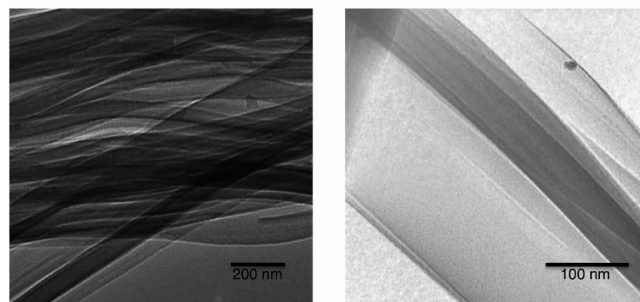
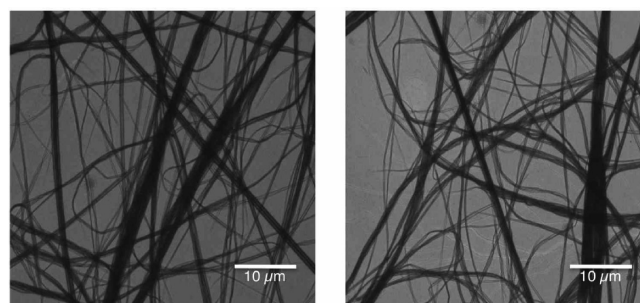


Figure 6. TEM images of LPDI nanobelts at different scales, fabricated by phase-transfer crystallization.

and BPDI in chloroform exhibit the same characteristics with a maximum at 526 nm, showing no evidence for aggregation (Figure S1, Supporting Information). LPDI molecules also yield aggregation in acetonitrile (ACN), with a marked red shift to 544 nm and the appearance of a new absorption band at around 585 nm (Figure S1, Supporting Information).

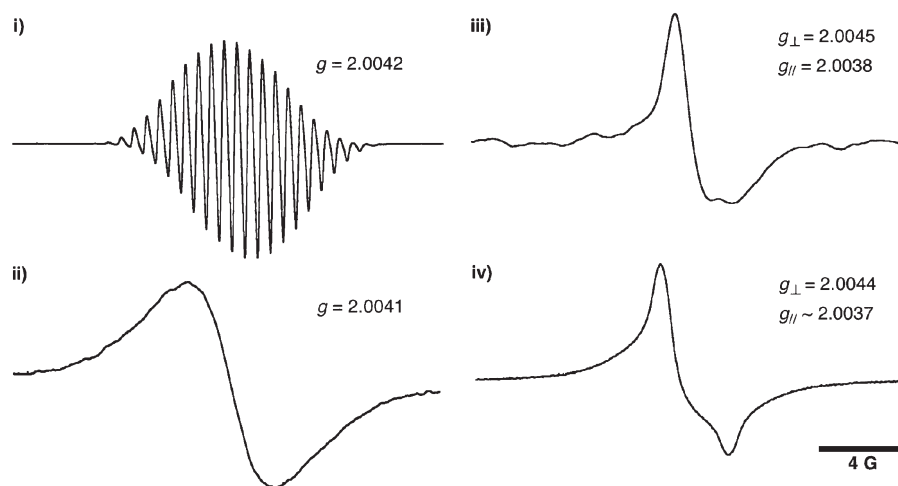


Figure 7. EPR spectra of (i,ii) the radical anion of BPDI (0.020 mM) at (i) room temperature and (ii) 77 K and (iii,iv) the radical anion of LPDI nanobelts (ca. 2.8 mM) at (iii) room temperature and (iv) 77 K in the presence of hydrazine (260 mM) in deaerated PhCN.

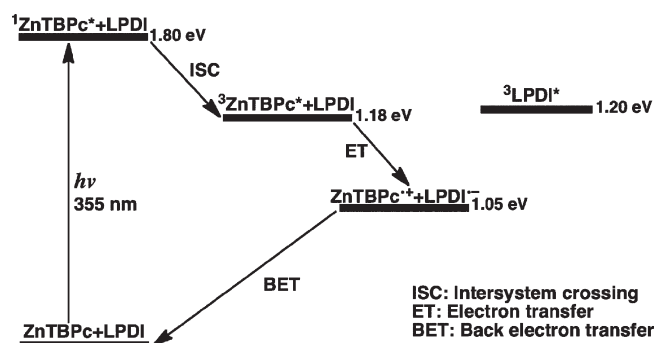


Figure 8. Energy level diagram (in eV) for the intermolecular ET process of the LPDI/ZnTBPc system through the triplet state of ZnTBPc.

The size distribution of LPDI aggregates in PhCN was examined by dynamic light scattering (DLS) measurements. The DLS diagram of LPDI aggregates reveals a size distribution ranging from 2300 to 4800 nm, with a mean size of 3312 nm (Figure 3). Dimensions at micrometer scale are most likely to result from the long lengths of the one-dimensional nanobelts as observed in solid state (vide infra).

LPDI molecules tend to dissolve in PhCN at high temperatures, as indicated by the absorption and emission spectra. The 0–0 transition at 530 nm is restored; compared to this recovery, electronic transitions at shorter wavelengths start to decrease gradually and the long-wavelength band at 590 nm disappears upon heating of the suspension to 85 °C (Figure 4). The full conversion of LPDI aggregates into free molecules as a result of decomposition of the molecular organization at the nanoscale can be recognized through a clear isosbestic point at 550 nm. As expected, the quenched fluorescence of LPDI molecules in the aggregate due to a symmetry-forbidden transition involving the lower-energy π -stacking state⁵ is recovered at high temperatures because of enhanced solubility (Figure 4). Hence, the aggregation yield^{2d,3} of LPDI molecules in PhCN was estimated to be 96% at room temperature by comparison of the emission intensities at room temperature and at 85 °C, where the LPDI molecules are assumed to dissolve completely and to have a quantum yield of the fluorescence close to unity.¹⁵ The decomposition of

LPDI aggregates can also be followed by DLS measurements at high temperatures (Figure S2, Supporting Information).

3.2. Characterization of LPDI Nanobelts in the Solid State.

The aggregation behavior of LPDIs in the solid state was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The π -stacked LPDI molecules form a one-dimensional nanobelt morphology, as shown in the SEM images (Figure 5). LPDI nanobelts were fabricated by phase-transfer self-assembly³ between excess acetonitrile or methanol and a concentrated chloroform solution. (See also Figure S3, Supporting Information.) The nanobelt structures appear to be surrounded by an emanating glow because of deposition of the electrons emitted from the electron gun of the SEM device. This can be explained by the semiconducting nature of PDIs. Indistinct patterns other than meaningful one-dimensional figures resulted from the roughness of the aluminum-foil surface.

Formation of the nanobelt arrangement can also be clearly seen in the TEM images (Figure 6 and Figure S4, Supporting Information). As shown in the SEM and TEM images, the average width was a few hundreds of nanometers and the length was in the range of a few tens of micrometers. This gives an average aspect ratio (length/width) of much more than 100.

X-ray diffraction measurements of powder LPDI nanobelts display the long axis of a unit cell to be 26.1 Å (Figure S5, Supporting Information), which is about 28% shorter than the full length of an LPDI molecule, which was calculated as 36.2 Å (Figure S6, Supporting Information) using density functional calculations at the B3LYP/6-31G level. From the average width of the nanobelts, it can be estimated that ca. 100 LPDI molecules with side-chain interdigitation fit laterally in a nanobelt. PDIs substituted with linear chains such as LPDI, as in many examples,^{2g,i,j,3,5} produce one-dimensional molecular organizations when phase-transfer techniques are applied, in contrast to those having branched appendages similarly to BPDI.^{3,5} Hence, the electrons transferred from a donor moiety are allowed to move along the one-dimensionally stacked LPDI molecules through the overlapping π -orbitals.

3.3. Spectral Characterization of Radical Anions of LPDI Nanobelts in Solution. Characterization of the radical anions of the LPDI aggregate $[(\text{LPDI})_n]^{\bullet-}$ and BPDI ($\text{BPDI}^{\bullet-}$) in PhCN

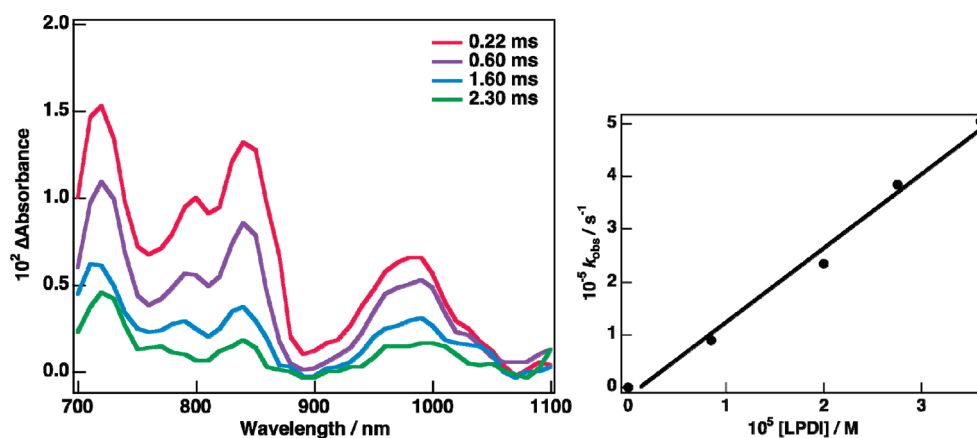


Figure 9. (Left) Nanosecond transient absorption spectra of ZnTBPC (0.06 mM) and LPDI aggregates (ca. 0.50 mM) in deaerated PhCN at the indicated time delays, $\lambda_{\text{ex}} = 355$ nm. (Right) Plot of the pseudo-first-order rate constant (k_{obs}) as a function of the concentration of LPDI determined from the absorbance change at 720 nm due to $\text{LPDI}^{\bullet-}$.

was done using electron paramagnetic resonance (EPR). $\text{BPDI}^{\bullet-}$ and $(\text{LPDI})_n^{\bullet-}$ are generated chemically by electron-donating hydrazine^{6d} in PhCN.¹⁶ The hyperfine coupling structure of $\text{BPDI}^{\bullet-}$, showing behavior corresponding to a nonaggregated molecule ($g = 2.0042$), matches quite well with the literature data (Figure 7 and Figure S5, Supporting Information).^{6d,9d,17} In the frozen solvent, the EPR spectrum of BPDI with a similar g value shows no hyperfine splitting. The spin distribution of the unpaired electrons of $(\text{LPDI})_n^{\bullet-}$, on the other hand, apparently has a different EPR spectrum, as shown in Figure 7. First, the hyperfine splitting disappeared because the unpaired electron averages many hyperfine environments by a fast hopping mechanism throughout the large LPDI aggregate on the microsecond time scale of the EPR experiment.^{6d,17} Second, the EPR spectrum of $(\text{LPDI})_n^{\bullet-}$ shows an asymmetric trait around the line center because of its anisotropic g tensor, which is x - y rotationally symmetric ($g_{\parallel} = 2.0038$). Anisotropy of the spectrum, which depends on the sample orientation in the magnetic field, implies that LPDI aggregates exhibit one-dimensional organization at room temperature rather than zero-dimensional aggregation because they have a very large radius of gyration compared to spherical species of the same molecular weight.¹⁷ In the frozen PhCN sample, the EPR spectrum of $(\text{LPDI})_n^{\bullet-}$ displayed the same powder pattern with the disappearance of hyperfine splitting and anisotropy due to the g tensor ($g_{\parallel} \approx 2.0037$). Thus, one can conclude that the electron chemically transferred from hydrazine delocalizes within the electron-accepting LPDI aggregate, which is ordered one-dimensionally by cofacial π - π stacking. The EPR spectrum of LPDI radical anion in ACN is consistent with that of LPDI in PhCN, also resulting in electron delocalization along the nanobelt structure (Figures S7 and S8, Supporting Information).

3.4. Intermolecular Photoinduced Electron-Transfer Dynamics. The PET of the LDI nanobelts with ZnTBPC was investigated in comparison with that of a mixture system comprising ZnTBPC and BPDI. Both systems in PhCN satisfy the necessary energy conditions for intermolecular PET from electron-donating ZnTBPC to electron-accepting LPDI nanobelts and BPDI molecules. As in similar intermolecular PET processes,¹⁸ the lifetime of the triplet excited state of ZnTBPC is long enough to allow PET reactions to occur.^{18a,b} PDIs are not convenient photosensitizers for these systems because the

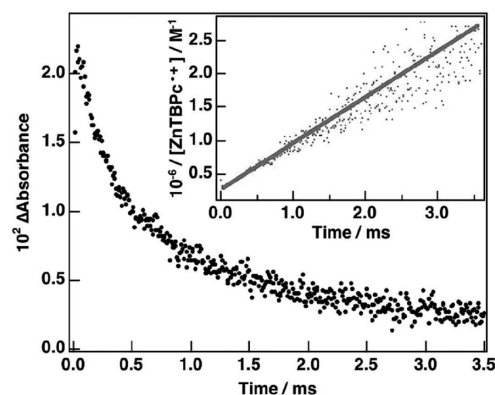


Figure 10. Decay time profile of the absorbance at 840 nm due to ZnTBPC^{*+} in deaerated PhCN, $\lambda_{\text{ex}} = 355$ nm. Inset: Second-order plot.

intersystem crossing pathway is extremely inefficient.¹⁹ In addition, the aggregation of LPDI molecules in PhCN already leads to fluorescence quenching, deactivating an efficient photosensitization.

Estimated intermolecular PET processes are compiled in the qualitative energy level diagram in Figure 8. The driving force for electron transfer ($\Delta G_{\text{et}}^{\text{T}}$) was determined according to the equation^{7,20}

$$\Delta G_{\text{et}}^{\text{T}} (\text{kcal mol}^{-1}) = 23.06(E_{\text{ox}} - E_{\text{red}}) - E_{\text{T}} - E_{\text{C}}$$

where E_{ox} is the first one-electron oxidation potential of the electron donor, E_{red} is the first one-electron reduction potential of the electron acceptor, E_{T} is the triplet-state energy of ZnTBPC (27.2 kcal mol⁻¹),²¹ and E_{C} is the Coulomb energy term (1.40 kcal mol⁻¹ in polar PhCN²²). The E_{ox} and E_{red} values of ZnTBPC and BPDI in PhCN were determined to be 0.58 and -0.53 V, respectively, by using a differential pulse voltammetry (DPV) technique (Figure S9, Supporting Information). BPDI was used for these measurements because of the low solubility of LPDI in PhCN. The side-chain substituents were found to have almost no effect on the electrochemical properties of the PDIs (vide supra).

Based on these values, the free energy change of electron transfer ($\Delta G_{\text{et}}^{\text{T}}$) through the triplet excited state of ZnTBPC was determined to be -3.0 kcal mol⁻¹ in PhCN.^{20,22,23} The negative

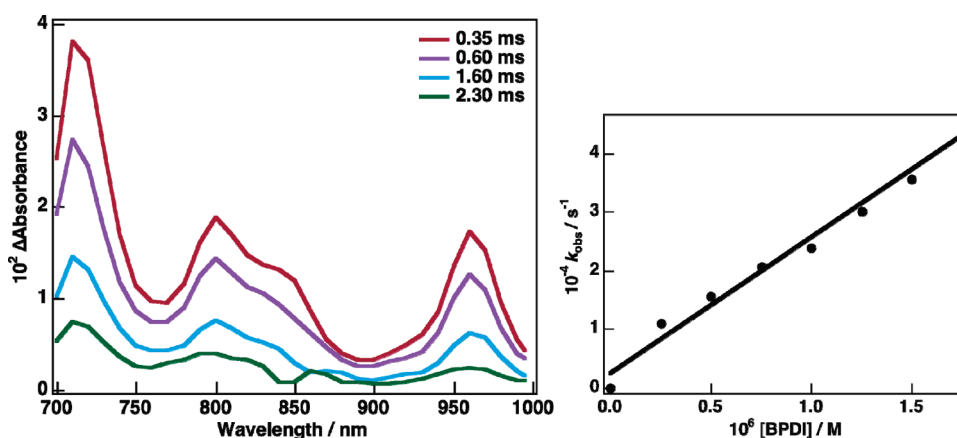


Figure 11. (Left) Nanosecond transient absorption spectra of ZnTBPC (0.06 mM) in the presence of BPDI (0.10 mM) in deaerated PhCN at the indicated time delays, $\lambda_{\text{ex}} = 355$ nm. (Right) Plot of the pseudo-first-order rate constant (k_{obs}) versus the concentration of ZnTBPC at 720 nm.

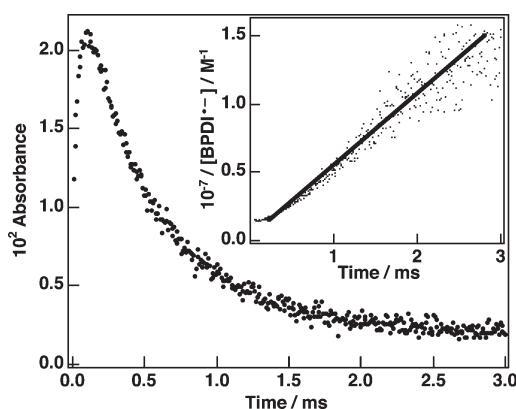


Figure 12. Decay time profile of the absorbance at 720 nm due to $\text{BPDI}^{\bullet-}$ in deaerated PhCN, $\lambda_{\text{ex}} = 355$ nm. Inset: Second-order plot.

$\Delta G_{\text{et}}^{\text{T}}$ value through the triplet excited state of ZnTBPC suggests that the quenching rate should be close to the diffusion-controlled limit (k_{diff}).^{24,25} Polar PhCN, stabilizing the radical ion pair of the radical cation ($\text{ZnTBPC}^{\bullet+}$) and the radical anion ($\text{LPDI}^{\bullet-}$), plays an important role in obtaining such an exothermic driving force.⁷ In addition, the BPDI/ZnTBPC mixture system has the same thermodynamic properties, because BPDI and LPDI have the same first one-electron reduction potentials.

Electron-Transfer Process of the $\text{ZnTBPC}/(\text{LPDI})_n$ Hybrid System. Nanosecond transient spectral measurements were performed to identify the products of the photoinduced electron transfer and to determine the kinetics of the electron-transfer and back-electron-transfer reactions. The transient absorption spectra of ZnTBPC and LPDI nanobelts in PhCN at selected time delays were obtained upon excitation at 355 nm. The maximum at 490 nm and the bleaching signal centered around 680 nm observed upon excitation are assigned to the triplet excited state of ZnTBPC in PhCN (Figure S10, Supporting Information). In the presence of the LPDI aggregates, the formation of the new peaks in the near-infrared (NIR) region following the quenching of $^3\text{ZnTBPC}^*$ was observed, as shown in Figure 9. The peaks with maxima at 720, 800, and 980 nm can be assigned to the radical anion of LPDI nanobelts by comparing with the steady-state absorption spectra of PDI radical anions obtained by the chemical reduction of PDI (Figure S11 in the Supporting Information).^{26,27}

The relatively sharp peak at 960 nm due to PDI radical anion in Figure S11 (Supporting Information) is red-shifted to 980 nm with a marked broadening up to 1070 nm for the radical anion of LPDI nanobelts in Figure 9. Such a broadening of the absorption band might result from an electron migration as reported for a similar oligomer system of PDI in solution.²⁸ In addition, one-dimensional aggregates of PDI containing reduced dopant molecules¹⁷ are reported to exhibit absorption in the NIR region similar to the transient spectra in Figure 9. This also indicates electron delocalization in the LPDI nanobelts following PET from ZnTBPC. The intense transient absorption peak at 840 nm in Figure 9 is attributed to radical cation of ZnTBPC, as recognized from the steady-state absorption spectra of ZnTBPC radical cation (Figure S12, Supporting Information).^{18a,b,29,30} Normally, BPDI has a molar extinction coefficient (ϵ) of $13500 \text{ M}^{-1} \text{ cm}^{-1}$ at 840 nm (Figure S11, Supporting Information), which is about twice that of $\text{ZnTBPC}^{\bullet+}$ at the same wavelength in PhCN.³¹ Because the formation of $\text{ZnTBPC}^{\bullet+}$ at 840 nm without any shielding can be clearly observed, it can be concluded that the ϵ value of $(\text{LPDI})_n^{\bullet-}$ is lower than that of the nonaggregated PDI molecule. Thus, the concentration of $\text{ZnTBPC}^{\bullet+}$ can be determined from the absorbance at 840 nm with the known ϵ value to analyze the kinetics of the back-electron-transfer reactions (vide infra). It should be noted that there is no transient signal due to the formation of the triplet excited state of LPDI¹⁹ through triplet–triplet energy transfer from $^3\text{ZnTBPC}^*$, even though their energy levels are very close (Figure 8). The rate of electron transfer obeys pseudo-first-order kinetics as shown in Figure 9 (see also Figure S13, Supporting Information). The pseudo-first-order rate constant increases linearly with increasing concentration of LPDI. From the slope of the linear plot in Figure 9 (right), the rate constant of electron transfer (k_{et}) from $^3\text{ZnTBPC}^*$ to LPDI was determined to be $1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The rate constant of back electron transfer (BET) from $(\text{LPDI})_n^{\bullet-}$ to $\text{ZnTBPC}^{\bullet+}$ (k_{bet}) indicates second-order kinetics. As shown in Figure 10, the decay profile of the absorbance at 840 nm due to $\text{ZnTBPC}^{\bullet+}$ was converted to a linear second-order plot. The k_{bet} value was determined from the slope in Figure 10 (inset), where the concentration of $\text{ZnTBPC}^{\bullet+}$ was estimated through the transient absorbance and molar absorptivity (ϵ) of $\text{ZnTBPC}^{\bullet+}$ at 840 nm.³¹ The slope affords the k_{bet} value of $6.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Second-order kinetics also confirms that ZnTBPC

and LPDI nanobelts have no noncovalent interactions, as was concluded from the steady-state absorption spectrum of the hybrid system.

Electron-Transfer Process of the ZnTBPC/BDPI Mixture System. The electron-transfer process of a mixture system comprising ZnTBPC and BPDI was investigated through nanosecond transient absorption spectroscopy techniques for comparison. Following excitation at 355 nm, the nanosecond differential spectra in Figure 11 display the same spectral features as were obtained chemically (Figure S11, Supporting Information), which can be interpreted in terms of PET from $^3\text{ZnTBPC}^*$ to BPDI in PhCN without π -electron delocalization. The electron-transfer rate from $^3\text{ZnTBPC}^*$ to BPDI also obeys pseudo-first-order kinetics, which was monitored by the absorbance change at 720 nm, as displayed in Figure 11 (see also Figure S14, Supporting Information). The pseudo-first-order rate constant of formation of $\text{BPDI}^{\bullet-}$ was found to increase linearly with increasing concentration of ZnTBPC. From the slope of the linear plot in Figure 11 (right), the k_{et} value was calculated as $2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is very close to that of the ZnTBPC/LPDI nanobelt mixture system.

It should be noted that the transient trait of ZnTBPC^{*+} at 840 nm overlaps with the shoulder of the transient absorption of $\text{BPDI}^{\bullet-}$ at 800 nm because of its low ϵ value compared to that of $\text{BPDI}^{\bullet-}$ (Figures S11 and S12, Supporting Information). Therefore, the back-electron-transfer kinetics can be assessed according to the absorbance of $\text{BPDI}^{\bullet-}$ at 720 nm.³² The BET from $\text{BPDI}^{\bullet-}$ to ZnTBPC^{*+} follows second-order kinetics (Figure 12). The k_{bet} value was determined from the slope of the linear plot in the inset of Figure 12 to be $4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is significantly larger than that of the ZnTBPC/LPDI nanobelt system ($6.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). The smaller k_{bet} value of the ZnTBPC/LPDI nanobelt system may be explained in terms of the electron delocalization within the π -system of the LPDI nanobelt. Even though the diffusion behaviors of suspended LPDI aggregates and dissolved BPDI molecules might be different in the solvent, the similar k_{et} values of the two systems show that the effects of this difference on the k_{bet} values can be neglected. Very fast delocalization inside the nanobelts might be compensating for a larger difference between the k_{bet} values. In any case, the distinctive transient absorption spectral characteristics of the radical anion of LPDI monitored in the NIR region clearly indicate the presence of delocalized electrons on the nanobelts after the occurrence of photoinduced electron transfer.

4. SUMMARY AND CONCLUSIONS

The LPDI nanobelt structure and its radical anion have been characterized spectroscopically. The photodynamics of electron-transfer events taking place (i) between LPDI nanobelts and ZnTBPC and (ii) between BPDI and ZnTBPC have been investigated by time-resolved transient absorption studies. Because of the stabilization effect of polar benzonitrile, low-energy $^3\text{ZnTBPC}^*$ was used as the driving force for photoinduced electron transfer. An explicit broadening of the radical anion peak of LPDI nanobelts at 980 nm was monitored by nanosecond transient absorption spectroscopy, confirming the delocalization of the transferred electron inside the LPDI nanobelts. The significantly lower rate of back electron transfer from $(\text{LPDI})_n^{\bullet-}$ to ZnTBPC^{*+} compared to that from $\text{BPDI}^{\bullet-}$ to ZnTBPC^{*+} might also indicate the effect of electron delocalization within the nanostructure.

■ ASSOCIATED CONTENT

S Supporting Information. Steady-state absorption spectra, DLS diagram, SEM and TEM images, EPR spectra, DPV voltammograms, X-ray diffraction pattern, optimized molecular structure, and nanosecond transient absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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