

Organic Electronics

Accessing the Triplet State in Heavy-Atom-Free Perylene Diimides

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Abstract: Previous studies of perylenediimides (PDIs) mostly utilized the lowest singlet excited state S1. Generation of a triplet excited state (T_1) in PDIs is important for applications ranging from photodynamic therapy to photovoltaics; however, it remains a formidable task. Herein, we developed a heavy-atom-free strategy to prompt the $T_1 \leftarrow S_1$ intersystem crossing (ISC) by introducing electrondonating aryl (Ar) groups at the head positions of an electron-deficient perylenediimide (PDI) core. We found that the ISC efficiency increases from 8 to 54% and then to 86% by increasing the electron-donating ability of headsubstituted aryl groups from phenyl (p-PDI) to methoxyphenyl (MeO-PDI) and then to methylthioxyphenyl (MeS-PDI). By enhancing the intramolecular charge-transfer (ICT) interaction from p-PDI to MeO-PDI, and then to MeS-PDI, singlet oxygen generation via energy-transfer reactions from T_1 of PDIs to ${}^{3}O_2$ was demonstrated with the highest yield of up to 80%. These results provide guidelines for developing new triplet-generating PDIs and related rylene diimides for optoelectronic applications.

Perylenediimide (PDI) derivatives have emerged as quintessential photofunctional materials owing to their high chemical robustness, photo- and thermostability, and chemically tunable optical and electronic properties,^[1] which render PDIs as promising candidates for applications in optical sensing,^[2] fluorescent tags,^[3] biological probes,^[4] organic electronics,^[5] and photosynthesis mimics.^[6] Note that most of these applications uti-

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lized the lowest singlet excited state S₁ of PDIs, such as fluorescence. Investigations on the triplet excited state T₁ of PDIs, however, have been limited, though T₁ of PDIs is important for understanding fundamental photochemistry and photophysics related to applications, such as phosphorescence, electroluminescence, photodynamic therapy (PDT), and photovoltaics. Especially, given recent reports highlighting that photovoltaic performance is remarkably increased by using a PDI derivative/ polymer as the photoactive layer,^[5a,d-f] access to the PDI triplet state clearly represents an attractive interest for solar energy conversion due to the prolonged exciton diffusion length.^[7] Therefore, the development of triplet-generating PDI chromophores is of crucial importance.

The PDI triplet can be approached by either an internal heavy-atom effect^[8] or complicated multicomponent excitonic interactions.^[9] Wurthner^[8a] and Castellano's^[8b] groups have independently introduced PDI chromophores linked with heavymetal atom (Ru, Ir, and Pt) at the bay positions of the perylene core and observed efficient and long-lived PDI triplet generation. Janssen and co-workers have investigated a cofacially stacked PDI dimer and characterized an enhanced intersystem crossing (ISC) to produce the PDI triplet via a high-energy charge-transfer state.^[9a] Recent studies by Wasielewski and coworkers on a slipped-stacked PDI polycrystalline film revealed the case of high triplet yield by a singlet fission process.^[9b] It is still a substantial challenge to develop PDI-based small molecules capable of efficient ISC, especially those without any heavy atoms.

Herein we propose a new approach to address this challenge by introducing substitutions at the headland positions of PDI (see Figure 1). We show that ISC systems can be designed on the basis of intramolecular charge-transfer interactions within the PDI framework, and we demonstrate this with a new class of triplet-generating materials, that is, N,N-bis(2ethylpropyl)-2,5,8,11-tetra(p-phenyl)perylene diimide (p-PDI),



Figure 1. The synthetic route of Ru-catalyzed four-fold arylation of PDI.

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N,N-bis(2-ethylpropyl)-2,5,8,11-tetra(*p*-methoxyphenyl)perylene diimide (MeO-PDI), and *N,N*-bis(2-ethylpropyl)-2,5,8,11-tetra(*p*-methylthioxyphenyl)perylene diimide (MeS-PDI). With this model system, we observe that intersystem crossing rate can be regulated through the modulation of CT interactions imparted by the appended aryl groups. The obtained PDI triplet can sensitize the molecular oxygen quantitatively to yield ${}^{1}O_{2}$, with efficiencies of singlet oxygen generation (Φ_{Δ}) as high as 0.80.

The Ar-PDI compounds were synthesized based on the Rucatalyzed reaction published previously.^[10] Figure 1 illustrates Ru-catalyzed fourfold arylation of PDIs. Bis(*N*-ethylpropyl)perylenediimide and phenyl boronic acid neopentyl glycol ester were mixed and heated in refluxing mesitylene and pinacolone at 140 °C for 40 h in the presence of 25 mol% of $[RuH_2(CO)(PPh_3)_3]$ (for details see the Experimental Section in the Supporting Information). After silica-gel separation, *p*-PDI was obtained in 59% yield and was characterized by ¹H NMR and MALDI-MS. MeO-PDI and MeS-PDI have been also synthesized with the same method.

The UV/Vis absorption and steady-state emission spectra of the headland-substituted Ar-PDIs in CH₂Cl₂ solution are presented in Figure 2. All compounds exhibit strong π - π * transition bands and vibronic progressions (Table 1), which is in accord with the well-established unsubstituted PDI dyes.^[11] A slight redshift is observed upon the attachment of the aryl groups. Despite their typical PDI-based spectral features, all



Figure 2. UV/Vis absorption (a) and steady-state emission (b) spectra of the headland-substituted Ar-PDIs in CH_2CI_2 solution. c) Near-IR phosphorescence spectra in N_2 -saturated CH_2CI_2 at 77 K. In (a), (b), and (c), red, green, and blue lines are for *p*-PDI, *MeO*-PDI, and *MeS*-PDI, respectively. d) The LUMO (top) and HOMO (bottom) obtained by density functional method at the B3LYP/6-31G(d) level. e) Approximate energy-level diagram and photophysical processes of Ar-PDIs in CH_2CI_2 solution.

| Table 1. Photophysical Parameters of Ar-PDIs in CH2Cl2 solutions. | | | | | | | | | | | |
|---|-------------------------|------------------------|-------------------|-------------------|--------------------|---|---|--|--|--|--|
| Sample | $\lambda_{ m Abs}$ [nm] | $\lambda_{\rm F}$ [nm] | $	au_{ m F}$ [ns] | $\varPhi_{\rm F}$ | λ_{P} [nm] | $	au_{\mathrm{T}} [\mathrm{\mu s}]^{\mathrm{[b]}}$ | $	au_{\mathrm{T}} [\mathrm{\mu s}]^{\mathrm{[c]}}$ | $arPsi_{	extsf{T}}$ [%] ^[d] | $\varPhi_{\boldsymbol{\Delta}}{}^{[\mathrm{e}]}$ | | |
| PDI ^[f] | 458, 488, 525 | 533, 572 | 5.55 | 0.88 | | | | | | | |
| p-PDI | 460, 493, 528 | 541, 581 | 0.96 | 0.16 | 897, 1060 | 0.69 | 30.6 | 8% | 0.05 | | |
| MeO-PDI | 462, 495, 532 | 536, 576 | within IRF | < 0.01 | 927, 1070 | 0.52 | 59.7 | 54% | 0.50 | | |
| MeS-PDI | 463, 496, 533 | 533, 572 | within IRF | < 0.01 | 938, 1077 | 0.71 | 61.4 | 86% | 0.80 | | |
| [a] $\tau_{\rm F}$ is the FL decay, and the $\Phi_{\rm F}$ is fluorescence quantum yield. [b] Triplet lifetime in air-saturated CH ₂ Cl ₂ . [c] Triplet lifetime in N ₂ -saturated CH ₂ Cl ₂ . [d] $\Phi_{\rm T}$ is the triplet yield. [e] $\Phi_{\rm A}$ is the quantum yield for singlet oxygen. [f] See ref. [11]. | | | | | | | | | | | |

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three samples are weakly emissive, with fluorescence quantum yields of 0.16 for p-PDI, <0.01 for MeO-PDI, and <0.01 for MeS-PDI, which is in sharp contrast to the parent PDI.^[11] We also note that the Stokes shift between the absorption and fluorescence peaks is largely reduced in MeO-PDI and MeS-PDI. Time-resolved fluorescence studies clarify that fluorescence time profiles of MeO-PDI and MeS-PDI can be well-fitted with a biexponential function, indicative of the significant chargetransfer character of the excited states.^[12] The emission of p-PDI decays in a simple monoexponential manner, resulting in a lifetime of 0.96 ± 0.01 ns (Table 1 and Figure S1, Supporting Information). The short-lived components of MeO-PDI and MeS-PDI cannot be well resolved due to the limitation of our instrumental response function (IRF), which is in agreement with the observed $\Phi_{\rm F}$ values. The enormous fluorescence quenching as well as the accelerated emission decay suggests the efficient nonradiative decay channel is active in the studied model system.

To unravel the origin of the unusual emission behavior and investigate the underlying photophysical processes of Ar-PDIs, femtosecond transient absorption spectra were recorded in CH₂Cl₂ after selective photoexcitation of Ar-PDI. Upon 480 nm pulsed photoexcitation of MeO-PDI, ground-state bleaching at ~530 and 600-730 nm positive absorption features emerge within IRF and are attributed to the generation of lowest singlet-excited PDI¹³. The ¹PDI* decays monoexponentially with a lifetime of 28 ± 3 ps, in line with the time-resolved fluorescence data. Meanwhile, an additional absorption band peaked at 555 nm increases in concert with the decay of the 720 nm feature, with a time constant of 27 ± 5 ps. The 555 nm absorption persists across the entire time window of the transient absorption measurement. We assign this long-lived feature to the triplet excited state of PDI^[10] (vide infra, see also in triplet sensitization measurements). Similar spectral dynamics are also shown in MeS-PDI. The transient absorption at 555 nm rises up with a time constant that corresponds to the decay at 720 nm. Global fitting of 720 and 555 nm traces (squares in Figure 3) show one decay component of 84 ± 5 ps and one rise component of 91 \pm 8 ps. A pseudoisosbestic point at ~590 nm is observed (Figure 3 c), which is direct evidence for a singlet-to-triplet intersystem crossing process. As for p-PDI, a triplet-oriented spectral pattern is also fairly observed (Figure 3 a).

Low-temperature phosphorescence spectroscopy and nanosecond flashlamp photolysis were conducted to estimate the energy level of the lowest triplet excited state and to obtain the related characters of the triplet state. In N₂-saturated solution, phosphorescence bands can be observed with 897 nm for *p*-PDI, 927 nm for MeO-PDI, and 938 nm for MeS-PDI, respectively. Figure 4a reveals the time profile of *p*-PDI in a nitrogen-saturated CH₂Cl₂ solution on the microsecond timescale. The T_n-T₁ absorption at 555 nm decays single-exponentially with a time constant of 30.6 µs. A much faster lifetime of 0.69 µs is obtained for *p*-PDI in an air-saturated solution. For MeO-PDI, the T_n-T₁ transient absorption was also monitored and resulted in τ_{EnT} =0.52 µs for the air-saturated solution and τ =59.7 µs for the nitrogen-saturated solution (Figure 4c). Similarly, the τ_{EnT} of Ms-PDI is 0.71 µs in aerated solution and 61.4 µs in deaerated solution. Apparently, the ³Ar-PDI* is efficiently quenched by the dissolved molecular oxygen due to energy transfer from Ar-PDIs' T₁ to ground-state ³O₂. Considering the highly electron-deficient structure of Ar-PDIs, the possibility of the electron-transfer reaction from ³Ar-PDI to ³O₂ is ruled out and the quantum efficiency of energy transfer $\Phi_{EnT=}$ (1– τ_{EnT}/τ_{T}) is estimated to be 98, 99, and 99% for *p*-PDI, MeO-PDI, and MeS-PDI, respectively.

We then use bimolecular triplet sensitization techniques to obtain triplet absorption cross-sections and to determine triplet quantum yields of the studied systems (for details, see Experimental Section in the Supporting Information). These triplets are optically probed to generate the triplet-induced absorption spectrum (Figure 4a) with long-lasting triplet lifetime and high extinction coefficient (18700, 16800, and 13400 M^{-1} cm⁻¹ for *p*-PDI, MeO-PDI, and MeS-PDI, respectively). The triplet sensitization experimental results agree well with the proposed T₁-induced absorption from femtosecond transient absorption spectroscopy, which confirms the triplet being formed on an ultrafast timescale following optical excitation of the studied Ar-PDI compounds. Note that all Ar-PDIs have a similar T₁ spectral pattern, although the overlapping groundstate bleaching makes different contributions to net transient absorption. It is straightforward to independently determine that the triplet yield for *p*-PDI is 8% in use of the single triplet absorption cross-section (for details see the Supporting Information). The values for MeO-PDI and MeS-PDI are 54 and 86%, respectively.

The above triplet generation upon direct photoexcitation and kinetics analysis prove clearly a highly efficient ISC process. We propose an energetic diagram for related photophysical processes. Theoretical computational studies were performed by using DFT methods at the B3LYP/6-31G(d) level. It can be found that the appended aromatic groups of Ar-PDIs exhibit ring twists relative to the planar PDI skeleton. In the optimized structure, the LUMOs of the PDIs are all localized on the polyaromatic core. However, the HOMOs exhibit distinct characters, in which the electronic density for p-PDI is located at the PDI moiety, whereas those for MeO-PDI and MeS-PDI are rather spread over the aryl groups. Strong charge-transfer interactions are introduced in the system. It has been reported that spatial separation of the HOMO and LUMO will result in the decreased singlet triplet energy offset (ΔE_{sT}) .^[14] The calculated excitation energy difference of the low-lying excited singlet (S_n) and triplet states (T_n) for Ar-PDIs are shown to largely reduce when n > 2. This would enhance the spin-orbital coupled intersystem crossing from singlet to triplet manifold, as is evidenced by the measured triplet yield sequence of MeS-PDI > MeO-PDI > p-PDI. Moreover, the replacement of the oxygen atom with a sulfur atom may also lead to an additional increase in the spin-orbital interactions. Furthermore, the higher energy of the Ar-PDI's T_1 state (~1.3 eV) than that of ${}^{1}O_2$ as well as its large electron affinity makes the energy-transfer reaction between them highly efficient. Comparison between p-PDI, MeO-PDI, and MeS-PDI suggests that the electron-donating ability of substitutions on the headland positions of PDIs influence the photophysics significantly.



Figure 3. a, c, and e) Femtosecond time-resolved absorption spectra in CH_2CI_2 at indicated delay times. b, d, and f) The corresponding time-absorption profiles at 532, 555, and 720 nm. The solid lines present the fitting.

The actual efficiency of ${}^{1}O_{2}$ generation (Φ_{Δ}) was also measured by using 9,10-diphenylanthracene (DPA) as a chemical trap and hypocrellin A (HA) as a standard (Φ_{Δ} =0.84 in CH₂Cl₂).^[15] Values of Φ_{Δ} =0.05, 0.50, and 0.80 were obtained for *p*-PDI, MeO-PDI, and MeS-PDI, respectively (Figure S8, Supporting Information). All of them show remarkable singlet oxygen generation upon 532 nm continuous laser irradiation. In addition, no detectable degradation of Ar-PDIs was observed upon laser exposure for over 24 h. This suggests the excellent photostability of Ar-PDIs, probably due to their resistance against photo-oxidation as a result of their large electron-deficient π -framework.

In conclusion, we have designed and characterized a new family of headland aryl-substituted PDI systems free from heavy atoms. The distorted aryl unit from the central PDI plane, as well as the frontier orbital separation due to strong charge-transfer interactions was suggested to promote a remarkably rapid $T \leftarrow S$ ISC process. Moreover, the higher energy of the PDI's T_1 state than that of ${}^{1}O_2$ combined with its long lifetime can sensitize ${}^{1}O_2$ generation efficiently. The heavy-atom-free character makes these materials especially environmentally-friendly and biocompatible. These prominent features of the studied Ar-PDIs render them a new structural alternative of PDI for the development of new optoelectronic materials.

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Figure 4. The nanosecond transient absorption spectra (a) and time-absorption profiles at 490 and 560 nm (b) recorded using flash photolysis of Ar-PDIs upon excitation with 532 nm, \sim 2 mJ, and 0.45 cm diameter laser pulse (d) Time-absorption profiles at 490 and 560 nm recorded by nanosecond flash photolysis for Ar-PDIs in N₂-saturated CH₂Cl₂ solutions at room temperature.

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Keywords: charge transfer • intersystem crossing • perylene diimide • singlet oxygen generation • triplet excited state

- F. Wurthner, C. R. Saha-Moller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmit. Chem. Rev. 2015, DOI: 10.1021/acs.chemrev.5b00188.
- [2] a) M. Xu, J. M. Han, Y. Zhang, X. Yang, L. Zang, *Chem. Commun.* 2013, 49, 11779–11781; b) L. Zang, R. Liu, M. W. Holman, K. T. Nguyen, D. M. A. Adams, J. Am. Chem. Soc. 2002, 124, 10640–10641.
- [3] T. Weil, T. Vosch, J. Hofkens, K. Peneva, K. Mullen, Angew. Chem. Int. Ed. 2010, 49, 9068–9093; Angew. Chem. 2010, 122, 9252–9278.
- [4] V. L. Malinovskii, D. Wenger, R. Haner, Chem. Soc. Rev. 2010, 39, 410– 422.
- [5] a) X. Zhang, Z. H. Lu, L. Ye, C. L. Zhan, J. H. Hou, S. Q. Zhang, B. Jiang, Y. Zhao, J. H. Huang, S. L. Zhang, Y. Liu, Q. Shi, Y. Q. Liu, J. N. Yao, Adv. Mater. 2013, 25, 5791–5797; b) C. Li, H. Wonneberger, Adv. Mater. 2012, 24, 613–636; c) W. Jiang, Y. Li, Z. H. Wang, Acc. Chem. Res. 2014, 47, 3135–3147; d) P. E. Hartnett, A. Timalsina, H. S. S. Ramakrishna-Matte, N. Zhou, X. Guo, W. Zhao, A. Facchetti, R. P. H. Chang, M. C. Hersam, M. R. Wasielewski, T. J. Marks, J. Am. Chem. Soc. 2014, 136, 16345–16356; e) Y. Zang, C. Z. Li, C. C. Chueh, S. T. Williams, W. Jiang, Z. H. Wang, J. S. Yu, A. K. Y. Jen, Adv. Mater. 2014, 26, 5708–5714; f) Y. Zhong, M. T. Trinh, R. Chen, W. Wang, P. P. Khlyabich, B. Kumar, Q. Xu, C. Y. Nam, M. Y. Sfeir, C. Black, M. L. Steigerwald, Y. L. Loo, S. Xiao, F. Ng, X. Y. Zhu, C. Nuckolls, J. Am. Chem. Soc. 2014, 136, 15215–15221.
- [6] M. R. Wasielewski, Acc. Chem. Res. 2009, 42, 1910-1921.
- [7] H. Najafov, B. Lee, Q. Zhou, L. C. Feldman, V. Podzorov, Nat. Mater. 2010, 9, 938–943.
- [8] a) M. Schulze, A. Steffen, F. Wurthner, Angew. Chem. Int. Ed. 2015, 54, 1570–1573; Angew. Chem. 2015, 127, 1590–1593; b) A. A. Rachford, S. Goeb, F. N. Castellano, J. Am. Chem. Soc. 2008, 130, 2766–2767.
- [9] a) D. Veldman, S. M. A. Chopin, S. C. J. Meskers, R. A. J. Janssen, *J. Phys. Chem. A* 2008, *112*, 8617–8632; b) S. W. Eaton, L. E. Shoer, S. D. Karlen, S. M. Dyar, E. A. Margulies, B. S. Veldkamp, C. Ramanan, D. A. Hartzler, S.

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Savikhin, T. J. Marks, M. R. Wasiekewski, *J. Am. Chem. Soc. J. Am. Chem. Soc* **2013**, *135*, 14701–14712; c) C. C. Hofmann, S. M. Lindner, M. Ruppert, A. Hirsch, S. A. Haque, M. Thelakkat, J. Kohler, *Phys. Chem. B* **2010**, *114*, 9148–9156.

- [10] S. Nakazono, S. Easwaramoorthi, D. Kim, H. Shinokubo, A. Osuka, Org. Lett. 2009, 11, 5426-5429.
- [11] F. Würthner, Chem. Commun. 2004, 1564-1579.
- [12] E. Busby, J. Xia, Q. Wu, J. Z. Low, R. Song, J. R. Miller, X. Y. Zhu, L. M. Campos, M. Y. Sfeir, *Nat. Mater.* 2015, *14*, 426–433.
- [13] A. Prodi, C. Chiorboli, F. Scandola, E. Lengo, E. Alessio, R. Dobrawa, F. Wurthner, J. Am. Chem. Soc. 2005, 127, 1454–1462.
- [14] a) U. Hiroku, G. Kenichi, S. Katsuyuki, N. Hiroko, C. Adachi, *Nature* 2012, 492, 234–238; b) G. Méhes, H. Nomura, Q. Zhang, T. Nakagawa, C. Adachi, *Angew. Chem. Int. Ed.* 2012, *51*, 11473–11477; *Angew. Chem.* 2012, *124*, 11640–11644.
- [15] Z. Diwu, J. W. Lown, J. Photochem. Photobiol. A 1992, 64, 273-287.

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