

Intersystem Crossing and Triplet-State Property of Anthryl- and Carbazole-[1,12]fused Perylenebisimide Derivatives with a Twisted π -Conjugation Framework

Zafar Mahmood,^{\perp} Andrey A. Sukhanov,^{\perp} Noreen Rehmat,^{\perp} Mengyu Hu, Ayhan Elmali, Yi Xiao, Jianzhang Zhao,^{*} Ahmet Karatay,^{*} Bernhard Dick,^{*} and Violeta K. Voronkova^{*}



efficient intersystem crossing (ISC) in planar neavy atom-free aromatic organic compounds is challenging. Herein, we demonstrate that two perylenebisimide (PBI) derivatives with anthryl and carbazole moieties fused at the bay position, showing twisted π conjugation frameworks and red-shifted UV–vis absorption as compared to the native PBI chromophore (by 75–1610 cm⁻¹), possess efficient ISC (singlet oxygen quantum yield: $\Phi_{\Delta} = 85\%$) and a long-lived triplet excited state ($\tau_{\rm T} = 382 \ \mu s$ in fluid solution and $\tau_{\rm T} = 4.28$ ms in solid polymer film). Femtosecond transient



absorption revealed ultrafast intramolecular charge-transfer (ICT) process in the twisted PBI derivatives (0.9 ps), and the ISC takes 3.7 ns. Pulsed laser excited time-resolved electron paramagnetic resonance (TREPR) spectra indicate that the triplet-state wave function of the twisted PBIs is mainly confined on the PBI core, demonstrated by the zero-field-splitting *D* parameter. Accordingly, the twisted derivatives have higher T_1 energy ($E_{T_1} = 1.48 - 1.56 \text{ eV}$) as compared to the native PBI chromophore (1.20 eV), which is an advantage for the application of the derivatives as triplet PSs. Theoretical computation of the Franck–Condon density of states, based on excited-state dynamics methods, shows that the efficient ISC in the twisted PBI derivatives is due to the increased spin– orbit coupling matrix elements for the S_1-T_1 and S_1-T_2 states [spin–orbit coupling matrix element (SOCME): 0.11–0.44 cm⁻¹. SOCME is zero for native PBI], as well as the Herzberg–Teller vibronic coupling. For the planar benzoPBI, the moderate ISC is due to $S_1 \rightarrow T_2$ transition (SOCME: 0.03 cm⁻¹. The two states share a similar energy, ca. 2.5 eV).

1. INTRODUCTION

Perylenebisimides (PBIs) are popular organic chromophores with extended π -conjugated molecular structure that offer excellent thermal, photochemical, and electrochemical stabilities and strong absorption of visible light.¹⁻³ PBIs have been widely used as light-absorbing or light-emitting chromophores in organic solar cells,⁴⁻⁶ light-emitting diodes,⁷ organic solidstate lasers,⁸ and so forth. Strong absorption of visible light and high fluorescence quantum yield make the PBIs an ideal candidate for application in molecular assemblies,⁹⁻¹² twophoton absorption dyes,¹³ fluorescence probes, and fluorescence bioimaging.¹⁴⁻¹⁶ Moreover, the PBI core provides a number of positions for functionalization; thus, chemical modification through substitution with different moieties on the PBI core can drastically change the photophysical properties of PBIs. However, the lack of intersystem crossing (ISC) ability restricts the application of PBIs in photochemistry. Many studies have been devoted to tune the singlet excited-state properties of PBIs,¹⁷⁻²⁰ but little effort has been made to improve their triplet excited-state generation ability.

The triplet excited state plays a crucial role in H₂ production through water splitting,^{21–23} photocatalysis,^{24–26} photodynamic therapy (PDT),^{27–29} and triplet-triplet annihilation (TTA) upconversion.^{30–32} ISC is the crucial property for the triplet photosensitizers (PSs).³³ Several strategies have been developed to enhance the ISC efficiency of triplet PSs, such as the heavy atom effect,^{34–37} but this method suffers from high cost, toxicity of heavy atoms (Ir, Ru, Pt, I, or Br atom), and the shortened triplet-state lifetimes. Other approaches to induce efficient ISC are the $n-\pi^* \leftrightarrow \pi-\pi^*$ transitions (El-

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Scheme 1. Synthesis of Twisted PBI Derivatives and the Reference Compounds^a



^{*a*}Key: (a) 3-Aminopentane, imidazole, refluxed at 140 °C for 4 h under a N₂ atmosphere, and yield: 95%; (b) Br₂, K₂CO₃, CHCl₃, refluxed at 60 °C for 2 h, under N₂, and yield: 45%; (c) 2-anthraceneboronic acid, K₂CO₃, PhCH₃/C₂H₅OH/H₂O (4:2:1, v/v), Pd(PPh₃)₄, refluxed at 90 °C for 8 h under a N₂ atmosphere, and yield: 75%; (d) $h\nu$, I₂, PhCH₃, stirred at rt for 4 h, and yield: 86%; (e) (9-phenyl-9*H*-carbazol-3-ylboronic acid), the reaction conditions are similar to that of (c), yield: 73%; (f) phenyl boronic acid, the reaction conditions are similar to that of (c), yield: 70%; and (h) reaction conditions are similar to that of (d), yield: 66%.

Sayed rule),³⁸ exciton coupling,^{39,40} use of spin converters,^{41–43} and the energy level matching of the S_n/T_n states.⁴⁴ Recently, the ISC of few twisted compounds has been studied, and it was observed that twisting of the π -conjugation framework of a chromophore can enhance the ISC.^{45–49}

PBI-based heavy atom-free triplet PSs are rarely reported. Several strategies were used to generate a triplet excited state in the PBI chromophore including triplet sensitization,⁵⁰ attaching heavy atoms or transition metals to the PBI core, ${}^{51-53}$ replacing the oxygen atoms of the carbonyl groups with sulfur atoms, 54 singlet fission, 55 charge recombination in electron donor-acceptor dyads, 56,57 attaching substituents at the ortho position,⁴⁴ or based on twisting of the PBI core.^{45,47} It is well known that attaching of bulky groups at the bay position of the PBI can twist its core, but the ISC capability of such system was not fully studied.58,59 The ISC of phenanthrene-fused PBI derivatives was studied.⁴⁶ These fused derivatives exhibit enhanced ISC, but the triplet quantum yield is low ($\Phi_{\rm T}$ = 10–30%) and the triplet excited state is short-lived (3.7–19.6 μ s). Triply bay-fused di-PBIs were also studied for enhanced ISC due to distorted structure.⁴⁷ A high singlet oxygen quantum yield (Φ_{Δ}) of 59–67% and a triplet lifetime up to $35-56 \ \mu s$ were observed for these derivatives, but the relationship of molecular structure and ISC efficiency and the triplet-state property were not studied in detail. For instance, the spatial localization of the triplet-state wave function was not studied. It is worthy to develop simple PBI derivatives with efficient ISC capability and long-lived triplet

excited state and to unravel the ISC mechanism and tripletstate property in these twisted compounds in detail.

Herein, we studied the ISC of PBI derivatives that have extended π -conjugation at the bay position. Previous studies demonstrate that the steric congestion at the bay position of PBI can cause twisting of the PBI core and result in enhanced ISC.^{45,46} We prepared two PBI-twisted derivatives by fusing anthryl and carbazole moieties (Scheme 1) at the bay position of PBI. The photophysical properties of these twisted derivatives were investigated in detail by using steady-state and time-resolved absorption and emission spectroscopic methods. We find that these derivatives have efficient ISC capability and a long-lived triplet excited state. Theoretical computation of the Franck-Condon density of states of the possible ISC pathways indicates that the efficient ISC of the twisted PBIs is due to the increased spin-orbit coupling matrix elements (SOCMEs) and the Herzberg-Teller vibronic coupling of $S_1 \rightarrow T_1$, induced by the twisted molecular structures, whereas the moderate ISC of the planar benzo-PBI is due to the non-negligible SOCME of $S_1 \rightarrow T_2$ ISC.

2. EXPERIMENTAL SECTION

2.1. General Methods. All chemicals used in the synthesis are of analytical grade and used as received. The solvents were dried before using for synthesis of the compounds. UV-vis absorption spectra were collected on a UV-2550 UV-vis spectrophotometer (Shimadzu Ltd., Japan). Fluorescence emission spectra were obtained on an RF-5301 PC

spectrofluorometer (Shimadzu Ltd., Japan). Fluorescence lifetimes were measured by an OB920 luminescence lifetime spectrometer (TCSPC detection mode. Edinburgh Instruments Ltd, U.K.) using an EPL 510 nm picosecond pulsed laser, and the instrument response function (IRF) is 100 ps; the repetition rates of the EPL picosecond laser for different lifetime ranges depend on the lifetime ranges to be measured: 20 MHz for 50 ns, 10 MHz for 100 ns, and 5 MHz for 200 ns.

2.2. Synthesis of PBI-1. Compound **2** (70 mg, 0.1 mmol) and I_2 (20 mg, 0.079 mmol) were dissolved in toluene (100 mL). The solution was photo-irradiated by white light (xenon lamp) for 3 h at room temperature. The reaction progress was monitored by TLC. After the completion of the reaction, the reaction mixture was concentrated under reduced pressure to obtain the crude product, which was further purified by column chromatography (silica gel, CH₂Cl₂). PBI-1 was obtained as a dark red solid (60 mg, yield: 86%). ¹H NMR $(CDCl_3, 400 \text{ MHz})$: δ 10.09 (s, 1H), 9.76 (s, 1H), 9.10 (s, 1H), 9.04–9.02 (m, 2H), 8.92–8.89 (m, 2H), 8.56 (d, 1H, J = 8.0 Hz, 8.47 (s, 1H), 8.12 (d, 1H, J = 8.0 Hz), 8.09-8.04 (m, J = 8.0 Hz), 8.2H), 7.65-7.55 (m, 2H), 5.24-5.13 (m, 2H), 2.43-2.27 (m, 4H), 2.14–2.03 (m, 4H), 1.05 (t, 12H, J = 8.0 Hz). ¹³C NMR (100 MHz, CDCl₃): δ132.8, 132.7, 131.9, 131.8, 130.9, 130.4, 129.9, 128.9, 128.5, 127.6, 127.1, 126.9, 126.7, 126.6, 126.5, 126.4, 123.8, 123.6, 123.4, 123.3, 122.7, 122.5, 120.1, 58.0, 57.9, 25.1, 25.1, 11.6, 11.6. TOF MALDI-HRMS $(C_{48}H_{36}N_2O_4^{-})$, calcd: m/z = 704.2675; found, m/z =704.2693.

2.3. Synthesis of PBI-2. PBI-2 was synthesized using compound 3 (75 mg, 0.1 mmol) as the starting material, following a similar method used for the synthesis of PBI-1. **PBI-2** was obtained as a dark red solid (54 mg, yield: 70%). ¹H NMR (CDCl₃, 500 MHz): δ 10.66 (s, 1H), 9.86 (s, 1H), 8.99–8.92 (m, 3H), 8.95 (d, 1H, J = 10.0 Hz), 8.75 (d, 2H, J = 10.0 Hz), 8.01 (d, 1H, J = 10.0 Hz), 7.82–7.77 (m, 4H), 7.71-7.67 (m, 1H), 7.61-7.58 (m, 2H), 7.46-7.42 (m, 1H), 5.22-5.12 (m, 2H), 2.42-2.26 (m, 4H), 2.14-2.02 (m, 4H), 1.06 (t, 6H, J = 10.1 Hz), 1.00 (t, 6H, J = 10.0 Hz). ¹³C NMR (100 MHz, CDCl₃): δ141.3, 141.3, 136.8, 133.2, 132.8, 130.3, 128.8, 128.6, 128.2, 127.2, 127.1, 126.7, 126.6, 126.4, 124.6, 124.1, 123.9, 123.7, 122.6, 122.4, 122.3, 121.7, 120.8, 116.9, 113.7, 110.9, 57.9, 57.7, 25.1, 25.1, 11.6. TOF MALDI-HRMS $(C_{52}H_{39}N_3O_4^{-})$, calcd: m/z = 769.2941; found, m/z =769.2962.

2.4. Synthesis of PBI-3. PBI-3 was synthesized using compound 4 (60 mg, 0.1 mmol) as the starting material, following a similar method used for the synthesis of **PBI-1**. **PBI-3** was obtained as an orange solid (40 mg, yield: 66%). ¹H NMR (CDCl₃, 400 MHz): δ 9.46 (s, 2H), 8.78–8.76 (m, 6H), 7.97 (s, 2H), 5.21–5.15 (m, 2H), 2.44–2.35 (m, 4H), 2.18–2.12 (m, 4H), 1.12–1.09 (m, 12H). TOF MALDI–HRMS ([C₄₀H₃₂N₂O₄]⁻), calcd: *m*/*z* = 604.2362; found, *m*/*z* = 604.2384.

2.5. Nanosecond Transient Absorption Spectroscopy. The nanosecond transient absorption spectra were recorded on an LP980 laser flash photolysis spectrometer (Edinburg Instruments, U.K.) equipped with a Tektronix TDS 3012B oscilloscope. The samples were deaerated with N_2 for 15 min prior to measurements and excited with a nanosecond pulsed laser (Opolette, the wavelength is tunable in the range of 210–2400 nm. OPOTEK, USA). The typical laser power is ca. 5 mJ per pulse. The data was processed by L900 software.

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2.6. Femtosecond Transient Absorption Spectroscopy. The femtosecond transient absorption spectroscopy instrument consists of a Ti:sapphire laser amplifier-optical parametric amplifier system with a 1 kHz repetition rate and 50 fs pulse duration (Spectra-Physics, Spitfire Pro XP, TOPAS) and a commercial pump-probe experimental device (Spectra-Physics, Helios); the signal is monitored by a white light continuum probe. The instrument resolution is 120 fs. The pump beam spot size was measured to be 400 μ m by using a profilometer and the knife edge method. According to the spot size and energy measurements (spot diameter = 400 μ m and pump laser energy = 1 μ J), the pump beam fluence is calculated as $\sim 8.0 \times 10^{-4}$ J cm⁻² on the sample in the pump probe experiment. The excitation wavelength was selected according to the absorption spectrum of the compounds. The angle between the probe and pump beam polarization directions was set up perpendicularly in the measurement. The data were subdivided and fitted using the Glotaran-Application 1.5.1 and Surface Xplorer,⁶⁰ and all data were chirp-corrected before global fitting.

2.7. Time-Resolved Electron Paramagnetic Resonance Spectroscopy. The time-resolved continuous-wave (TR CW) EPR measurements were performed on an X-band EPR Elexsys E-580 spectrometer (Bruker) at 80 K. The samples were dissolved in toluene/MeTHF (3:1, v/v). The oxygen was removed by a few freeze-pump-thaw circles. The samples were excited by the second harmonic of a Nd:YAG pulsed laser pumped optical parameter oscillator (Quantel Brilliant, $\lambda = 500$ nm, pulse length = 5 ns; E/pulse = ca. 10 mJ). The spectra were simulated using the EasySpin package based on Matlab.⁶¹

2.8. Photoreduction Experiment. A xenon lamp (20 mW/cm^2 , 35 W) was used to perform the photoreduction experiment. Triethanolamine (TEOA) was used as a sacrificial electron donor. An Agilent 8453 UV–vis spectrophotometer was employed to record the absorption spectra. The sample solution (compound + TEOA) was deaerated with N₂ for 10 min prior to photoirradiation.

2.9. Theoretical Computations. All calculations were carried out with the ORCA programs.^{62,63} All electronic structure calculations used DFT with the B3LYP functional and the SVP atomic basis set. The geometry of the ground-state S_0 was optimized with the RHF-type calculation (the standard for singlet ground states with DFT). The T_1 states were optimized with the unrestricted open-shell DFT method. For S_1 and T_2 states, the TD-DFT method was used. For each of the four states S_0 , S_1 , T_1 , and T_2 , the Hessian matrices were calculated, all eigenvalues are positive. The next step used TD-DFT at all four optimized geometries in order to get the relative level ordering in each geometry. This also allowed us to arrange all energies within the same scale, with the S_0 state at the optimized S_0 geometry as the global zero.

3. RESULTS AND DISCUSSION

3.1. Molecular Design and Structure Confirmation. PBI is highly fluorescent, and it is feasible to functionalize at the bay position and ortho position.^{44,64–66} Recently, a few studies have shown that by modification at the bay position, core-twisted PBI derivatives were obtained, leading to drastically different photophysical properties.^{46,47} However, the ISC ability of such system mostly remained unclear.⁶⁷ Inspired by previous reports, we are interested to study the ISC of twisted PBI derivatives with an aryl moiety fused at the bay



Figure 1. Partial 2D ${}^{1}H{-}^{1}H$ COSY spectra of PBI-2 recorded in CDCl₃ at 20 °C along with two possible molecular structures of PBI-2. The expected structure was proposed previously for an analogue with an alkyl substituent at the N position of the carbazole moiety.⁶⁸

Table 1. I notophysical I alameters of the Compound	Table 1	. Photophysica	l Parameters	of the	Compounds
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	$\lambda_{ m abs}^{a}$	ϵ^{b}	$\lambda_{ m em}$	$\Phi_{\mathrm{F}}{}^{c}$	$\tau_{\rm F}^{\ d}/({\rm ns})$	$ au_{\mathrm{T}} \; \left(\mu \mathrm{s} ight)^{e}$	$\Phi_{\Delta}{}^{g}$
PBI-1	492/558	0.52/0.10	638	0.09	8.1/9.1 ^h	343	$0.55/0.45^i/0.42^i$
PBI-2	514	0.30	636	0.05	3.7/3.5 ^h	382	$0.85/0.60^i/0.57^i$
PBI-3	503	0.67	514	0.90	5.1/4.3 ^h	212	$0.01/0.001^i/0.15^j$
2	361/528	0.13/0.33	579	0.01	6.1 ^{<i>h</i>}	131.7	0.01/0.57 ⁱ /0.001 ^j
3	485/530	0.24/0.20	712	0.01	8.8 ^h	110.1 ^{<i>f</i>}	1
4	531	0.37	576	75	5.9/5.5 ^h	48.5	0.06/0.23 ⁱ /0.24 ^j
PBI	512	0.90	532	0.86	4.8/4.5 ^h	129.4 ^{<i>f</i>}	k

^{*a*}In dichloromethane $(1.0 \times 10^{-5} \text{ M})$ and in nanometer. ^{*b*}Molar absorption coefficient $(10^5 \text{ M}^{-1} \text{ cm}^{-1})$. ^{*c*}Fluorescence quantum yield with Bodipy as a standard ($\Phi_F = 72\%$ in tetrahydrofuran). ^{*d*}Fluorescence lifetimes, $\lambda_{ex} = 510 \text{ nm}$ (EPL picosecond pulsed laser). ^{*e*}Triplet state lifetime. ^{*f*}Obtained by TTET with PtOEP as the triplet energy donor, and the data was analyzed with global fitting. ^{*g*}Singlet oxygen quantum yield measured with 2,6-diiodobodipy as a standard ($\Phi_{\Delta} = 0.87$ in acetonitrile). ^{*h*}In *n*-hexane. ^{*i*}In toluene. ^{*j*}In acetonitrile. ^{*k*}Not determined. ^{*l*}Not observed.

region. For this purpose, we synthesized two PBI derivatives by fusing organic moieties of different electron-donating ability (carbazole and anthracene) at the bay position of PBI (Scheme 1). Moreover, this modification will cause steric congestion at the bay region and leads to twisting of the core. The synthesis of these compounds was reported previously, but their photophysical properties were not studied in detail.^{67,68}

Previously, the carbazole-fused PBI derivatives were reported for optoelectronic study, and it was concluded that the direct cyclization of carbazole affixed at the bay position of PBI leads to planar geometry (carbazole fuse from 2-position with the PBI core).⁶⁸ However, Lu et al. demonstrated that the 4-position of carbazole is more reactive toward the reductive cyclization reaction as compared to the 2-position of the carbazole.⁶⁹ To confirm the molecular structure of the carbazole-fused PBI (**PBI-2**), we investigated the 1D ¹H NMR and also performed the 2D COSY NMR spectra of the isolated product (Figures 1 and S12).

The ¹H NMR spectrum of **PBI-2** showed two characteristic doublet peaks of protons of the carbazole unit (H_A and H_B in Figure 1), which confirmed that the carbazole fused at the 4-position instead of the 2-position as stated in a previous report, and it leads to twisted geometry (the planar structure was observed for the previously proposed structure).⁶⁸ The two doublet peaks for the protons of the carbazole unit are only possible in the structure with carbazole fused at the 4-position, while in the planar structure (in which the carbazole fused at

the 2-position), the protons (H_A and H_B) at the 1- and 4postion of carbazole will exhibit singlet peaks. The assignment of doublet peaks to the protons was further verified by 2D ${}^1H^{-1}H$ COSY NMR, in which the interaction between these two doublets was confirmed. However, this interaction is impossible for the previously assigned structure, at least for the isolated product (no 2D NMR spectral study was presented in the previous study).⁶⁸ The absorption and emission data of **PBI-2** (Table 1) are identical to the previously reported data;⁶⁸ thus, we believe that at least in our case, we isolated a different product, and the structure is presented in Figure 1.

Moreover, the low fluorescence quantum yield and good solubility of **PBI-2** compared to the phenyl-fused PBI (**PBI-3**) planar derivative also support the twisted structure of **PBI-2**, as it is established that twisting of the PBI core improves the solubility.^{46,70} Moreover, previously it was reported that photocyclization of anthracene at the bay position of PBI (**PBI-1**) leads to a zigzag (twisted) geometry,⁶⁷ while the phenyl-fused PBI (**PBI-3**) has a planar structure.⁷¹ On the basis of previous reports on the core-twisted PBI derivatives, we suppose that the extended π -conjugation at the core region of PBI and the twisted geometry will induce ISC in these derivatives.^{46,47}

In order to study the molecular conformation, the groundstate geometries of the fused PBI derivatives were optimized with the DFT method. For both **PBI-1** and **PBI-2**, twisted geometries were found (Figure 2a,b), while reference **PBI-3**

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Figure 2. Optimized geometries and the twist angles at the bay regions of PBI derivatives (a) PBI-1, (b) PBI-2, and (c) PBI-3. Calculated by DFT [B3LYP/6-31G (d)] using Gaussian 09.



Figure 3. UV–vis absorption spectra of twisted PBI derivatives along with reference compounds. (a) **PBI-1**, **PBI-2**, **2**, and **3**. (b) **PBI-3** and **PBI**. $c = 1.0 \times 10^{-5}$ M in dichloromethane. (c) Fluorescence emission spectra of PBI derivatives in dichloromethane, $\lambda_{ex} = 465$ nm (A = 0.10). Optically matched solutions were used (all the solutions have the same absorbance at the excitation wavelength $c \approx 1.0 \times 10^{-5}$ M, A = 0.1), 20 °C.



Figure 4. Fluorescence emission spectra of PBI-fused derivatives in solvents of different polarity; (a) **PBI-1**, (b) **PBI-2**, and (c) **PBI-3**, $\lambda_{ex} = 465$ nm (A = 0.10). Optically matched solutions were used (all the solution of the compounds have the same absorbance at the excitation wavelength. $c \approx 1.0 \times 10^{-5}$ M, A = 0.1), 20 °C.

has a planar structure (Figure 2c). Due to the steric hindrance of hydrogen atoms at the bay region, the π -conjugation plane of **PBI-1** is twisted with an angle of 32°, while **PBI-2** shows twisting of 34°. Previously, phenanthrene-fused PBI derivatives with a highly twisted geometry (torsion angle of 40.7–44.3°) were reported, but the triplet yield was quite low.⁴⁶

3.2. UV–Vis Absorption and Fluorescence Spectra. The UV–vis absorption spectra and the fluorescence emission spectra of the compounds were studied (Figures 3 and 4). The absorption spectrum of **PBI-1** contains two sharp peaks centered at 460 and 490 nm (Figure 3a), which is the characteristic PBI vibronic progression.⁶⁷ A shoulder band at 560 nm was also observed, which is very sensitive to solvent polarity (Figure S13). However, the absorption spectrum of

the precursor compound 2 is slightly red-shifted, and the absorption peaks are not well resolved.

For **PBI-2**, a broad absorption band centered at 513 nm without any fine structure was observed (Figure 3a), which is different from its precursor (compound 3). The absorption spectrum of 3 consists of two poorly resolved broad bands. In the case of a previously studied phenanthracene-fused PBI derivative, the absorption profile possesses a structure similar to that of the PBI chromophore but slightly red-shifted.⁴⁶ The reported diPBI-fused derivatives also showed structured and red-shifted absorption due to a large π -conjugation system.⁴⁷ However, for **PBI-2**, the strong electron-donating ability of the fused carbazole moiety perturb the molecular orbitals of the PBI chromophore, which results in a totally different

absorption profile. The reference compound **PBI-3** shows a similar absorption profile as that of the unsubstituted PBI (Figure 3b). The absorption of compounds was also studied in other solvents (Figure S13). It is worth to note that **PBI-1** and **PBI-2** show good solubility in organic solvents due to their twisted nature as compared to rigid and planar **PBI-3**.

The fluorescence emission spectra of the compounds were studied (Figure 3c). **PBI-3** is highly fluorescent ($\Phi_F = 0.90$), and it shows the characteristic emission profile similar to that of the unsubstituted PBI, except the 10–20 nm of blue shifting.⁷¹ For **PBI-1** and **PBI-2**, a red-shifted and broad structureless emission band centered at ca. 635 nm was observed.^{67,68} The fluorescence of **PBI-1** and **PBI-2** is greatly quenched as compared to the reference compounds. The fluorescence quantum yields of **PBI-1** and **PBI-2** in dichloromethane are 0.09 and 0.05, respectively, which are much lower than the unsubstituted PBI ($\Phi_F = 0.86$).

These two compounds showed red-shifting and quenching of emission with increasing solvent polarity (Figure 4a,b). The large Stokes shifts $(3700-5500 \text{ cm}^{-1})$ and the weak emission in polar solvents of the twisted PBI derivatives indicate the intramolecular charge-transfer (ICT) character of the emissive state. For PBI-3 and PBI, however, no clear trend in emission was observed with increasing solvent polarity (Figures 4c and S14). Previously, the fluorescence property of the twisted phenanthrene-fused PBI derivative was studied and no such ICT feature was observed.⁴⁶ Those derivatives exhibited a vibronically resolved structured emission profile, and a small Stokes shift of ca. 330 cm⁻¹ was observed (in which one phenanthrene unit was fused at the bay position of PBI). The small Stokes shift and structured emission indicate that emission takes place from the LE (locally excited) state in these derivatives.⁴

The fluorescence emission decay kinetics of the compounds was studied (Figure S15). For PBI-1 and PBI-2, drastically different fluorescence lifetimes were observed in dichloromethane. The fluorescence of PBI-1 decays with the monoexponential feature with a lifetime of 8.1 ns, while the fluorescence of PBI-2 decays much faster, showing a shorter lifetime of 3.7 ns, which is slightly shorter than the unsubstituted PBI ($\tau_F = 4.8$ ns). The difference in the fluorescence lifetimes of PBI-1 and PBI-2 may be due to the different ICT nature of the excited singlet states. The fluorescence lifetime of 5.1 ns is comparable to that of the unsubstituted PBI (Figure S17).

The singlet oxygen quantum yields (Φ_{Δ}) of the twisted PBI derivatives were studied (Table 1), as a preliminary estimate of the triplet-state production of the compounds. Previously, the singlet excited-state properties of the current twisted derivatives were studied, but the triplet excited-state properties remained unraveled.^{67,68} The twisted PBI-1 and PBI-2 show very high Φ_{Λ} values of 0.55 and 0.85, respectively, but a much lower Φ_{Λ} value (0.01 in dichloromethane) was observed for PBI-3, which has a planar geometry. Since the PBI moiety is devoid of ISC ability, the enhanced ISC in these derivatives is due to the twisting of the core of the molecules Moreover, these derivatives show efficient singlet oxygen generation ability in solvents of different polarity. Previously, phenanthrene-fused PBI derivatives with twisted geometry have been studied, but the ISC efficiency in those derivatives is low (<0.3).46

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3.3. Nanosecond Transient Absorption Spectroscopy: Triplet-State Properties. In a previous report of the bayfused PBI derivatives, the triplet state of the twisted derivatives was not studied, such as using nanosecond transient absorption (ns-TA) spectra.^{67,68} Thus, in order to confirm the triplet excited-state population in the twisted PBI derivatives, the ns-TA spectra of the compounds were measured (Figure 5).



Figure 5. Nanosecond transient absorption spectra of the twisted PBI derivatives (a) **PBI-1** and (b) **PBI-2** upon nanosecond pulsed laser excitation ($\lambda_{ex} = 500$ nm). (c,d) Respective decay curves monitored at 535 nm in deaerated dichloromethane, $c = 1.0 \times 10^{-5}$ M at 20 °C. The τ values in (c,d) are the intrinsic triplet-state lifetimes of the compounds.

Upon photoexcitation, both twisted derivatives exhibited a nearly identical absorption profile, only a slight change in the ground-state bleach (GSB) was observed due to the difference in their ground-state absorption (Figure 5a,b). For PBI-1, two GSB absorption bands centered at 380 and 485 nm, respectively, were observed; one excited-state absorption (ESA) band centered at 540 nm was observed, which is the characteristic $T_1 \rightarrow T_n$ exited-state absorption of the PBI moiety.^{44,53,72} It should be noted that the ESA band overlaps with the GSB band. For PBI-2, a GSB band in the range of 300-450 nm was observed, as well as an ESA band in the range of 450-700 nm. Similar results were observed in other solvents (Figures \$19 and \$20). The overlap of the ESA and GSB bands in the current twisted derivatives is different from the unsubstituted PBI chromophore,57 or less twisted PBI moiety,⁷² because the molecular orbital and $T_1 \rightarrow T_n$ transitions are different for the current twisted PBI compounds and the unsubstituted PBI compounds (see the theoretical computation section).

For **PBI-1** and **PBI-2**, apparent triplet lifetimes of 115.8 and 78.5 μ s were observed, respectively, by monitoring the decay traces at 535 nm and using the imbedded software of the ns-TA spectrometer (L900 software). However, this apparent lifetime should be significantly shorter than the actual triplet lifetime of the compounds due to the TTA quenching effect, as a result of the strong absorption, efficient ISC, and the long triplet lifetime of **PBI-1** and **PBI-2**. For this reason, the



Figure 6. (a) Femtosecond transient absorption spectra of **PBI-1** at different delay times, (b) corresponding evolution associated difference spectra (EADS), and (c) decay traces at selected wavelengths. (d) Femtosecond transient absorption spectra of **PBI-2**, (e) corresponding EADS, and (f) decay traces at selected wavelengths. λ_{ex} = 500 nm, in dichloromethane, 20 °C.

intrinsic triplet lifetime of the compounds was determined by fitting the decay traces at two different concentrations with a special kinetic model, which was developed by some of us previously, to eliminate the self-quenching TTA effect.^{73,74} For **PBI-1**, a long-lived triplet excited state was observed (Figure 5c), with an intrinsic triplet lifetime of 343 μ s (vs. apparent τ_T = 115.8 μ s). For **PBI-2**, an intrinsic triplet lifetime of 382 μ s was observed (Figure 5d, vs. apparent triplet lifetime of τ_T = 78.5 μ s) by fitting of the decay traces with the TTA kinetic model (in dichloromethane). The triplet decay feature of the twisted derivative was also studied in polar solvent, and it was observed that the triplet decay becomes slightly faster in polar solvent; for instance, the apparent triplet lifetime of **PBI-1** in acetonitrile is 83.2 μ s (Figure S20).

The triplet-state lifetimes observed for PBI-1 and PBI-2 are much longer than those of the previously reported twisted PBI derivatives. For instance, in mono- and bis-phenanthrene-fused PBI derivatives, the triplet-state lifetimes were determined as 3.7 and 19.6 μ s.⁴⁶ For the di(perylenebisimide)s showing a twisted π -conjugation framework, the triplet-state lifetimes were observed as $35-56 \ \mu s$.⁴⁷ For the Pt(II) bisacetylide complex with PBI as the ligand (ISC is enhanced by the heavy atom effect), a short-lived triplet state ($\tau_{\rm T}$ = 0.37 μ s) was observed.⁷⁵ Ir(III) and Pt(II) complexes containing PBI ligands also exhibited a short-lived PBI-localized triplet state $(\tau_{\rm T} = 22.3 \ \mu s \text{ and } 0.25 \ \mu s, \text{ respectively}).^{51,53}$ 1,6,7,12-TetrabromoPBI gives a short triplet-state lifetime ($\tau_{\rm T} = 1.04$ μ s).⁴⁴ Previously, it was reported that some PBI derivatives with aryl substituents attached at the ortho position of the PBI core exhibit efficient ISC, but the triplet lifetime (30.6 μ s) is also much shorter.⁷⁶

The triplet excited state of the twisted derivatives was also studied in a solid polymer film (Figures S21–S23. Doped in Clear Flux 50, polyurethrene precursors, a flexible transparent rubber). The transient absorption profile of the twisted derivatives in a thin film is similar to that observed in a fluid solution. Interestingly, for **PBI-1**, a much longer triplet lifetime of 5.18 ms in a N₂ atmosphere was observed (4.74 ms under air atmosphere). The minor quenching of the triplet state under aerated atmosphere is attributed to the poor O₂ diffusion in the polymer matrix), while **PBI-2** in polymer film showed $\tau_{\rm T}$ = 4.74 ms in a N₂ atmosphere (4.52 ms under aerated condition). These results indicate that in solution, the triplet lifetime is not only quenched by TTA but also other relaxation channels such as vibration relaxation, which is inhibited in the solid matrix so that the triplet lifetime is prolonged.^{77,78} This is beneficial for some applications of the triplet PSs such as PDT; in some cases, the PDT agents were doped in the solid matrix.⁴⁹

3.4. Femtosecond Transient Absorption Spectroscopy. To gain further insights into the excited-state dynamics in the twisted PBI derivatives, the femtosecond transient absorption (fs-TA) spectra of the compounds were measured (Figures 6 and S26). The fs-TA spectral studies were performed in two different solvents (toluene and dichloromethane). Upon photoexcitation of PBI-1 at 490 nm in dichloromethane, intense GSB centered at 492 nm appeared promptly, as well as a broad ESA band in the range of 575-800 nm, assigned to $S_1 \rightarrow S_n$ transition (Figure 6a).^{44,76,79} Previously, the fs-TA spectra studies on twisted phenanthrenefused PBI and triply linked di-PBIs derivatives also showed the singlet excited-state absorption in a similar range (700-900 nm).46,47 Within 1 ps, the ESA band slightly blue-shifted, which is attributed to the vibrational relaxation/ICT process. Remarkably, within few picoseconds, the singlet ESA band decreased in intensity and a new band centered at 538 nm rises gradually, which is assigned to $T_1 \rightarrow T_n$ transition. The triplet absorption band (538 nm) continues to grow on a nanosecond timescale similar to that as previously observed in phenanthrene-fused PBI derivatives, in which ISC takes 1 ns.⁴

To obtain the exact rate constants of the excited state dynamics, global fitting and target analysis of transient absorption data were performed to obtain the evolutionassociated difference spectra (EADS). For **PBI-1**, four components were required for the satisfactory fitting of the data. The initial spectral component represents the population

of Frank-Condon (FC) singlet excited state as is evident by the GSB and a broad positive excited-state absorption (Figure 6b). The second spectral component (red line) appearing with a time of 0.5 ps represents the relaxation from the FC state to form the ICT state. In the following evolution, occurring in 138 ps (blue line), the ¹ICT* partially relaxed. We suppose that this might be due to some solvation relaxation. Finally, the triplet state populates as is indicated by the final spectral evolution which appears with 8.2 ns and persists for a long time. The spectral feature of the final component resembles well the ns-TA spectral profile of the compound. Thus, for PBI-1, the ISC rate or the triplet rise time is 8.2 ns, nearly identical to the ¹ICT* decay time ($\tau_{\rm F}$ = 8.1 ns). The brominated twisted PBI derivative and doubly phenanthrenefused PBI derivatives were previously reported to have ultrafast ISC (0.38 or 0.25 ps).^{46,80} In contrast, singly phenanthrenefused PBI ($\tau_{ISC} = 1$ ns) and triply linked DIPBIs derivatives ($\tau_{\rm ISC}$ = 970 ps) showed ISC at a relatively slower timescale.^{46,47} Thus, the ISC rate significantly varied (from few picoseconds to nanoseconds) in the different twisted derivatives having different extents of the π -conjugated framework.

For **PBI-2** in dichloromethane upon excitation at 510 nm, the transient absorption spectra exhibited a negative absorption band at 524 nm, which can be attributed to GSB (Figure 6d), and it is consistent with UV–vis absorption (Figure 3a). An ESA band in the range of 600–800 nm corresponding to $S_1 \rightarrow S_n$ transition was also observed.^{46,47} The global analysis shows that the vibrational relaxation or the ICT takes place at 0.9 ps (Figure 6e), while the triplet state in **PBI-2** also populates at a relatively longer time scale ($\tau_{ISC} = 3.7$ ns), similar to that observed previously in a twisted thiophene-fused diPBI derivative ($\tau_{ISC} = 4.7$ ns).⁸¹

To further verify the ISC mechanism, the decay traces at singlet- and triplet-state ESA bands were compared, and it was observed that within the singlet-state decay, the triplet state populates gradually (Figure 6c,f). fs-TA spectral measurements of twisted PBI derivatives were also performed in toluene (Figure S26). The excited-state dynamics of the compounds shows a slight change in toluene. The ISC takes 7.9 and 2.5 ns for **PBI-1** and **PBI-2**, respectively.

3.5. TREPR Spectra: Electron Spin Selectivity of the ISC and the Triplet-State Wave Function Confinement in the Twisted π -Conjugation Framework. To further investigate the electron spin selectivity of the ISC induced by the twisted π -conjugation system and the spatial confinement of the triplet-state wave function of the PBI derivatives, time-resolved electron paramagnetic resonance (TREPR) spectral study was carried out (Figures 7 and S27). This information can hardly be obtained with ordinary optical spectroscopic methods. TREPR spectroscopy is a useful tool to investigate the ISC mechanism, the spatial localization of the triplet excited state, and the electron spin selectivity of the ISC based on the electron spin polarization (ESP) phase pattern and ZFS parameters (*D* and *E* values) observed with TREPR spectra, respectively.^{74,82-84}

The TREPR spectra of **PBI-1** and **PBI-2** observed in frozen toluene:MeTHF (3:1, v/v) at 0.25 μ s are presented in Figure 7a,b, respectively. For both **PBI-1** and **PBI-2**, the TREPR spectra of the triplet state show the ESP phase pattern of (*e*, *a*, *e*, *a*, *e*, *a*), which is different from the ESP of the PBI triplet state (*e*, *e*, *e*, *a*, *a*, *a*) accessed by the normal SOC effect.⁵⁶ Interestingly, the ESP of the triplet state is very close to that generated by charge recombination.^{56,57} A similar ESP pattern



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Figure 7. Representative TREPR spectra of the frozen solutions (T = 80-130 K) of (a) **PBI-1** and (b) **PBI-2** in toluene/MTHF (3:1, v/v) obtained upon excitation at 500 nm with pulsed laser at energies of 10 mJ per pulse. $c = 3.0 \times 10^{-5}$ M. The spectra in red are the simulations.

(*e*, *a*, *e*, *a*, *e*, *a*) was observed in twisted hexaphyrin derivatives. 85,86

The zero-field splitting (ZFS) parameters of **PBI-1** are |D| = 47.1 mT and |E| = 1.9 mT, while for **PBI-2**, |D| = 44.6 mT and |E| = 2.2 mT were obtained by the simulation of TREPR spectra (Table 2). The *D* value is similar to the planar PBI

Table 2. ZFS Parameters (D and E) and Relative Population Rates ($P_{x,y,z}$) of the Zero-Field Spin States of the Twisted PBI Derivatives and Reference Compound^{*a*}

	D(mT)	E(mT)	P_x	P_y	P_z	$\Delta P^{*^{b}}$
PBI-1 ^c	47.1	-1.9	0.4	0.6	0	0.33
PBI-1 ^d	- 47.1	1.9	0.3	0	0.7	0.43
PBI-2 ^c	44.6	-2.2	0.2	0.8	0	0.75
PBI-2 ^d	- 44.6	2.2	0.43	0	0.57	0.75

^{*a*}Obtained from simulation parameters of the triplet-state TREPR spectra of the indicated molecule in a toluene/MTHF (3:1, v/v) solvent matrix at 80 K. ^{*b*} $\Delta P^* = |P_x - P_y|/|P_z - P_y|$. ^{*c*}By assuming D > 0. ^{*d*}By assuming D < 0.

moiety (|D| = ca. 46.5 mT), previously observed with the PBI-Cz donor/acceptor dyads exhibiting the SOCT-ISC mechanism of triplet population.⁵⁷ However, the *E* value is significantly smaller than those of planar PBI triplet PSs (|E|= ca. 4.2 mT). On the basis of ZFS parameters, we conclude that the triplet wave function in twisted derivatives is predominantly localized on the PBI core, the distribution of the spin density on the fused anthracene and carbazole moieties should not be significant; otherwise, a much smaller *D* parameter should be observed (this is supported by the spin density surface analysis of the triplet state, see later section). In other words, the relatively smaller *E* value compared to *D* in twisted PBI derivatives suggest that the unpaired electrons are not delocalized in the twisted framework, as previously observed in the twisted hexapyrin derivative.⁸⁵

The relative population of the triplet sublevel was determined by assuming the two conditions, that is, D > 0 and D < 0 (Table 2). It is worth to mention that different conventions for assigning the D/E sign result in different spin level referencing. Predicting the exact sign of the D/E value from EPR experiment is challenging. For some compounds with large D values, sometimes the sign was determined, from the temperature dependence of the EPR spectra, based on the change of the ratio of the intensities of the weak-field and strong-field signals. However, in the case of compounds with a small D value, the difference is small. By comparison of the

Assuming D > 0, the relative population rates of the three triplet sublevels for **PBI-1** is $P_x/P_y/P_z = 0.4:0.6:0$, which is similar to that of the previously reported PBI-Ph1-PTZ dyad $(P_x/P_y/P_z = 0.35:1:0)$, both showed overpopulation of the T_y state $(P_v > P_x, P_z)$.⁵⁶ Note that previously the ZFS D and E parameters of the triplet state of PBI derivatives with phenoxy substituents at the bay position were assigned as positive and negative, respectively. Another twisted derivative (PBI-2) also showed overpopulation of the T_{ν} state with relative population rates of $P_x/P_y/P_z = 0.2:0.8:0$. However, the ESP pattern of twisted PBI derivatives was similar to that of the previously reported PBI-Cz dyads, but the relative population rates of the triplet sublevels are different. The PBI-Cz dyads showed overpopulation of the T_x state $(P_x/P_y/P_z = 1:1.08:0)$.⁵⁷ This is a consequence of the different choice of the sign of Eparameters.

3.6. Theoretical Computations. In order to rationalize the photophysical properties, the frontier molecular orbitals of PBI-fused derivatives were studied. The frontier molecular orbitals of compounds **PBI-1**, **PBI-2**, and **PBI-3** are depicted in Scheme 2. For **PBI-1**, HOMO is mainly localized on the

Scheme 2. Selected Frontier Molecular Orbitals of PBI-1, PBI-2, and PBI-3 Calculated at the DFT (B3LYP/6-31G (d)) Level with Gaussian 09W in Toluene^a



^aThe energy levels of the orbitals are presented (in eV).

fused anthryl unit while LUMO is mainly confined on the PBI moiety but also spreads slightly to the fused anthryl chromophore. This result indicates the possibility of charge transfer in **PBI-1** upon photoexcitation.⁶⁷ Similar results were observed for **PBI-2**. For **PBI-3**, which has the planar geometry, the HOMO and LUMO are not separated, thus no CT behavior is expected for the S_1 state. These results are in agreement with the solvent polarity-dependent fluorescence emission wavelength of the compounds (Figure 4).

The electron spin density surfaces of the T_1 states of the twisted PBI derivatives were also studied (Figure 8). For **PBI-1**, the spin density of the triplet state is mainly confined on the PBI moiety, and only minor spin leakage to the anthryl moiety was observed. Similar results were observed for **PBI-2**. For **PBI-3**, the spin density of the triplet state is also mainly localized on the PBI unit, slightly leaked to the fused phenyl ring. These results are in agreement with the ZFS *D* parameter of the twisted PBI derivatives observed in the TREPR spectral study, which are similar to the native PBI chromophore.⁵⁷

In addition to the electronic ground state S_{0} , the geometries of the excited states S_1 , T_1 , and T_2 were optimized. Figure 9 shows the energy level diagrams at each of these optimized geometries (indicated at the top of each column). All energies are given relative to the energy of the optimized ground state S_0 .

Analysis of the TDDFT wave functions shows that these excited states originate from excitations from the two highest occupied orbitals (HOMO, HOMO – 1) to the two lowest virtual orbitals (LUMO, LUMO + 1). All of these orbitals are part of the π -electron system, except for HOMO – 1 of **PBI**, which is a linear combination of the oxygen lone pairs.

According to these calculations, **PBI** and **PBI-3** have a similar S₁ excitation energy (21075 and 20800 cm⁻¹). The S₁ and T₁ states of **PBI** originate from the HOMO \rightarrow LUMO excitation. Since this orbital pair has a large exchange integral, the energy gap is rather large (10944 cm⁻¹). The T₂ state is above the S₁ state at all geometries; hence, it is most likely not involved in ISC. The situation is similar for the other planar molecule **PBI-3** with a slightly smaller adiabatic S₁/T₁ energy gap (8695 cm⁻¹). In contrast to **PBI**, the T₂ state is now slightly below S₁ and ISC to this state should be considered.

Fusion of the PBI chromophore with either anthracene in **PBI-1** or with carbazole in **PBI-2** not only forces twisting of the π -electron system but also introduces a possible electron donor. Indeed, analysis of the wave functions reveals that the S₁ state in these compounds has a substantial CT character. As a proof, we show the static dipole moments of all four states of the four compounds in Table 3.

In line with this observation, the calculated $S_0 \rightarrow S_1$ excitation energy in **PBI-1** (15651 cm⁻¹) and **PBI-2** (16692 cm⁻¹) is substantially red-shifted with considerably lower oscillator strength. Judging from the dipole moments, the corresponding triplet state is the T_2 state. As the dipole moment shows, the T_1 state corresponds to the local excitation (as in compounds **PBI** and **PBI-3**). Hence, two possible channels exist for ISC, $S_1(CT) \rightarrow T_1(LE)$ and $S_1(CT) \rightarrow T_2(CT)$. Due to the different excitation characteristics of S_1 and T_1 , the gap in **PBI-2** (4836 cm⁻¹) is only half of the size compared to **PBI** and considerably smaller in **PBI-1** (2999 cm⁻¹). This smaller energy gap should result in a larger FC-weighted density of states and hence in larger ISC rate constants.

The ISC process is caused by coupling between the initial singlet and the final triplet state via the spin-orbit operator. The matrix elements of this operator were calculated with the TD-DFT method at the equilibrium geometries of T_1 and T_2 and are listed in Table 4. The matrix elements are given in Cartesian coordinates; for the orientation of the molecules, see Figure S36. The *z*-component is identical to the M = 0 component of the triplet state, the M = 1 and M = -1 components are complex conjugate linear combinations of the *x*- and *y*-components.

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Figure 8. Spin density distribution of the triplet state of PBI-1, PBI-2, and PBI-3 in toluene. Calculated at the B3LYP/6-31G (d) level using Gaussian 09W.



Figure 9. Energy diagram of the compounds (a) **PBI**, (b) **PBI-1**, (c) **PBI-2**, and (d) **PBI-3** at the optimized geometries of the four states S_0 , S_1 , T_1 , and T_2 (indicated at the top of every column), respectively. Singlet states are marked in black and triplet states in red. The large dot in each column indicates the state that was optimized.

In **PBI** and **PBI-3**, the S₁ state and the T₁ state have the same leading configuration. Hence, the coupling S₁/T₁ is forbidden by the high symmetry in **PBI** (D_{2h}) and **PBI-3** (C_{2v}). The planarity of the compounds **PBI** and **PBI-3** also results in very small values for the S₁/T₂ coupling (El-Sayed rule). For

the non-planar systems **PBI-1** and **PBI-2**, non-zero coupling elements are found. The square modulus of the three Cartesian components is 0.11 cm^{-1} for **PBI-1**, and for **PBI-2**, the value is 0.44 cm⁻¹. This is a clear indication that the SOCME is increased by the twisted π -conjugation system in the carbazole

Table 3. Static Dipole Moments (Debye) of the States S_0 , S_1 , T_1 , and T_2 of the Four Compounds

	S ₀	S ₁	T_1	T_2
PBI	0.00	0.00	0.00	0.00
PBI-1	2.73	16.54	3.33	15.15
PBI-2	5.34	18.91	7.08	17.74
PBI-3	1.39	4.67	1.78	4.93

or anthryl-fused PBI derivatives. These values are, however, still smaller than 1 cm⁻¹. As we will see below, the FC term leads only to a minor contribution to the ISC rates, whereas the main contribution is from the Herzberg–Teller term.

The rate constant for ISC from an initial electronic state $|i\rangle$ to a final electronic state $|f\rangle$ can be expressed by Fermi's golden rule as eq 1

$$k_{\rm ISC} = \frac{2\pi}{\hbar} \sum_{uv} \left| \langle iu | H^{\rm SO} | fv \rangle \right|^2 \frac{1}{Z} e^{-E_{uv}/kT} \delta(E_{iu} - E_{jv})$$
(1)

where H^{SO} is the spin-orbit coupling operator, u and v label the vibrational states within the two electronic states, E_{iu} is the vibronic energy of each state, $\delta()$ is the Dirac function, and eq 2 shows the partition function

$$Z = \sum_{iu} e^{-E_{iu}/kT}$$
(2)

The integral over the electronic coordinates is a function of the nuclear coordinates and is usually expanded in powers of the normal coordinates q (eq 3)

$$\langle i|H^{\rm SO}(q)|f\rangle = \langle i|H^{\rm SO}|f\rangle + \sum_{q} \frac{\partial \langle i|H^{\rm SO}|f\rangle}{\partial q}q$$
(3)

ORCA uses the geometry of the final state as the reference. When only the first term is retained, we obtain the FC rate constant

$$k^{\rm FC} = \frac{2\pi}{\hbar} \left| \langle i | H^{\rm SO} | f \rangle \right|^2 (\rm FCWD) \tag{4}$$

where the FC-weighted density of states is given by eq 5

$$(FCWD) = \frac{1}{Z} \sum_{uv} |\langle u|v \rangle|^2 e^{-E_{iu}/kT} \delta(E_{iu} - E_{jv})$$
(5)

When the SOCME at the equilibrium geometry of the final states vanishes (e.g., due to symmetry), the vibronic coupling term remains as eq 6

$$k^{\rm HT} = \frac{2\pi}{\hbar} \sum_{q, u, v} \left| \frac{\partial \langle i | H^{\rm SO} | f \rangle}{\partial q} \langle u | q | v \rangle \right|^2 \frac{1}{Z} e^{-E_{iu}/kT}$$
$$\delta(E_{iu} - E_{jv}) \tag{6}$$

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In the general case, interference terms occur and are calculated in ORCA.

The ISC rates of the compounds were calculated by the socalled excited-state dynamics (ESD) technique implemented in ORCA. This technique considers the FC density of states as well as the vibronic contributions (Herzberg–Teller, HT) to the ISC rate constant. The rate constants can be studied as a function of energy gap (Figure 10) and temperature, while the



Figure 10. ISC rate constants calculated with the ESD method for the S_1-T_1 transitions (filled symbols) and the S_1-T_2 transitions (open symbols) vs. variation of the energy gap in a range ±2000 cm⁻¹ from the predicted energy gap by TD-DFT. The rate constants are shown on a logarithmic scale.

SOCMEs and their vibronic derivatives need to be calculated only once for each M-sublevel of the triplet state. For these calculations, the SOCMEs from TD-DFT calculations were used. Since the experimental S_1-T_1 energy gap is not known, the ISC rate constants were calculated in a range ± 2000 cm⁻¹ from the predicted energy gap. The rate constants are shown on a logarithmic scale; hence, a straight line corresponds to an exponential energy gap law. Apparently, PBI and PBI-3 obey this rule perfectly (Figure 10). The SOCMEs are zero for both molecules, and the ISC rate is entirely due to vibronic coupling. At the calculated energy gap, $k_{\rm ISC} = 1.54 \times 10^2 \, {\rm s}^{-1}$ for **PBI** and 1.73×10^3 s⁻¹ for **PBI-3**. Both rates are so small that they could not lead to significant population of the triplet state. This explains the negligible triplet yield of PBI, but not the moderate yield of **PBI-3** ($\Phi_{\Lambda} = 15\%$). On the other hand, **PBI-**1 and **PBI-2** show similar and large rates $(5.59 \times 10^5 \text{ and } 1.01)$ \times 10⁶ s⁻¹, respectively). Although these values are more than 2 orders of magnitude larger than those for PBI and PBI-3, they

Table 4. SOCMEs (cm⁻¹ units) for the State Pairs (S_1 , T_1) and (S_1 , T_2) Evaluated at the Optimized Geometry of the Triplet State^{*a*}

		$S_1 - T_1$			$S_1 - T_2$	
	Ζ	X	Y	Z	X	Y
PBI	0.0000	0.0000	0.0000	0.0000	0.0015	0.0004
PBI-1	-0.0977	0.0439	-0.0280	-0.0303	0.0303	-0.0103
PBI-2	-0.4178	-0.0545	-0.0462	0.1239	0.0008	0.0822
PBI-3	-0.0001	0.0003	0.0000	0.0004	0.0000	-0.0260

^aAll values are purely imaginary numbers.



Figure 11. (a) UV–vis absorption spectra of **PBI-1** in the presence of TEOA in dearated ACN upon photoirradiation; (b) reversibility of the formation of PBI^{-•} radical anion upon photoirradiation and re-exposure to air (oxidize the radical anion to the neutral form); (c) photographs showing the reversible color change of the **PBI-1**/TEOA mixed solution upon sequential photoirradiation and re-exposure to air. c [**PBI-1**] = 1.0 × 10⁻⁵ M, c [TEOA] = 1.0 × 10⁻⁴ M. The white light source is an un-filtered xenon lamp; the power density is 20 mW/cm². 20 °C.

can only account for a triplet yield of ca. 0.4% given that the singlet lifetimes are 8.1 and 3.7 ns (Table 1), respectively.

Hence, we need to consider the contribution of the S_1-T_2 coupling (Figure 10). All three molecules have a non-zero SOCME for the S_1-T_2 coupling: 0.04 cm⁻¹ for PBI-1, 0.14 cm⁻¹ for PBI-2, and 0.03 cm⁻¹ for PBI-3. We find the following values for the adiabatic energy gap and the rate constant: $\Delta E = 1899 \text{ cm}^{-1}$ and $k_{\text{ISC}} = 2.20 \times 10^6 \text{ s}^{-1}$ for PBI-1, $\Delta E = 1298 \text{ cm}^{-1} \text{ and } k_{\text{ISC}} = 7.78 \times 10^5 \text{ s}^{-1} \text{ for PBI-2, and } \Delta E = 1054 \text{ cm}^{-1} \text{ and } k_{\text{ISC}} = 3.93 \times 10^7 \text{ s}^{-1} \text{ for PBI-3. These values}$ would account for triplet yields in the range 2-20% for the observed singlet lifetimes. Although these rates depend on the energy gap, this dependence is not simply exponential, as can be seen in Figure 10 (open symbols). Since these calculations are based on a harmonic approximation of the vibrations, the results contain some uncertainty. Nevertheless, they are in the right range to explain the observed triplet yields of PBI-1, PBI-2, and PBI-3 and the vanishing triplet yield of PBI. Thus, the $S_1 \rightarrow T_2 \rightarrow T_1$ route is possible (note that it is difficult to observe the T₂ state with femtosecond transient absorption spectra).

3.7. Photochemical Studies: Reversible Photoproduction of Radical Anion in the Presence of Sacrificial Electron Donor TEOA. PBIs are an excellent class of organic dyes which are of particular interest in photocatalysis,⁸ photoconduction,⁸⁸ and n-type transistor fabrication¹ due to feasible reduction into their radical anion.⁸⁹ Previously, the PBI radical anion was prepared by electrochemical reduction,^{90,91} or in the presence of a chemical reductant such as tetrabutyl ammonium cyanide or dithionite $(Na_2S_2O_4)_{,}^{92-94}$ and by photochemical method.^{44,57} However, formation of a radical anion of twisted PBI derivatives was not reported. Herein, we demonstrated the reversible radical anion formation of twisted, fused PBI derivatives by photochemical method, which is in the presence of sacrificial electron donor upon photoirradiation and transformation to neutral compounds again upon exposure to air (Figure 11). PBI-1 was easily reduced to its radical anion (PBI^{-•}) in the presence of sacrificial electron donor triethanolamine (TEOA) even by irradiating with a simple torch light within few seconds (Figures 11, S28, and S29).

The evolution of the UV-vis absorption changes of the compound (**PBI-1**) upon photoirradiation in the presence of typical sacrificial electron donor TEOA was monitored (Figure 11a). Upon photoirradiation, the initial absorption bands centered at 487 nm decreased with concomitant appearance of new absorption bands centered at 676, 758, and 896 nm, and these new NIR bands gradually rise and attain maximum

intensity within 80 s. On the basis of theoretical computations and comparison with previous reports, we assigned these NIR absorption bands to the absorption of **PBI-1** radical anion (**PBI-1**)^{-•}, that is $D_0 \rightarrow D_n$ transitions of the **PBI-1** radical anion (Figures S32 and S33 and Table S2). The (**PBI-1**)^{-•} absorption is quite different from radical anion absorption of the native PBI chromophore.^{57,95} Previously, carbazoleperylenebisimide (PBI-Cz) donor/acceptor dyads were studied for the generation of PBI^{-•} by a photochemical method. The PBI^{-•} absorption in those dyads appeared at 698, 794, and 953 nm, respectively, which is different from the current twisted **PBI-1**.⁵⁷

After the photoreduction, the **PBI-1**^{-•} solution was exposed to air, the PBI-1^{-•} absorption bands centered at 676, 758, and 896 nm decreased, and the ground-state PBI-1 absorption band at 487 nm was fully recovered. These results indicated the oxidation of radical anion PBI-1^{-•} by the O_2 in air. The orange color of PBI-1 changes to light blue upon radical anion formation and the original color of the compound gets restored upon exposure of the photoirradiated solution to air (Figure 11c). The radical formation and re-oxidation to its neutral precursor is reversible until more than five cycles without any significant decomposition, which indicates the excellent reversibility of persistent PBI-1^{-•} radical anion formation (Figures 11b and S30). Similar results were observed for PBI-2 (Figure S28). It is also worthy to note that the twisted derivatives can act as an excellent candidate for dye-sensitized solar cells (DSSCs), as the oxidation potential of the PBI-2 radical anion $(-1.24 \text{ V vs. Fc/Fc}^+)$ is more negative compared to the conduction band of TiO₂ $(-1.19 \text{ V vs. Fc/Fc}^+)$.

The photophysical processes of PBI-2 are summarized in Scheme 3. Upon photoexcitation, its singlet excited state is populated, and then the CT state is formed, which is supported by the solvent polarity-dependent fluorescence emission wavelength. Then, from the ICT state, the ISC occurs based on theoretical computation, which indicates the energy matching of S_1-T_2 states in PBI-2, which assists direct transition of S1 state to the triplet state. However, advance theoretical computations and femtosecond transient absorption studies support that the major ISC channel is SOC between the S₁ and T₁ states caused by twisted geometry. The other competing pathway which PBI-2 follows is the radiative relaxation of singlet excited state through the ICT process. From the ICT state, it decays back to the ground state by emitting radiation or contribute in triplet population. A similar photophysical process was observed in PBI-1. While in PBI-3, which has a planar geometry, the singlet excited state directly

Scheme 3. Jablonski Diagram Demonstrating the Photophysical Processes Involved in PBI-2 upon Photoexcitation^a



"The energy levels of the excited state are derived from the spectroscopic data. CT energy levels in different solvents are derived from the CT emission. The triplet energy levels are estimated by the TD-DFT method. The numbers in superscripts indicates the spin multiplicity.

relaxed back to the ground state by radiative decay, which is in accordance with its high fluorescence quantum yield and low triplet yield (Scheme S2).

It should be pointed out that the states S_1 and T_2 have a similar orbital constitution (i.e., CT characteristic); hence, the possibility of a $S_1 \rightarrow T_2$ ISC must be considered. According to the calculations, the energy gap is negative for **PBI** and less than 2000 cm⁻¹ for the other compounds. When solvent effects for DCM are included in the energy calculations, these gaps reduce to 1448, 497, and 534 cm⁻¹ for **PBI-1**, **PBI-2**, and **PBI-3**, respectively. For toluene as a solvent, the gaps become even smaller, namely, 1410, 379, and 312 cm⁻¹. These values are smaller than the typical accuracy of TD-DFT calculations. The fact that no singlet oxygen production was observed with **PBI-3** in toluene or dichloromethane can be explained if we assume that the $S_1 \rightarrow T_2$ path is energetically not accessible in these solvents for **PBI-3**.

4. CONCLUSIONS

In summary, we studied the detailed photophysical property of anthryl- and carbazole-fused PBI derivatives (PBI-1 and PBI-2, respectively) showing twisted π -conjugation frameworks. Through the nuclear magnetic resonance (1D and 2D COSY HNMR) study, we confirmed the nonplanar structure of the carbazole-fused PBI (PBI-2), which is different from that of the previously reported planar analogue (fusing position is different). Efficient ISC (singlet oxygen quantum yield Φ_{Δ} = 85%) and long-lived triplet excited state ($\tau_{\rm T}$ = 382 μ s) were observed for the twisted PBI derivatives, whereas the planar analogue benzo-PBI (**PBI-3**) exhibits poor ISC ability (Φ_{Δ} = 15%). The triplet-state lifetimes are much longer than that observed with the previously reported twisted PBI derivatives $(0.1-67 \ \mu s)$. Femtosecond transient absorption spectra show that the ISC takes 3.7-8.2 ns in the current twisted PBI derivatives, which is slower than the ISC of the previously reported twisted PBI derivatives. The pulsed laser excited timeresolved electron paramagnetic resonance (TREPR) spectroscopy indicates that the electron spin polarization (ESP) phase pattern of the triplet state is (e, a, e, a, e, a), which is different from the native PBI triplet state accessed with the normal spin orbital coupling effect, which shows the ESP phase pattern of (e, e, e, a, a, a) in the triplet-state TREPR spectrum.

Furthermore, the ZFS parameter |D| was determined as 47.1 mT, which is similar to the native PBI chromophore showing | D = 46.5 mT, indicating that the spin density of the triplet excited state of the twisted PBI derivatives are mainly distributed on the PBI core and spreading to the fused anthryl or the carbazole moiety is not significant; otherwise, the D value should be smaller. This postulation is supported by theoretical computation on the triplet-state spin density. Theoretical computation of the FC density of states of the coupling $S_1 - T_n$ (*n* = 1,2) states, based on excited-state dynamics (ESD) methods, indicates that the twisting of the π conjugation framework indeed increases the SOCMEs magnitudes of S₁-T₁ and S₁-T₂ states (SOCME: 0.11-0.44 cm⁻¹), as well as the Herzberg-Teller vibronic coupling, in comparison the planar native PBI compounds shows negligible SOCME values (at least <0.01 cm⁻¹). For the planar benzoPBI, the computation indicates that the moderate triplet-state yield is due to $S_1 \rightarrow T_2$ ISC (SOCME: 0.03 cm⁻¹) and the small S_1-T_2 energy gap (1054 cm⁻¹). Upon photoexcitation in the presence of sacrificial electron donor, the twisted derivatives exhibited efficient and reversible conversion into the near-infrared-absorbing PBI radical anion, which demonstrate their potential application in photocatalysis and photovoltaics. These results are useful for designing of new heavy atom-free triplet PSs showing twisted π -conjugation-induced ISC.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.1c05032.

General experimental methods; ¹H NMR, 2D NMR, and HRMS spectra of the compounds; theoretical computation data; and photophysical data (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Jianzhang Zhao State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China; orcid.org/ 0000-0002-5405-6398; Email: zhaojzh@dlut.edu.cn
- Ahmet Karatay Department of Engineering Physics, Faculty of Engineering, Ankara University, Ankara 06100, Turkey; Email: Ahmet.Karatay@eng.ankara.edu.tr
- Bernhard Dick Lehrstuhl für Physikalische Chemie, Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Regensburg 93053, Germany; Ocrid.org/ 0000-0002-9693-5243; Email: Bernhard.Dick@ chemie.uni-regensburg.de
- Violeta K. Voronkova Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of Russian Academy of Sciences, Kazan 420029, Russia; Email: voi@kfti.knc.ru

Authors

- Zafar Mahmood State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China
- Andrey A. Sukhanov Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of Russian Academy of Sciences, Kazan 420029, Russia

- Noreen Rehmat State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China
- Mengyu Hu State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China
- Ayhan Elmali Department of Engineering Physics, Faculty of Engineering, Ankara University, Ankara 06100, Turkey
- Yi Xiao State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcb.1c05032

Author Contributions

[⊥]Z.M., A.A.S., and N.R. contributed equally to this work. **Notes**

The authors declare no competing financial interest.

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