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Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Published on 25 January 2020. Downloaded by UNIVERSITE PARIS SUD on 1/25/2020 10:36:47 PM

Carbazole-Perylenebisimide Electron Donor/Acceptor Dyads Showing Efficient Spin Orbit Charge Transfer Intersystem Crossing (SOCT-ISC) and Photo-Driven Intermolecular Electron Transfer

Noreen Rehmat,^a Antonio Toffoletti,^b Zafar Mahmood,^c Xue Zhang,^a Jianzhang Zhao^{*a} and Antonio Barbon^{*b}

Perylenebisimide-Carbazole (PBI-Cz) dyads were prepared to study the charge-recombination (CR) induced intersystem crossing (ISC) in these electron donor-acceptor dyads. The distance and the mutual orientation of the perylenebisimide (PBI) and carbazole (Cz) moieties were varied to study its effect on the photophysical properties. Steady state and time-resolved optical spectroscopies show that the electronic coupling between the electron donor and acceptor is negligible at ground state. The fluorescence of the PBI moiety is strongly quenched in the dyads, larger separation between the donor and acceptor results in the less fluorescence quenching. The Gibbs free energy changes of the electron transfer and the energy level of the charge transfer state were studied by electrochemical and optical spectra data. Singlet oxygen quantum yields (Φ_a) of the dyads are up to 72% for the dyad with shortest separation between the donor and acceptor. Nanosecond transient absorption spectra confirmed the formation of the PBI-localized long lived triplet state (the lifetime is up to 190 µs). Notably these non-orthogonal dyads show efficient spin orbit charge transfer (SOCT-ISC), which is different from the previously proposed orthogonal molecular structure for SOCT-ISC. Time-resolved electron paramagnetic resonance (TREPR) spectroscopy show that all three dyads give the same electron spin polarization of *eae/aea*, thus radical pair ISC (RP ISC) mechanism is excluded, which is different from the previously reported PBI-phenothiazine analogues. Efficient and reversible transformation of dyads to their radical anion was observed in the presence of sacrificial electron donor triethanolamine under inert atmosphere with photo-irradiation.

Introduction

Triplet photosensitizers (PSs) are versatile materials for applications in photocatalysis,^{1–4} photovoltaics,^{5–7} photodynamic therapy (PDT),^{8–15} and triplet-triplet annihilation (TTA) upconversion.^{16–23} Intersystem crossing (ISC) is the crucial property for the triplet PSs.²⁴ Heavy atom effect is the typical method to enhance the ISC such as by using Ir, Ru, Pt, I or Br atoms.^{25–31} However, concerning some applications, dark toxicity and the high cost of these heavy atom containing compounds are the disadvantages,^{24,32} thus it is highly desired to develop heavy atom free triplet PSs, which are also

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fundamentally interesting in photochemistry studies. Various ISC mechanisms have been studied, for instance the above mentioned heavy atom effect, $n-\pi^* \rightarrow \pi-\pi^*$ transitions,³³ exciton coupling,³⁴⁻³⁶ systems based on spin converters³⁷⁻⁴⁰ and the energy level matching of S_n/T_n states.^{24,41} In comparison, the charge recombination (CR) induced ISC was less investigated. It is known that the CR in electron donor/acceptor dyads, with long separation between the donor and acceptor, may induce ISC, given the electron exchange integral is extremely small ($J < 0.1 \text{ cm}^{-1}$).⁴² Under this circumstance, the radical pair ISC (RP-ISC) may occur by the magnetic coupling between the electron and the magnetic nuclei, i.e. ISC of ¹CT to ³CT. The subsequent electron spin-selective CR would produce a locally excited triplet state (³LE), given the ³LE state is with lower energy level than the CT state.

It is worthy to mention that the charge separation (CS) and CR are electron spin selective, which means ${}^{1}LE \rightarrow S_{0}$, ${}^{1}CT \rightarrow S_{0}$ are bound to prevail than the ${}^{1}LE \rightarrow {}^{3}LE$ and ${}^{1}CT \rightarrow {}^{3}CT$, respectively. Therefore prerequisites are required for ${}^{1}CT \rightarrow {}^{3}CT$ (RP-ISC). In order to facilitate the states mixing of ${}^{1}CT$ and ${}^{3}CT$ states, the energy gap of these two states should be very small (J value should be on the scale of Zeeman effect, < 0.1 cm⁻¹), which requires decoupling between the donor and acceptor, achieved by large separation of the donor and acceptor, which makes the synthesis difficult.⁴³⁻⁴⁵ Moreover, due to the coupling

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Scheme 1. Synthetic routes to perylenebisimide-carbazole Dyads and reference compound.

of electron magnetic dipole and the nuclear magnetic dipole, the ${}^{1}CT \rightarrow {}^{3}CT$ is usually slow, thus the ISC yield is not expected to be high, due to the competing ${}^{1}CT \rightarrow S_{0}$ process. Normally, the ISC yields and the triplet state properties (the lifetimes and the application in electron transfer) were not studied in detail for molecular systems showing RP-ISC.42

Recently, compact electron donor/acceptor dyads were reported to show ISC, in this case, the π -conjugation planes of the donor and acceptor take orthogonal geometry, thus the electron spin angular momentum change during ISC is compensated by the molecular orbital angular momentum change of the CR process, and it is the so-called spin orbit charge transfer ISC (SOCT-ISC).⁴⁶⁻⁵¹ For these molecules, RP-ISC can be excluded, because of the significant J values (large ¹CT/³CT energy gaps) caused by the strong coupling of the electron donor/acceptor.⁵² Anthracene, acridinium, bodipy and perylene moieties have been used for construction of the compact electron donor/acceptor dyads showing SOCT-ISC.46,47,53-55 These dyads share a common feature, i.e. the electron donor and acceptor are directly connected, and the π -conjugation planes of the electron donor/acceptor adopt close-toorthogonal geometry. It will be interesting to explore the application of other chromophores and molecular structures for the construction of such SOCT-ISC dyads. Herein we prepared perylenebisimide (PBI)-carbazole (Cz) derived electron donor/acceptor dyads to study the above issues (Scheme 1). PBI is used as electron acceptor in the dyads, and Cz moiety was used as electron donor. To the best of our knowledge, PBI was not used for SOCT-ISC dyads. Moreover, the molecular structure (geometry) is different from the recently reported SOCT-ISC dyads, which usually show orthogonal geometry, as a result of large conformation restriction. The PBI-Cz dyads studied herein are with medium separation distance between the electron donor and acceptor, and the orientation of the electron donor and acceptor is not orthogonal. The photophysical properties of the PBI-Cz dyads were studied with steady-state and timeresolved optical spectroscopies, as well as time-resolved electron paramagnetic resonance (TREPR) spectroscopy. Interestingly, we found satisfactory SOCT-ISC yields for the PBI-Cz dyads, and TREPR spectroscopy excluded the RP-ISC mechanism. Although some of the current PBI-Cz dyads are with similar structure to that of previously reported PBI-Phenothiazine (PTZ) dyads, which show RP-ISC.⁴²

Results and discussion

Molecular design and synthesis

Previously bay-substituted carbazole-perylenebisimide donor-

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acceptor system has been investigated, which show strong ground state electronic coupling, but no ISC was observed.⁵⁶ Considering that the chemical modification at imide position will result in weak to moderate electronic coupling between donor and acceptor moieties. It is of scientific interest to investigate the ISC ability of imide substituted PBI-Cz donor/acceptor system. For this study, three PBI-Cz dyads were designed by attaching carbazole donor at the imide position of PBI acceptor. The linker length between the PBI and the carbazole moiety was varied from one phenyl moiety (**PBI-Cz-1** and **PBI-Cz-3**) to two phenyl moieties (**PBI-Cz-2**). The orientation of the PBI and the carbazole moieties was also varied, to study the relationship between the molecular structure and the SOCT-ISC efficiency.

UV-Vis absorption and emission

The UV-Vis absorption spectra of the compounds were studied (Fig. 1a). All the three PBI-Cz dyads and reference compound PBI-Ph display very similar absorption feature. The structured absorption bands between 400 and 550 nm are assigned to the $S_0 \rightarrow S_1$ transition of the PBI core. The spectral features indicate that substitution of carbazole on imide position of PBI has little influence on the electronic structure of the PBI core. In other words, no electronic coupling between carbazole and PBI moiety was observed at ground state. However, in case of previously reported bay-substituted PBIphenothiazine (PBI-PTZ) dyads in which PTZ is attached to PBI through different orientation, different absorption spectra were observed. For the dyad with orthogonal geometry, the PBI and PTZ are completely electronically decoupled, the absorption spectrum was similar to un-substituted PBI but for the dyad with nonorthogonal geometry, the absorption spectrum was broad and structureless and strong electronic coupling between PBI and PTZ moieties was observed.⁵⁷ Moreover, in case of previously reported bay substituted PBI-carbazole derivatives, red shifted and broad structureless absorption spectra was observed, which indicate that strong ground state electronic coupling is present in bay substituted PBI-carbazole derivatives due to π -conjugation,⁵⁶ while imide substituted PBI-Cz dyads (Scheme 1) inherit photophysical characteristics from the PBI.

The fluorescence of PBI-Cz dyads and reference compound were studied (Fig. 1b). All the compounds shows similar emission wave-



Fig. 1 (a) spectra UV–Vis absorption spectra of PBI-Cz dyads, $c = 1.0 \times 10^{-5}$ M in toluene; (b) Fluorescence emission spectra of PBI-Cz dyads in toluene ($\lambda_{ex} = 475$ nm). Optically matched solutions were used (all the compounds have same absorbance at the excitation wavelength $c \approx 1.0 \times 10^{-5}$ M, absorbance A = 0.23), 20 °C. Inset: enlarged emission spectra of **PBI-Cz-1** and **PBI-Cz-2**.

ARTICLE

length, structured emission peak appears at 535/ienmtidWithling pronounced vibrational shoulder at 575 nmPThelenission of PBPC2 dyads is quenched even in low polar solvent toluene as compared to reference compound **PBI-Ph**, which is highly fluorescent (optically matched solution was used). The fluorescence quantum yield (Φ_F) of **PBI-Cz-2** is 0.44 (in toluene), which is lower than that of reference compound **PBI-Ph** (Φ_F = 0.90). Although the linker between the PBI and the Cz moieties in **PBI-Cz-1** and **PBI-Cz-2** are one and two phenyl rings respectively, yet we observed the different fluorescence quantum yield in these two dyads.

It should be noted that fluorescence is strongly quenched in case of **PBI-Cz-1** ($\Phi_F = 0.02$) and **PBI-Cz-3** ($\Phi_F = 0.01$) in toluene (Table 1), the photo-induced charge separation (CS) is possible reason for fluorescence quenching (Cz moiety as electron donor). We proposed this different fluorescence quenching in PBI-Cz dyads is due to different length of spacer which controls the electronic interaction between Cz and PBI moieties. As the length of spacer increases, the electronic interaction between two moieties decreases which results in less fluorescence quantum yield in **PBI-Cz-2** as compared to other two dyads. The solvent-dependent fluorescence of dyads was also studied (see ESI[†], Fig. S16). In all solvents only structured emission band were observed in case of PBI-Cz dyads, no CT emission band was observed. Although with increasing polarity the quenching of fluorescence becomes more pronounced which confirms the PET process in the PBI-Cz dyads.

Fluorescence emission spectra of these imide substituted PBI derivatives are different from the previously reported bay substituted PBI-carbazole derivatives (1,6- and 1,7-substitution). Those derivatives showed the red shifted structureless emission band due to strong electronic coupling.⁵⁶ Moreover, in case of bay substituted PBI-PTZ dyads, structureless red shifted emission band



Fig. 2 Fluorescence decay traces of PBI-Cz dyads; (a) PBI-Cz-1 (λ_{em} = 535 nm); (b) PBI-Cz-2 (λ_{em} = 535 nm); (c) PBI-Cz-3 (λ_{em} = 535 nm); (d) PBI-Ph (λ_{em} = 535 nm), λ_{ex} = 510 nm c = 1.0 × 10⁻⁵ M in toluene, 20 °C.

Table 1. Photophysical parameters of the compounds.

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	$\lambda_{ m abs}{}^a$	\mathcal{E}^{b}	$\lambda_{ m em}$	$\Phi_{\rm F}{}^{\rm c}$	$\tau_{F}{}^{d}$	$\Phi_{\Delta}{}^{e}$	τ_T^f
PBI-Cz-1	526	0.65	535	0.02	1.85	0.45	179.6
PBI-Cz-2	526	0.62	535	0.44	3.87	0.38	188.8
PBI-Cz-3	526	0.66	535	0.01	1.02	0.72	109.7
PBI-Ph	526	0.65	535	0.90	4.29	g	

^{*a*} In toluene $(1.0 \times 10^{-5} \text{ M})$ and in nm. ^{*b*} Molar absorption coefficient $(10^5 \text{ M}^{-1} \text{cm}^{-1})$. ^{*c*} Fluorescence quantum yield with Bodipy as a standard ($\Phi_{\text{F}} = 72\%$ in tetrahydrofuran). ^{*d*} Fluorescence lifetimes (ns) in toluene, $\lambda_{\text{ex}} = 510$ nm (EPL picosecond pulsed laser), ^{*e*} Singlet oxygen quantum yield in toluene with 2,6-diiodobodipy as a standard ($\Phi_{\Delta} = 0.83$ in DCM) and excited at 531 nm.⁷ Triplet state lifetime (µs) in toluene, determined with nanosecond transient absorption spectroscopy. ^{*g*} Not applicable.

around 780 nm, along with structured emission (locally excited) band at 524 nm was observed, which indicates the existence of strong electronic coupling between donor PTZ and PBI moieties.⁵⁷

The fluorescence lifetime of PBI-Cz dyads was also studied (Fig. 2). In all dyads the fluorescence emission decays faster as compared to reference compound and exhibits biexponential feature, which confirm the PET process in these dyads. For **PBI-Ph**, the decay of fluorescence at 520 nm (LE emission) is with lifetime of 4.3 ns, similar to that of unsubstituted PBI moiety which has fluorescence lifetime of 4.4 ns (see ESI[†], Fig. S18)

For **PBI-Cz-2** (Fig. 2b), the fluorescence decay is with minor biexponential feature of 0.6 ns (population ratio 13%) and 3.9 ns (87%), respectively. For the dyads, **PBI-Cz-1** and **PBI-Cz-3**, showing weak fluorescence, the biexponential decay feature is more significant. In case of **PBI-Cz-1** fluorescence lifetime is 0.1 ns (population ratio 82%) and 3.6 ns (18%); while for **PBI-Cz-3**, the fluorescence lifetime is 0.6 ns (population ratio 84%) and 4.3 ns (16%). The fast decaying components of **PBI-Cz-1** and **PBI-Cz-3**, generally indicate the quenching channel of the ¹LE state, e.g. photo-induced CS.⁵⁸ Fluorescence decay of PBI-Cz dyads were also studied in polar solvent such as dichloromethane (see ESI[†], Fig. S17). In polar solvent the fluorescence also decays faster and exhibit biexponential feature which support above results.

The singlet oxygen quantum yields (Φ_{Δ}) of the PBI-Cz dyads were studied (Table 1), as a preliminary evolution of the triplet state production ability of the compounds. The detailed method for measurement of Φ_{Δ} values is given in ESI[†]. PBI-Cz dyads show very high singlet oxygen quantum yields in toluene (Φ_{Δ} = 0.72 for **PBI-Cz-**3). Since PBI moiety is devoid of ISC ability, the ISC is attributed to the charge transfer mediated triplet state population in these dyads. It was found that by increasing the 'effective' spacer length in the dyads, the Φ_{Λ} decreases. Moreover, in polar solvents, the Φ_{Λ} decreases sharply as well. In toluene, the $\Phi_{\!\Delta}$ values are in the range of 38% ~ 72%, in dichloromethane, the PBI-Cz dyads showed Φ_{Δ} of only 4-10 %, whereas no singlet oxygen generation was observed in acetonitrile. The solvent polarity dependency of Φ_{Λ} indicates that CT state is involved the ISC, which is character of SOCT-ISC mechanism. It is interesting that the Cz and the PBI π -conjugation planes do not adopt orthogonal geometry, but the ISC is efficient. This result is different from the previously proposed orthogonal molecular geometries for electron donor-acceptor dyads showing efficient SOCT-ISC.46-48



Fig. 3 Cyclic voltammogram of (a) **PBI-Cz-1**; (b) **PBI-Cz-2**; (c) **PBI-Cz-3** and (c) **PBI-Ph**. In deaerated dichloromethane containing 0.10 M Bu₄NPF₆ as supporting electrolyte, Ferrocene (Fc) was used as the internal reference. Scan rates: 50 mV/s. $c = 5.0 \times 10^{-4}$ M, 20 °C.

Electrochemical studies

In order to study the Gibbs free energy changes of electron transfer and to determine the energy levels of charge transfer (CT) states of the PBI-Cz dyads, electrochemical measurements were carried out (Fig. 3). For PBI-Cz-1, two reversible reduction potential waves at -1.25 and -1.06 V were observed which can be attributed to PBI moiety (Table 2). One reversible oxidation potential wave at +0.81 V was also recorded, which can be assigned to Cz moiety. In case of PBI-Cz-2, one reversible oxidation wave potential at +0.87 V was observed which can be assigned to Cz moiety. Two reversible reduction potential waves similar to that of PBI moiety at -1.09 V and -1.24 V were also observed. In case of PBI-Cz-3, one reversible oxidation wave at +0.84 V was observed, this can be assigned to the Cz moiety. Two reversible reduction waves similar to that of PBI moiety at -1.07 V and -1.24 V were also observed. For the reference compound PBI-Ph only two reversible reduction waves at -1.11 V and -1.33 V were observed and no oxidation potential wave was

ARTICLE

observed within potential range used in the electrochemical measurements, which indicates that the PBI moiety is an electron acceptor rather than electron donor (Fig. 3d).

Journal of Materials Chemistry C

The Weller equation is used to calculate the free energy changes of PET process (Equation 1–3): 59,60

$$\Delta G^{0}_{cs} = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_{S}$$
(1)

$$\Delta G_{\rm S} = -\frac{e^2}{4\pi\varepsilon_{\rm s}\varepsilon_0 R_{\rm CC}} - \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{R_{\rm D}} + \frac{1}{R_{\rm A}}\right) \left(\frac{1}{\varepsilon_{\rm REF}} - \frac{1}{\varepsilon_{\rm S}}\right)$$
(2)

$$\Delta G_{\rm CR} = -(\Delta G_{\rm CS} + E_{00}) \tag{3}$$

where $\Delta G_{\rm S}$ is the static Coulombic energy, which is described by equation 2, e = electronic charge, $E_{OX} =$ half-wave potential for oneelectron oxidation of the electron-donor unit, E_{RED} = half-wave potential for one-electron reduction of the electron-acceptor unit; E_{00} = energy level approximated with the crossing point of UV–Vis absorption and fluorescence emission after normalization at the singlet excited state, ε_{s} = static dielectric constant of the solvent, R_{cc} = center-to-center separation distance between the electron donor (carbazole) and electron acceptor (perylenebisimide), determined by DFT optimization of the geometry, R_{CC} (PBI-Cz-1) = 13.57 Å, R_{CC} (PBI-Cz-2) = 13.57 Å, R_{CC} (PBI-Cz-3) = 10.69 Å, R_{D} is the radius of the electron donor, $R_{\rm A}$ is the radius of the electron acceptor, $\varepsilon_{\rm RFF}$ is the static dielectric constant of the solvent used for the electrochemical studies, ε_0 is permittivity of free space. The solvents used in the calculation of free energy of the electron transfer is Toluene ($\varepsilon_s = 2.4$), CH_2Cl_2 ($\varepsilon_s = 8.9$) and acetonitrile ($\varepsilon_s = 37.5$).

The free energy changes of intermolecular electron transfer and charge recombination process are listed in Table 3. Both **PBI-Cz-1** and **PBI-Cz-2** show the comparable ΔG^0_{CS} value in low polar solvent toluene i.e. -0.06 eV and -0.07 eV respectively and also have similar CSS energy level of 2.27 eV. However, in polar solvent the E_{CSS} of **PBI-Cz-1** becomes lower as compared to **PBI-Cz-2**. For **PBI-Cz-3**, in which Cz is linked with PBI moiety using a spacer of short length, the E_{CSS} is 2.20 eV which is lower compared to other two dyads and ΔG^0_{CS} is -0.14 eV in toluene. These results indicate the strong PET process in the **PBI-Cz-3** which also support the low fluorescence quantum yield ($\Phi_{\Delta} = 0.01$) and high singlet oxygen quantum yield ($\Phi_{\Delta} = 0.72$).

The ΔG^0_{CS} values also indicate that the CS is thermodynamically allowed for all PBI-Cz dyads even in non-polar solvent such as toluene which is in agreement with experimental observations (Fig. 1b, Table 3). This prediction was also confirmed by the fluorescence quenching of compounds in non-polar solvent. Moreover, we found that the CT state energy levels decrease in polar solvents (Table 3).

Table 2. Electrochemical redox potentials of the compounds ^a

Compounds	<i>E</i> (ox) (V)	<i>E</i> (red) (V)
PBI-Cz-1	+0.81	-1.25, -1.06
PBI-Cz-2	+0.87	-1.24, -1.09
PBI-Cz-3	+0.84	-1.25, -1.07
PBI-Ph	_b	-1.11, -1.33

^{*a*} Cyclic voltammetry in N₂-saturated DCM containing a 0.10 M Bu₄NPF₆. Counter electrode is Pt electrode and working electrode is glassy carbon electrode, Ag/AgNO₃ couple as the reference electrode. ^{*b*} Not observed.

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Perylenebisimide (PBI) chromophore devoid ISC ability and is highly fluorescent.⁶¹ However, PBI-Cz dyads show significant singlet oxygen production (Table 1), which indicates efficient ISC ability. For instance, the singlet oxygen quantum yield (Φ_{Δ}) of **PBI-Cz-3** is 72% in toluene, for **PBI-Cz-1** and **PBI-Cz-2**, the singlet oxygen quantum yields in toluene are 45% and 38%, respectively. To study the triplet excited states of the PBI-Cz dyads, nanosecond transient absorption spectra were studied (Fig. 4). Upon 532 nm pulsed laser excitation, a prominent excited state absorption (ESA) band was observed in the range of 400–650 nm that is similar to typical $T_1 \rightarrow T_n$ absorption profile of PBI moiety.⁶²

For **PBI-Cz-1**, **PBI-Cz-2** and **PBI-Cz-3**, ground state bleach bands (GSB) were observed at 528 nm. To monitor the lifetime of triplet excited state, the decay traces at 470 nm were studied. Interestingly, longer lifetime (110–189 μ s) was observed in the case of PBI-Cz dyads. The lifetime of transient species detected in case of PBI-Cz dyads are greatly quenched in the presence of air, which confirms the formation of triplet species. The PBI-localized triplet state is much longer-lived than that observed with heavy atom effect in a Pt(II) complex (246 ns ~ 1.0 μ s).^{63,64} The triplet state lifetimes are also much longer than that observed with the S₁/T_n (n > 1) energy level matching approach (30 ~ 60 μ s).⁶⁵ However, in a PBI derivative with phenyl acetylides substituents at 2, 5, 8, 11-position of the PBI core, a much longer triplet state lifetime was observed (505 μ s).⁶⁶

Time-resolved EPR spectral study

In order to study the triplet state property and the ISC mechanisms of the dyads, time-resolved electron paramagnetic resonance (TR-EPR) spectra of the dyads were recorded. Based on the UV–Vis absorption spectrum (Fig. 1a), we acquired the TR-EPR spectra of the compounds (Fig. 5) upon photoexcitation at 355 and 530–536 nm, where the Cz (355 nm) and/or the PBI (at 530 ca and 355 nm) moieties show absorption maxima, respectively.

Upon pulsed photoexcitation at 530–536 nm, all the dyads show similar TREPR spectra, with *eae/aea* electron spin polarization (ESP, *a* and *e* refer to enhanced absorption or emission, respectively). On the base of the ZFS parameters, D = 469 MHz and E = 44 MHz (Table 4), the triplet state is localized on the PBI moiety for all three dyads.

The polarization is not typical triplet state accessed with a regular SO-ISC,⁴² for its polarization would be *eee/aaa* (see the spectrum labeled PBI-ISC in Fig. 5a, simulated with the parameters taken from reference,⁴² and presented in Table 4). The spectral features are, instead, rather similar to those for a compact PBI-PTZ dyads, where the triplet was obtained by SOCT-ISC.⁴² Moreover, similar ESP pattern was observed in case of Julolidine-Anthracene (DMJ-AN) dyads exhibiting SOCT-ISC.⁴⁶ For this type of ISC process, we still have a population of the ZFS states, but the population rates of the sublevels of the triplet state is different from that obtained from a regular SO-ISC. The population of the ZFS states (molecular frame) will be carried over to the high-field energy levels (laboratory frame), thus highly polarized TREPR spectra of the triplet state were observed. It should be pointed out that the typical ESP of the triplet state accessed with RP ISC (either *aee/aae* or *eaa/eea*⁴²) was not observed, and we didn't observe any narrow bands relative to spin correlated radical pair (SC

Journal of Materials Chemistry C

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Table 3. Driving forces of charge recombination (ΔG^{0}_{CR}) and charge separation (ΔG^{0}_{CS}) and the energy of charge separated state (CSS) for dyads in different solvents ^a

	ΔG^{0}_{CS} (eV)			ΔG^{0}_{CR} (eV)			E _{css} (eV)		
	TOL	DCM	ACN	TOL	DCM	ACN	TOL	DCM	ACN
PBI-Cz-1	-0.06	-0.57	-0.71	-2.27	-1.76	-1.62	2.27	1.76	1.62
PBI-Cz-2	-0.07	-0.49	-0.64	-2.27	-1.85	-1.70	2.27	1.85	1.70
PBI-Cz-3	-0.14	-0.57	-0.69	-2.20	-1.77	-1.65	2.20	1.77	1.65

^aE₀₀ = 2.34 eV was used for all PBI-Cz dyads. E₀₀ is the approximated energy level with the cross point of UV–Vis absorption and fluorescence emission after normalization. The calculation of ΔG^{0}_{CS} , ΔG^{0}_{CR} and E_{CSS} values are based on electrochemical and optical measurements.



Fig. 4 Nanosecond transient absorption spectra of (a) PBI-Cz-1, (b) PBI-Cz-2, (c) PBI-Cz-3, decay curves of (d) f PBI-Cz-1 (470 nm), (e) PBI-Cz-2 (470 nm) and (f) PBI-Cz-3 (470 nm). λ_{ex} = 525 nm (nanosecond pulsed laser), $c = 1.0 \times 10^{-5}$ M in deaerated toluene. 20 °C.

RP) species, thus, the ISC of the dyads discussed in this manuscript is not due to RP ISC.⁶⁷ The TR-EPR spectra of the dyads were also recorded upon excitation at 355 nm (Fig. 5b). PBI-Cz-1 and PBI-Cz-3 gave similar spectra (Fig. 5b), both show the formation of two triplet states, localized on the PBI and the Cz moiety, respectively. Instead, PBI-Cz-2 leads to a spectrum in which only the Cz triplet is present. Also for this species, the polarization is different from that obtained from a regular SO-ISC of carbazole (Table 4).68 This result indicate that the intramolecular triplet energy transfer is retarded at low temperature.⁶⁹ Notably, PBI-Cz-2 is with two intervening phenyl moieties between the PBI and the Cz moieties, yet no RP ISC was observed for this dyad, based on the ESP of the triplet state TREPR spectrum. Interestingly, for the previously reported PBI-Ph₂-PTZ dyad, RP-ISC contributes significantly above 150 K (at low temperature, the SO-ISC contributes more, accordingly the ESP changed from *aee/aae* to *eee/aaa* with decreasing temperature).⁴² Another interesting result is that the tilting of the ZFS principal axes of the PBI and the Cz moieties in the three dyads are different, yet the ESP of the triplet state of the PBI moiety formed via the SOCT-ISC are the same for the three dyads. This result is different from the



Fig. 5 TR-EPR spectra with excitation at (a) 530 nm and (b) 355 nm in frozen solutions (T = 80 - 130 K) of **PBI-Cz-1**, **PBI-Cz-2**, **PBI-Cz-3** in toluene/MTHF (3: 1, v/v). The concentration was 3.0×10^{-5} M, but for PBI-Cz-2, the concentration was doubled because of the poor signal intensity. The spectra in red are the simulations of the experimental curves. Curve with PBI-ISC label in (a) refers to a simulation of a PBI triplet.⁴² and Cz-ISC in (b) refers to a simulation of a Cz triplet state,⁶⁸ both populated by a regular SO-ISC mechanism, taken as reference.

previous report that the ESP is sensitive to the mutual orientation of the electron donor and acceptor in SOCT-ISC electron donor/acceptor dyads.^{53,69} Although SO-ISC was expected for all PBI-Ph_n-PTZ (n = 1 – 5) at low temperature, yet the population ratio of the three sublevels are different, for PBI-Ph_n-PTZ (n = 2 – 5), the X and Y sublevels are almost equally populated. For PBI-Ph₁-PTZ, however, only one of the sublevels is overwhelmingly populated. Our results for the three dyads are similar to the compact dyad PBI-Ph₁-PTZ (n = 1 – 5) accessed with the SO ISC can be either *eee/aaa* (PBI-Ph_n-PTZ (n = 2 – 5), or *eae/aea* (PBI-Ph₁-PTZ).⁴² In case of previously reported PBI-PTZ derivatives, *E* value is negative (*E* < 0).⁴² But its sign depends on the labelling of the components (see Fig. 5). Given *D* > 0 and *E* > 0 (Table 4), the alignment of the three sublevels of the T₁ state is in the order of Y > X > Z (Y, X > 0, Z < 0).⁴⁶

Photochemical studies: reversible formation of radical anion in the presence of sacrificial electron donor TEOA

Photoreduction experiments were conducted in order to confirm the potential application of the dyads in photocatalysis (Fig. 6). The PBI-Cz dyads show efficient ISC, thus these compounds can be potentially used as photocatalysts, to derive electron transfer.⁴¹ The UV-Vis absorption changes of the dyads were monitored upon photo-irradiation by xenon lamp in the presence of TEOA in acetonitrile. Upon photo-irradiation, **PBI-Cz-1** and **PBI-Cz-3** show the formation of PBI radical anion (**PBI⁻⁺**) absorption bands at 698 nm, 794 nm and 953 nm, in the presence of sacrificial electron donor triethanolamine (TEOA).⁷⁰⁻⁷² Emergence of of new absorption bands at 698 nm, 794 nm and 953 nm, indicate the characteristic $D_0 \rightarrow D_n$ absorption of PBI radical anion (**PBI⁻⁺**).⁷⁰⁻⁷²

For dyad **PBI-Cz-3**, the absorption band at 519 nm gradually decreased in intensity under deaerated conditions in the presence of TEOA upon photoirradiation. New absorption bands at 698 nm, 794 nm and 953 nm appeared and gradually increase in intensity with time of irradiation (Fig. 6a). These gradually intensifying new NIR bands indicates the formation of PBI radical anion (**PBI⁻⁺**). These new NIR absorption bands attains maximum intensity upon 15 minutes of photoirradiation under N₂ environment and absorbance band at 519 nm was reduced to about 66% of the original signal intensity. When the photoirradiated solution was exposed to air, the absorption peaks in the near IR region disappeared, due to the oxidation of radical anion (**PBI⁻⁺**). Reversibility of the persistent radical anion formation was examined by photoirradiating the solution until 3 cycles (see ESI[†], Fig. S20). The orange color of **PBI-Cz-3** changed to light blue upon radical anion formation and original color of

Table 4. Simulation parameters of the TR-EPR spectra of the PBI and Cz references in Figure 5. The population rates of the different sublevels (P_x , P_Y and P_Z) and the calculated ZFS principle values are also presented, together with the selected experimental values from literatures.

	<i>D</i> (mT)	<i>E</i> (mT)	Px	Ру	Pz
PBI-ISC ^a	39.9	7.7	0.8	1.0	0.0
PBI (calc)	51.1	5.1	-	-	-
Cz-ISC ^b	107.1	12.9	1.0	1.0	0.0
Cz (calc)	131.7	0.6	_	-	-

 o From compound ${\bf 3}$ in ref. 42 Two electron-donating groups slightly reduce the ZFS-values of the triplet state of PBI moiety. b Literature value. 68

Table 5. Zero-field splitting parameters (*D* and *E*) and relative population rates P_{OVEW} the zero-field spin states of the dyads PBI-Cz-1, PBI-Cz-2 and PBI-Cz-3 and PBI-Cz-3 and PBI-Cz-3 and PBI-Cz-3 and PBI-Cz-3 and PBI-Cz-3 and Cz, which refer to triplets localized on either the PBI or the Cz moieties. The relative weight is presented in the parenthesis. The excitation wavelength (λ_{ex} . In nm) used for recording the spectra was presented

	λ_{ex}	<i>D</i> (mT)	<i>E</i> (mT)	Pz	Pz	Pz	
PBI-Cz-1	530	46.5 (100%)	4.2	1	0.18	0	
PBI-Cz-2	530	46.8 (100%)	4.4	1	0.15	0	
PBI-Cz-3	530	46.5 (100%)	4.3	1	0.25	0	
PBI-Cz-1	355	47.1 (20%)	4.4	1	0.2	0	
(two triplet states)		118.8 (80%)	30.1	0	1	0.8	
PBI-Cz-2	355	47.1 (100%)	4.4	1	0.2	0	
PBI-Cz-3	355	47.1 (70%)	4.4	1	0.2	0	
(two triplet states)		118.8 (30%)	30.1	0	1	0.8	

 $^{\it o}$ Obtained from simulations of the triplet-state TREPR spectra of the indicated molecules in a frozen toluene matrix at 80 K upon excitation at 530 nm and 355 nm.

compound was restored upon exposure of the photoirradiated solution to air (Fig. 6b). Similar phenomenon was observed in the case another dyad **PBI-Cz-1** (see ESI[†], Fig. S19). For **PBI-Cz-2**, no radical anion formation was observed as it aggregates in acetonitrile.



Fig. 6 (a) UV–Vis absorption spectra changes of **PBI-Cz-3** upon continuous photoirradiation in the presence of TEOA in the deaerated ACN and reversibility of the formation of PBI-* radical anion upon photoirradiation; (b) Photos showing the reversible color change of the **PBI-Cz-3**/TEOA mixed solution upon photoirradiation and reexposure to air: *c* [**PBI-Cz-3**] = 1.0×10^{-5} M, *c* [TEOA] = 1.0×10^{-4} M. The light source is a xenon lamp, power density is 180 mW/cm², photoirradiation time: 15 min. 20 °C.

DFT calculations

In order to rationalize the photophysical properties, the ground state geometries of the perylenebisimide-carbazole (PBI-Cz) dyads were optimized with DFT method by using CAM-B3LYP/6-31G (d) basis set.

The frontier molecular orbitals of the dyads were presented (Scheme 2). For all the three dyads, the HOMO is mainly localized on the Cz moiety, the LUMO is localized on the PBI moiety. This result indicates the possibility of the electron transfer from Cz to PBI moiety in the dyads upon photoexcitation. Moreover, the electron density

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Journal of Materials Chemistry C



Scheme 2. Selected frontier molecular orbitals of PBI-Cz-1, PBI-Cz-2, and PBI-Cz-3 calculated at DFT (CAM-B3LYP/6-31G (d)) level with Guassian 09W. The energy levels of the orbitals are presented (in eV).

of HOMO orbital also spread to the intervening phenyl moieties in all the dyads, but to a slightly less extent in **PBI-Cz-2** compared to other dyads. In principle the separation of the HOMO/LUMO molecular orbitals is prerequisite for the SOCT-ISC. Fully overlapped HOMO/LUMO orbits usually do not facilitate ISC.⁷³

The ground state geometries of the dyads were optimized (Fig. 7). For **PBI-CZ-1** and **PBI-CZ-3**, the dihedral angle between the PBI and the intervening phenyl moiety is 85.5°, almost orthogonal (Fig. 7).

This geometry indicates the conformation restriction of the two carbonyl moieties. On the other hand the dihedral angle between the intervening phenyl ring and the Cz moiety is 37.3°, indicating the conformation restriction is weak.

The dihedral angle between the planes of carbazole and PBI in PBI-Cz dyads was also determined (see ESI[†], Fig S21). For **PBI-Cz-1** and **PBI-Cz-3**, the dihedral angle between carbazole and PBI planes is ca. 49.2° and 24.7° respectively. It should be pointed out that the Cz and the PBI moiety are not in orthogonal geometry, yet the ISC is efficient. This result is different from previously reported electron



Fig. 7 Optimized conformations and the dihedral angles (degree) of the PBI and Cz units in the dyads calculated by DFT (B3LYP/6-31G (d)) with Gaussian 09W.



Fig. 8 Spin density distribution of the triplet states of the PBI-Cz dyads obtained by computation with DFT theory at (CAM-B3LYP/6-31G (d)) level using Gaussian 09W.

Journal of Materials Chemistry C



Fig. 9 Spin Density distribution of the PBI-Cz dyads anions and cations, obtained by computation with DFT theory at (UB3LYP/6-31G (d)) level using Gaussian 09W.

donor/acceptor dyads showing SOCT-ISC, in which orthogonal geometry was desired. $^{\rm 46-48,52}$

The electron spin density surfaces of the T_1 states of the dyads were studied (Fig. 8). For all the three dyads, the triplet states are all confined on the PBI moieties; there is no spin leakage to the intervening phenyl moieties. These results are in agreement with the TREPR results (*D* and *E* parameters, Table 4). The electron spin density surfaces of the radical anion and radical cations of the dyads were also studied (Fig. 9). This characterization shows the localization of the hole and electron of the CT states. The results show the hole is confined on the electron donor carbazole moiety and the intervening phenyl rings. The electron is localized on the electron acceptor PBI units.

The photophysical processes of the dyads upon photoexcitation are summarized in Scheme 3. PBI is a visible light-harvesting chromophore, upon photoexcitation, ultrafast CS occurs (supported by the quenched fluorescence of the PBI moiety and fast decay of the LE emission), CT state is formed. The subsequent CR will lead to formation of ³LE states. Since the CT state energy level will decrease in polar solvents, the matching of the ¹CT state and the T_n state may change, as a result, the ISC efficiency is highly solvent polaritydependent. The singlet oxygen quantum yields are high in toluene (Table 1), but the singlet oxygen quantum yields in polar solvents are much lower. Another possible reason for inefficient triplet



Scheme 3. Jablonski diagram demonstrating the photophysical processes involved in PBI-Cz-3 upon photoexcitation. The energy levels of the excited state are derived from the spectroscopic data and energy level of charge separated (CS) state are determined from electrochemical data. The triplet energy levels are estimated by TD-DFT method (in toluene). The numbers in superscripts indicates the spin multiplicity. population in high polar solvent can be the fast CR process which competes strongly with SOCT-ISC. The Jablonski diagrams demonstrating photophysical process involved in other two dyads (**PBI-Cz-1** and **PBI-Cz-2**, see ESI[†])

Conclusions

In summary, we prepared a series perylenebisimide (PBI)-carbazole (Cz) electron donor/acceptor dyads to study the spin orbital charge transfer (SOCT-ISC) induced intersystem crossing in these dyads. The molecular conformation was varied by changing the mutual orientation and distance between perylenebisimide donor and carbazole acceptor. Negligible ground state electronic coupling between the PBI and Cz moiety was observed in all the dyads. High singlet oxygen quantum yields (Φ_{Δ} = 38 ~ 72%) were observed, especially in case of PBI-Cz-3 in which the donor and acceptor are separated by smallest distance. All the dyads shows the long-lived PBI localized triplet state (τ_T is up to 190 μ s), confirmed by nanosecond transient absorption spectroscopy. It should be noted that dyads (PBI-Cz-1 and PBI-Cz-3) with one phenyl spacer between donor and acceptor adopts non-orthogonal geometry, but the ISC is still efficient, which is different from the previously reported molecular structural profiles which require orthogonal geometry for efficient SOCT-ISC. Time-resolved electron paramagnetic resonance (TREPR) spectroscopy reveals that all three dyads have same electron spin polarization of eae/aea, which is different from the SO-ISC (eee/aaa), thus confirming the SOCT-ISC mechanism. Moreover, upon photoirradiation, PBI-Cz-1 and PBI-Cz-3 show the formation of near-IR absorbing PBI radical anion (PBI-•) in the presence of sacrificial electron donor (TEOA). These results are useful for future design of heavy atom-free triplet photosensitizers and for study of the charge recombination in the electron donor/acceptor dyads.

Experimental section

Materials and methods

All chemical used in the study are of analytical grade and used as received. UV–Vis absorption spectra were recorded on a UV-2550 UV–Vis spectrophotometer (Shimadzu Ltd., Japan). Fluorescence spectra were obtained with a RF-5301PC spectrofluorometer (Shimadzu Ltd., Japan). Fluorescence lifetimes were measured by OB920 luminescence lifetime spectrometer (Edinburgh Instruments Ltd, U.K.).

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Synthesis

The detail of the synthesis and characterization of compounds **1**, **2**, **3** and **PBI-Ph** are given in the ESI[†].

Synthesis of PBI-Cz-1: Under N₂ atmosphere, compound 1 (100 mg, 0.16 mmol), 9-phenyl-9H-carbazol-3-ylboronic acid (92 mg, 0.32 mmol) and K₂CO₃ (100 mg, 0.72 mmol) were dissolved in 25 mL mixed solvent of PhCH₃/EtOH/H₂O (4/2/1, v/v). The reaction mixture was deoxygenated by using vacuum pump and N₂ purging for 20 minutes. Then Pd(PPh₃)₄ (20 mg, 5 mol%) was added and reaction mixture was refluxed for 8 h under nitrogen atmosphere. After completion of reaction, the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (30 mL), washed with water (2 × 100 mL) and dried over anhydrous sodium sulfate. After evaporation of solvent under reduced pressure, the crude product was further purified with column chromatography (Silica gel, CH_2Cl_2 /petroleum ether, 2/1, v/v) to give red solid (75 mg, yield: 60 %). mp > 250 °C. ^1H NMR (CDCl_3, 400 MHz); δ 8.79 (d, 2H, J = 8.0 Hz), 8.72–8.67 (m, 6H), 8.43 (s, 1H), 8.22 (d, 1H, J = 4.0 Hz), 7.92 (d, 2H, J = 8.0 Hz), 7.73 (dd, 1H, J = 8.0 Hz), 7.67-7.61 (m, 4H), 7.52-7.44 (m, 6H), 7.36-7.30 (m, 1H), 5.12-5.05 (m, 1H), 2.32–2.23 (m, 2H), 2.02–1.91 (m, 2H), 0.94 (t, 6H, J = 8.1 Hz). TOF MALDI-HRMS ($[C_{53}H_{35}N_3O_4]^-$) Calcd: m/z = 777.2628. Found: *m*/*z* = 777.2606.

Synthesis of PBI-Cz-2: Under N_2 atmosphere, compound $\boldsymbol{1}$ (100 mg, 0.16 mmol), (4-(9-carbazolyl)benzeneboronic acid (92 mg, 0.32 mmol) and K₂CO₃ (100 mg, 0.72 mmol) were dissolved in 25 mL mixture of PhCH₃/EtOH/H₂O (4/2/1, v/v). The reaction mixture was deoxygenated by N₂ purging for 20 minutes. Then Pd(PPh₃)₄ (20 mg, 5 mol%) was added and reaction mixture was refluxed for 8 h under N₂ atmosphere. After completion of reaction, the reaction mixture was cooled to room temperature, extracted with CH₂Cl₂ (30 mL), washed with water (2 × 100 mL) and dried over anhydrous sodium sulfate. After evaporation of solvent under reduced pressure, the crude product was further purified with column chromatography (silica gel, CH₂Cl₂/petroleum ether, 2/1, v/v) to give red solid (60 mg, yield: 48 %). mp > 250 °C. ¹H NMR (CDCl_{3.} 500 MHz); δ 8.81 (d, 2H, J = 10.0 Hz), 8.73-8.72 (m, 6H), 8.18 (d, 2H, J = 5.0 Hz), 7.90-7.89 (m, 4H), 7.70 (d, 2H, J = 10.0 Hz), 7.53-7.50 (m, 4H), 7.47-7.44 (m, 4H), 5.13-5.06 (m, 1H), 2.33-2.25 (m, 2H), 1.99-1.93 (m, 2H), 0.94 (t, 6H, J = 8.0 Hz). TOF MALDI-HRMS ([$C_{53}H_{35}N_3O_4$]⁻) Calcd: m/z = 777.2628. Found: *m*/*z* = 777.2637.

Synthesis of PBI-Cz-3: Under N₂ atmosphere, the mixture of compound **3** (100 mg, 0.21 mmol), compound 5 (81 mg, 0.31 mmol) and imidazole (500 mg, 7.35 mmol) was stirred at 140 °C for 4 h. After completion of reaction, temperature of reaction mixture was reduced to 90 °C, water (5 mL) was added and continue stirring for 30 min. Then reaction mixture was filtered and residue solid was washed with 20 % KOH aqueous solution (3 × 20 mL). The crude product was dried in oven overnight and purified with column chromatography (silica gel, CH₂Cl₂) give red solid (60 mg, yield: 40 %). mp > 250 °C. ¹H NMR (CDCl₃, 500 MHz); δ 8.83 (d, 2H, *J* = 5.0 Hz), 8.75–8.71 (m, 6H), 8.18 (d, 2H, *J* = 10.0 Hz), 7.82 (d, 2H, *J* = 10.0 Hz), 7.62 (m, 4H), 7.48 (dd, 2H, *J* = 10.0, 5.0 Hz), 7.35–7.32 (m, 2H), 5.13–5.06 (m, 1H), 2.35–2.25 (m, 2H), 2.01–1.93 (m, 2H), 0.95 (t, 6H, *J* = 10.0 Hz). TOF MALDI–HRMS ([C₄₇H₃₁N₃O₄]⁻) Calcd: *m/z* = 701.2315. Found: *m/z* = 701.2303.

Nanosecond transient absorption spectroscopy

LP980 laser flash photolysis spectrometer (Edinburg Instruments, U.K.) equipped with Tektronix TDS 3012B oscilloscope was used to study the nano- and microsecond dynamics. The samples were deaerated with N₂ for 15 min prior to investigations. The data was processed by L900 software.

Journal of Materials Chemistry C

Time-resolved electron paramagnetic resonance (TREPR) spectroscopy

The solutions containing the compounds **PBI-Cz-1**, **PBI-Cz-2**, **PBI-Cz-3** (Scheme 1) in toluene/MTHF (3:1, v/v) 3×10^{-5} M were prepared, the solutions were transferred into 3 mm (i.d.) quartz tubes and sealed under vacuum after removing dissolved gas by a few freeze-pump-thaw cycles. TR-EPR spectra were recorded with an Elexsys Bruker EPR spectrometer, equipped with a dielectric cavity placed inside an Oxford CF595 cryostat with an optical access for irradiation of the sample by a pulsed laser. A Quantel Nd:YAG laser provided pulsed light (6 *ns* duration) for the photoexcitation of the sample in the visible range with an OPO pumped by 355 nm pulses (also available for irradiation of the sample).

Acknowledgements

J. Z. thanks the NSFC (21673031, 21761142005, 219911530095 and 21421005), the State Key Laboratory of Fine Chemicals (ZYTS201901), the Fundamental Research Funds for the Central Universities (DUT2019TA06) and Department of Chemical Science, University of Padua, Italy (Visiting Scientist) for support.

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Published on 25 January 2020.

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Carbazole-Perylenebisimide Electron Donor/Acceptor Dyads Showing Efficient Spin Orbit Charge Transfer Intersystem Crossing (SOCT-ISC) and Photo-Driven Intermolecular Electron Transfer

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Efficient spin orbit charge transfer intersystem crossing (SOCT-ISC) was demonstrated in nonorthogonal compact carbazole-perylenebisimide electron donor/acceptor dyads.