

Article

Metal-Free Triplet Photosensitizers via Arene–BODIPY Charge Transfer and Iodine-Induced Spin Conversion

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Abstract

BODIPY derivatives are promising scaffolds for triplet photosensitizers because of their strong absorption and tunable absorption range, but their dominant fluorescence decay and weak spin–orbit coupling hinder efficient intersystem crossing (ISC). Here, we report iodine-substituted BODIPY photosensitizers bearing anthracene, pyrene, and perylene units (**BI-Ant**, **BI-Pyr**, and **BI-Per**), designed to combine the heavy-atom effect with the spin–orbit charge-transfer ISC (SOCT-ISC) process. Spectroscopic and computational analyses revealed charge-transfer character and efficient triplet formation in all three compounds. Transient absorption measurements showed that **BI-Ant** and **BI-Pyr** undergo an ISC process to BODIPY-centered triplet state, whereas **BI-Per** exhibits intermediate strong charge-transfer-state evolution and the fastest ISC process. Solvent-dependent results further indicate that charge-transfer-state stabilization accelerates ISC process, supporting an additional SOCT contribution. These findings provide an effective strategy for developing highly efficient metal-free triplet photosensitizers.

Keywords: triplet photosensitizer; BODIPY; intersystem crossing; spin–orbit charge transfer; heavy atom effect

1. Introduction

The electronic excited states of molecular systems are fundamentally categorized into singlet and triplet states based on their spin multiplicity [1]. Unlike singlet excitons, which are primarily governed by radiative and non-radiative decay pathways, triplet excitons exhibit a unique spin-active character due to their parallel spin alignment [2]. This distinct nature enables a variety of sophisticated photophysical phenomena that are inaccessible via singlet excited states, such as thermally activated delayed fluorescence [3–5], triplet–triplet annihilation upconversion [6–8], and the generation of singlet oxygen for photodynamic therapy [9,10]. Despite these scientific and technological advantages, the direct population of the triplet state from the ground and singlet excited states is quantum mechanically spin-forbidden. Consequently, achieving efficient intersystem crossing (ISC), a transition from singlet to triplet state, is key in the utilization of triplet-mediated processes [11–13].

To overcome the spin-forbidden nature of triplet generation, several fundamental strategies have been developed to facilitate ISC in triplet photosensitizers. These primarily include the heavy-atom effect, which introduces metals with a large atomic number to



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enhance spin–orbit coupling (SOC) [14]. Also, El-Sayed’s rule leverages $n \rightarrow \pi^*$ transitions to promote spin-flip, where the change in orbital angular momentum between the two different types of orbitals effectively compensates for the spin-flip to satisfy the conservation of total angular momentum [15]. Additionally, spin–orbit charge-transfer intersystem crossing (SOCT-ISC) has emerged as a metal-free pathway for triplet generation through the formation of photoinduced charge transfer (CT) state, and electron density is transferred from donor to acceptor subunits. Because the CT and locally excited (LE) states differ substantially in electronic configuration, their interconversion involves a change in orbital angular momentum that promotes spin-flip and thus enhances ISC [16]. However, their application as practical triplet sensitizers is limited by several challenges. Heavy metals are often restricted by environmental toxicity [17], a tendency to shorten triplet lifetimes and high costs, while systems relying on El-Sayed’s rule suffer from low molar absorption coefficients and high-energy $n \rightarrow \pi^*$ transitions, which confine their applicability to the UV region, limiting their photoactivity in the visible spectrum [18]. Moreover, SOCT-ISC demands rigorous control over molecular geometry and electronic energy levels, which requires extensive trial-and-error optimization [19].

In this context, significant scientific interest has been focused on 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) molecule to develop highly efficient triplet photosensitizer [20]. BODIPY derivatives are well-known as outstanding molecular dyes due to their intense visible-light absorption, high fluorescence quantum yields, and excellent photostability. A key advantage of the BODIPY molecular skeleton is its remarkable structural versatility, which allows for precise chemical modification to tune its photophysical properties [21]. Furthermore, the BODIPY core enables strong donor–acceptor interactions with various aromatic units, which facilitates charge-transfer-mediated processes [22]. By strategically integrating multiple ISC-promoting mechanisms, rather than relying on a single pathway, it is possible to exploit synergistic effects to transform the typically fluorescent BODIPY into a highly efficient triplet photosensitizer.

Herein, we focused on a metal-free BODIPY-based photosensitizers that are capable of simultaneously inducing the heavy-atom effect and SOCT-ISC. In BODIPY systems, the introduction of iodine, one of the most widely used non-metal heavy atoms, is known to promote triplet exciton generation efficiently. However, because BODIPY intrinsically exhibits strong fluorescence emission, radiative decay is not completely suppressed even after iodine substitution, which limits the triplet formation quantum yield [23,24]. Overcoming this limitation often requires the incorporation of heavy metals that provide substantially stronger spin–orbit coupling. To address this issue, we introduced arene substituents to additionally induce SOCT-ISC through donor–acceptor interactions with the BODIPY core, thereby enabling more efficient ISC without the use of metals. From this perspective, we thoroughly investigated the ISC processes of iodine-substituted BODIPY photosensitizers bearing anthracene, pyrene, or perylene units. In these systems, the heavy-atom effect and SOCT-ISC can occur simultaneously. Their photophysical behavior was analyzed using time-resolved spectroscopies and DFT calculations. In all three cases, electronic donor–acceptor interactions between BODIPY and the appended arene generated pronounced CT character, which led to enhanced ISC efficiency in polar environments through SOCT-ISC. Notably, the perylene-substituted system exhibited particularly strong electronic coupling with the BODIPY core because of its favorable energetic alignment, which enabled remarkably rapid ISC even in nonpolar toluene. These findings provide a new strategy for designing advanced triplet photosensitizers that overcome the conventional trade-offs in triplet-state engineering.

2. Results and Discussion

2.1. Characterization of Molecular Structures and Photophysical Properties

In this study, we synthesized a series of BODIPY-based photosensitizers, **BI-Ant**, **BI-Pyr**, and **BI-Per**, according to previously reported procedures (Figure 1) [25]. In all compounds, iodine atoms are directly introduced at the 2,6-positions of the BODIPY core by which the heavy-atom effect can be most effectively induced. Moreover, the anthracene, pyrene, or perylene moieties are attached at the *meso*-position, and methyl groups at the 1,7-positions are employed to maintain an orthogonal arrangement between the arene groups and the BODIPY core. These conformations are clearly supported by DFT optimization results, which reveal dihedral angles of 90.0°, 84.1°, and 84.3° for **BI-Ant**, **BI-Pyr**, and **BI-Per**, respectively (Figure S1). These molecular geometries effectively minimize π -conjugative interactions between the BODIPY core and the arene substituents, while facilitating the role of the BODIPY core and arene units as independent intramolecular electron acceptor and donor units.

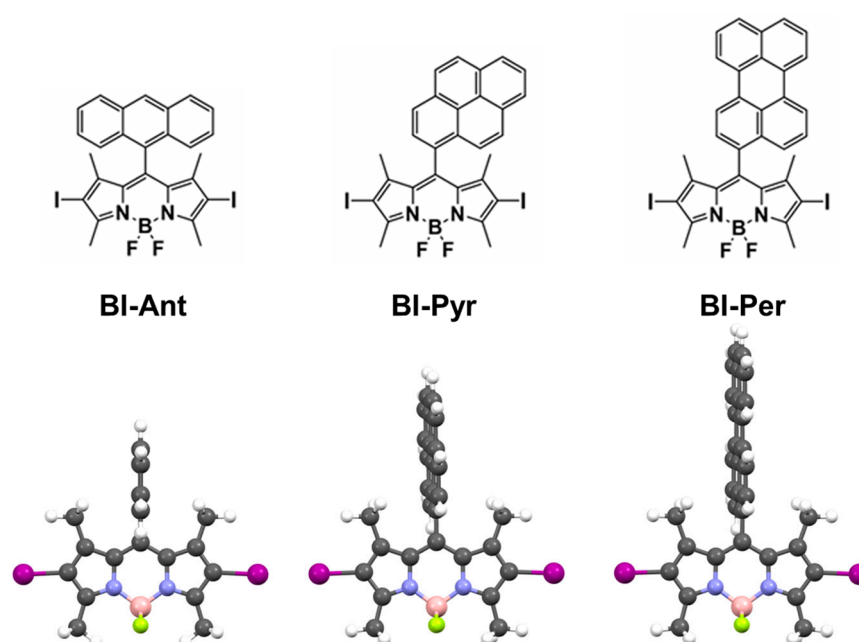


Figure 1. Molecular structures of **BI-Ant**, **BI-Pyr**, and **BI-Per**. Carbon, hydrogen, nitrogen, boron, fluorine, and iodine atoms are represented in gray, white, pale blue, apricot, light green, and purple, respectively.

2.2. Absorption and Fluorescence Emission Properties

Figure 2 shows the absorption and fluorescence emission spectra of **BI-Ant**, **BI-Pyr**, and **BI-Per** in various solvents. All three compounds exhibit similar overall spectral features despite changes in solvent polarity. In the absorption spectra, a common intense band is observed around 540 nm, which can be assigned to the characteristic absorption of the BODIPY core [26]. In addition, extra absorption bands appear in the 300–450 nm region and gradually shift to shorter wavelengths in the order of **BI-Per**, **BI-Ant**, and **BI-Pyr**. These bands correspond to the absorption of the perylene, anthracene, and pyrene moieties in **BI-Per**, **BI-Ant**, and **BI-Pyr**, respectively. This result clearly indicates that, as suggested by the molecular structures, the orthogonal geometry effectively minimizes π -conjugative interactions between the BODIPY core and the arene groups, which allows their π -electronic structures to remain largely independent [27].

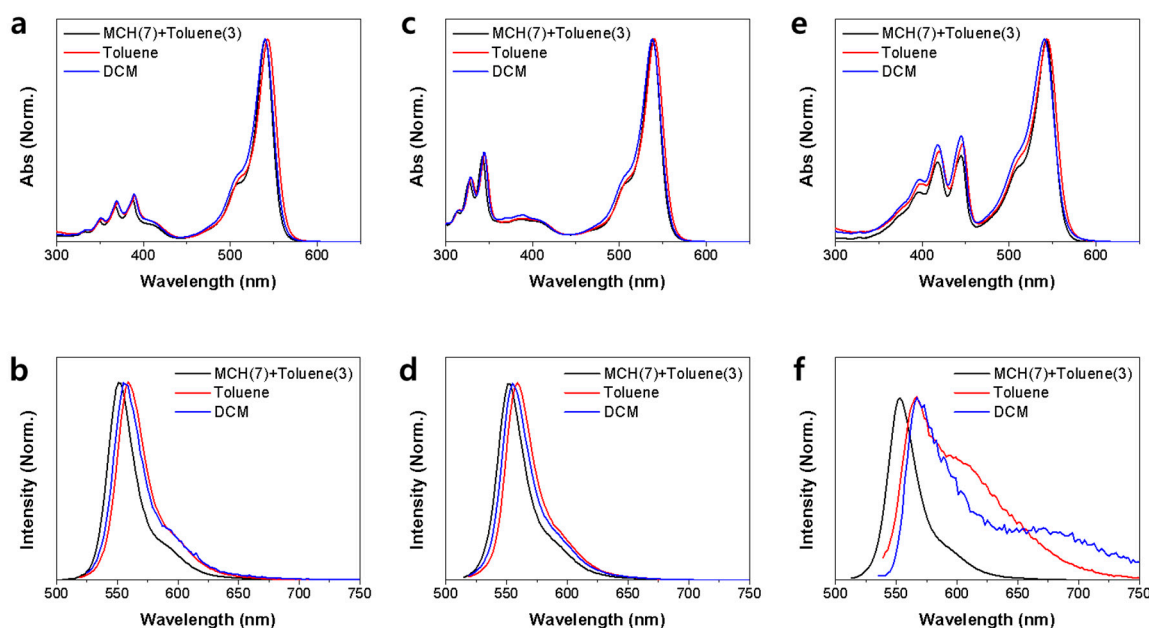


Figure 2. UV-vis absorption and fluorescence emission spectra of (a,b) **BI-Ant**, (c,d) **BI-Pyr**, and (e,f) **BI-Per** in methylcyclohexane (MCH) and toluene mixture (7:3), toluene, and dichloromethane (DCM). Fluorescence emission spectra were measured with photoexcitation in the 500–520 nm region.

In contrast to their similar absorption spectral features, the three compounds exhibit sharply different emission behaviors. **BI-Ant** and **BI-Pyr** show fluorescence maxima around 555 nm regardless of the solvent (Figure 2b,d), which are well matched with the characteristic fluorescence emission of the BODIPY core [28]. By contrast, **BI-Per** displays BODIPY-centered emission in a mixed solvent of methylcyclohexane (MCH) and toluene (7:3), similar to **BI-Ant** and **BI-Pyr**. However, as the solvent polarity increases from toluene to dichloromethane (DCM), an additional emission band emerges at longer wavelengths with a pronounced red shift (Figure 2f). Furthermore, spectral analysis of the time-resolved fluorescence emission in toluene reveals no noticeable time-dependent spectral changes for **BI-Ant** or **BI-Pyr**, whereas **BI-Per** exhibits clear spectral evolution over time, although the earliest changes could not be fully resolved because of the limited time resolution (Figure 3). These polarity- and time-dependent spectral changes in **BI-Per** clearly indicate the formation of a pronounced photoinduced CT state [29]. In particular, the emergence of a red-shifted emission band in more polar solvents suggests stabilization of the CT state, whereas the time-dependent spectral evolution supports its dynamic formation from the populated LE state to the CT state.

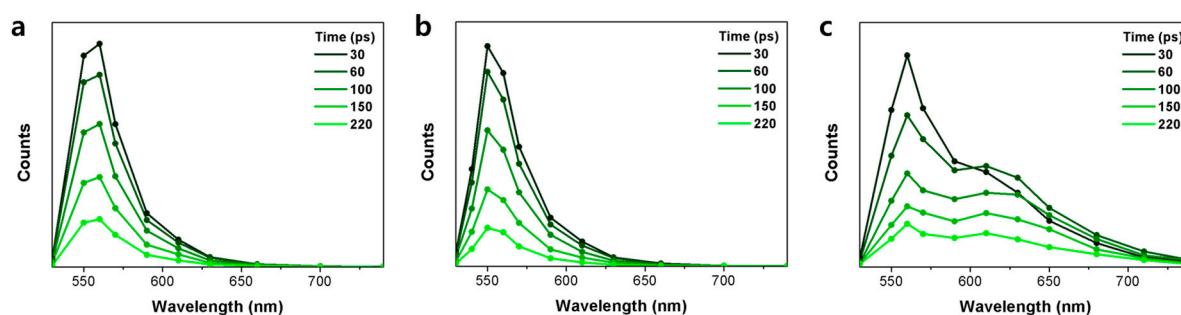


Figure 3. Time-resolved fluorescence decay spectra of (a) **BI-Ant**, (b) **BI-Pyr**, and (c) **BI-Per** in toluene. The spectra were measured with a photoexcitation at 515 nm.

To further clarify these photophysical features, we measured the fluorescence quantum yields of all compounds. The fluorescence quantum yield analysis reveals that **BI-Per** shows

a substantial decrease in quantum yield value even in nonpolar toluene compared with the MCH/toluene mixed solvent (Table 1). This result strongly indicates the emergence of a CT process in **BI-Per** [30], due to the orthogonal arrangement between the perylene and BODIPY units. **BI-Ant** and **BI-Pyr** also show gradual decreases in fluorescence quantum yield with an increase in solvent polarity. This trend suggests that the anthracene and pyrene moieties, being similar to the perylene moiety, can also interact with the BODIPY unit, which results in the donor–acceptor interactions to generate CT character. In particular, **BI-Ant** shows a much larger difference in fluorescence quantum yield between toluene and DCM than **BI-Pyr**, which further indicates that the extent of CT character depends on the interaction between the arene and BODIPY units and becomes stronger as their energy gap between the two moieties decreases.

Table 1. Fluorescence emission properties.

	MCH/Toluene (7:3)		Toluene		DCM	
	Φ_F ^a	λ_f (nm) ^b	Φ_F	λ_f (nm)	Φ_F	λ_f (nm)
BI-Ant	2.03 ± 0.01	551	1.39 ± 0.01	559	0.30 ± 0.01	557
BI-Pyr	1.52 ± 0.01	550	1.37 ± 0.01	554	0.95 ± 0.01	551, 610
BI-Per	1.49 ± 0.01	554	0.24 ± 0.01	557	0.09 ± 0.01	556, 670

^a Fluorescence quantum yield (%). ^b Maximum emission band wavelength.

We also examined the singlet oxygen ($^1O_2$) emission and $^1O_2$ quantum yields (Φ_Δ) to confirm triplet formation and quantitatively evaluate its efficiency. All compounds display clear singlet oxygen emission at 1270 nm in all solvents (Figures S2–S4). Because singlet oxygen is produced by energy transfer from the triplet excited species to ground-state oxygen [31], this result indicates that all compounds undergo ISC to the triplet state efficiently in all solvent environments. In toluene, the $^1O_2$ quantum yields of **BI-Ant**, **BI-Pyr**, and **BI-Per** were determined to be $86 \pm 3\%$, $86 \pm 3\%$, and $90 \pm 2\%$, respectively (Table S1). All of these values are higher than that of 2,6-diiodo-1,3,5,7-tetramethyl-8-phenyl-BODIPY ($\Phi_\Delta = 83\%$), whose arene unit is simply a benzene ring and is known to show negligible CT character [32]. This suggests that **BI-Ant**, **BI-Pyr**, and **BI-Per** exhibit enhanced ISC through an additional SOCT contribution arising from their CT character, consistent with the fluorescence results. In particular, the highest value observed for **BI-Per**, which also shows the most pronounced CT character, strongly supports that ISC is most efficiently promoted in this system by an additional SOCT contribution.

2.3. Excited-State Dynamics

To examine the highly efficient ISC behavior of **BI-Ant**, **BI-Pyr**, and **BI-Per** in detail, we carried out femtosecond and nanosecond transient absorption (fs- and ns-TA) measurements. Because TA spectra measure the photoinduced change in absorbance (ΔA), they are generally composed of three major contributions of ground-state bleaching (GSB), excited-state absorption (ESA), and stimulated emission (SE) [33,34]. GSB appears as a negative signal at wavelengths of the steady-state absorption band owing to ground-state depopulation upon photoexcitation, whereas ESA gives positive signals from absorption by excited species and SE gives negative signals from probe-induced emission overlapping with the fluorescence band. Consistent with the singlet oxygen emission results, all compounds exhibited long-lived TA signals beyond 10 μs in the ns-TA spectra, which directly demonstrates the efficient formation of triplet states (Figure S5). Notably, the ns-TA spectra of **BI-Per** are clearly distinct from those of **BI-Ant** and **BI-Pyr**. For **BI-Ant** and **BI-Pyr**, the ESA signals appear on the longer wavelength side relative to the GSB band, whereas **BI-Per**

shows ESA signals on the shorter wavelength side of the GSB. The ns-TA spectral features of **BI-Ant** and **BI-Pyr** are in good agreement with the reported triplet TA spectrum of iodine-substituted BODIPY [35,36]. In contrast, the ns-TA spectrum of **BI-Per** matches well with previously reported ns-TA spectra of perylene [37]. These spectral correspondences clearly indicate that the triplet exciton is formed on the BODIPY core in **BI-Ant** and **BI-Pyr**, whereas in **BI-Per**, it is localized on the perylene unit. This assignment is also consistent with the lower triplet-state energy level of perylene [38].

fs-TA measurements in toluene reveal the singlet excited-state dynamics of these compounds as well as the TA spectral evolution associated with the ISC process, in which **BI-Ant**, **BI-Pyr**, and **BI-Per** also exhibit clearly contrasting spectral features (Figure 4). **BI-Ant** and **BI-Pyr** show very similar TA behaviors with strong negative signals initially dominating the 500–650 nm region. Based on the spectral matching with their absorption and fluorescence emission spectra, the negative signals can be assigned to a combination of GSB and SE features. As these initial TA spectra evolve into the spectra that are consistent with their ns-TA spectra, the fast decay time constants of 75 and 67 ps for **BI-Ant** and **BI-Pyr**, respectively, can be assigned to their ISC time constant. **BI-Per** also initially exhibits a TA spectrum dominated by negative signals in the 500–650 nm region, similar to **BI-Ant** and **BI-Pyr**. Although this initial TA spectrum also evolves into the triplet-exciton TA spectrum observed in the ns-TA measurement, a distinct intermediate spectral change is clearly observed, in which an ESA band with a maximum at 575 nm rises and decays rapidly. The TA decay profile of **BI-Per** contains two extra decay time constants of 2.7 and 50 ps, together with a long-lived component. Given the fluorescence emission features of **BI-Per**, these two decay components can be assigned to the strong CT process between BODIPY and perylene units and the subsequent ISC process, respectively. Here, the fastest ISC observed for **BI-Per**, together with the appearance of a distinct intermediate ESA band at 575 nm and a preceding 2.7 ps CT-related component, indicates that spin conversion is not governed solely by the iodine-induced heavy-atom effect but is further accelerated by an additional SOCT contribution.

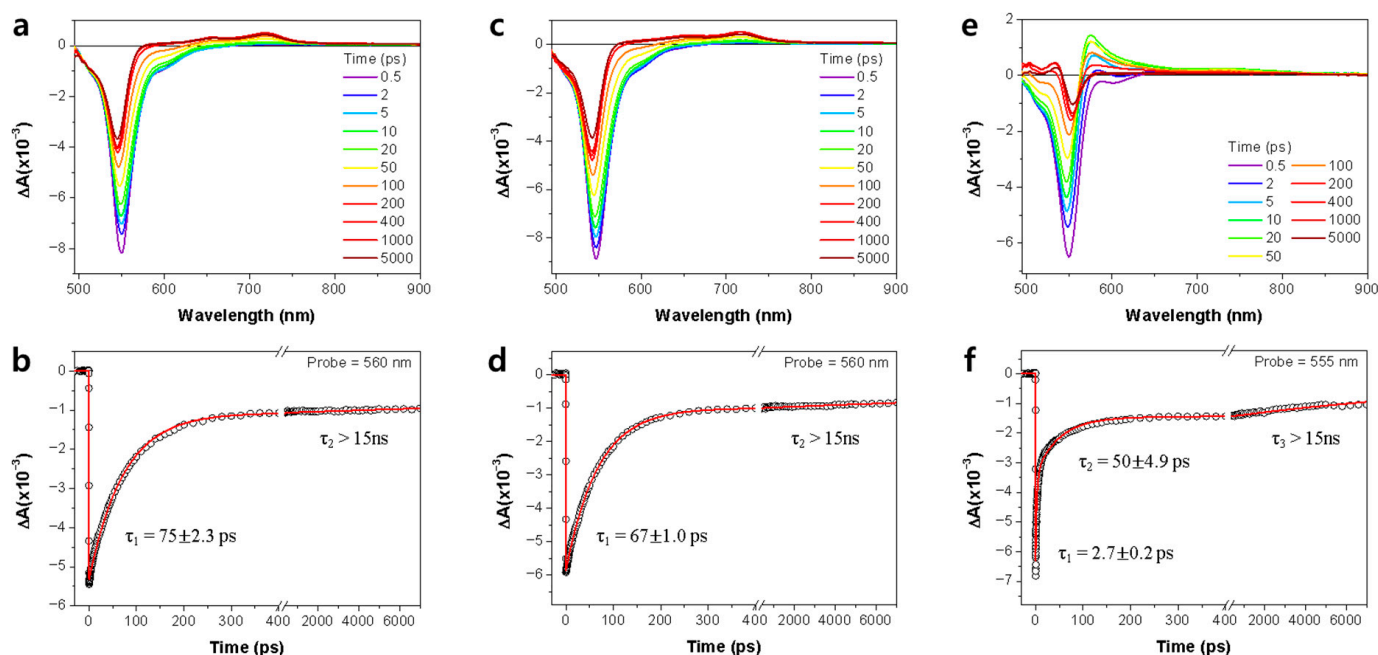


Figure 4. Femtosecond transient absorption spectra and decay profiles of (a,b) **BI-Ant**, (c,d) **BI-Pyr**, and (e,f) **BI-Per** in toluene upon photoexcitation at 540 nm.

To gain deeper insight into the CT character, fs-TA measurements were performed in solvents of varying polarity. For **BI-Per**, increasing solvent polarity clearly led to a progressive increase in the amplitude of the ESA band centered at 575 nm (Figure 5). This feature causes the CT and ISC processes to become shorter as solvent polarity increased. These observations suggest that higher solvent polarity stabilizes the CT state more effectively, which increases the difference in π -electron density distribution between the LE and CT states. As a result, SOCT becomes more pronounced and leads to a faster ISC process. A similar polarity-dependent acceleration of the ISC rate was also observed for **BI-Ant** and **BI-Pyr** (Figures S6 and S7). In particular, the fs-TA result of **BI-Ant** in DCM reveals a distinct intermediate spectral evolution accompanied by the appearance of an ESA band with a maximum at 575 nm (Figure S6e), closely resembling the fs-TA results of **BI-Per** (Figure 4e). This finding clearly indicates that, in a polar environment, strong donor-acceptor interactions between the anthracene and BODIPY units give rise to substantial CT character in **BI-Ant**. More broadly, it directly demonstrates that sufficiently stabilizing the electronic interaction between the arene and BODIPY units can induce pronounced CT interactions. Moreover, whereas the ISC process in typical 2,6-diiodo-substituted BODIPY derivatives generally occurs with a time constant on hundreds of ps [39–41], **BI-Ant**, **BI-Pyr**, and **BI-Per** exhibit much faster ISC on the timescale of several tens of ps, and this process is further accelerated with an increase in solvent polarity. Given the fs-TA result of **BI-Ant** in DCM, it is strongly suggested that ISC in all three compounds is not governed solely by the heavy-atom effect, but is additionally promoted by SOCT, resulting in markedly enhanced ISC efficiency.

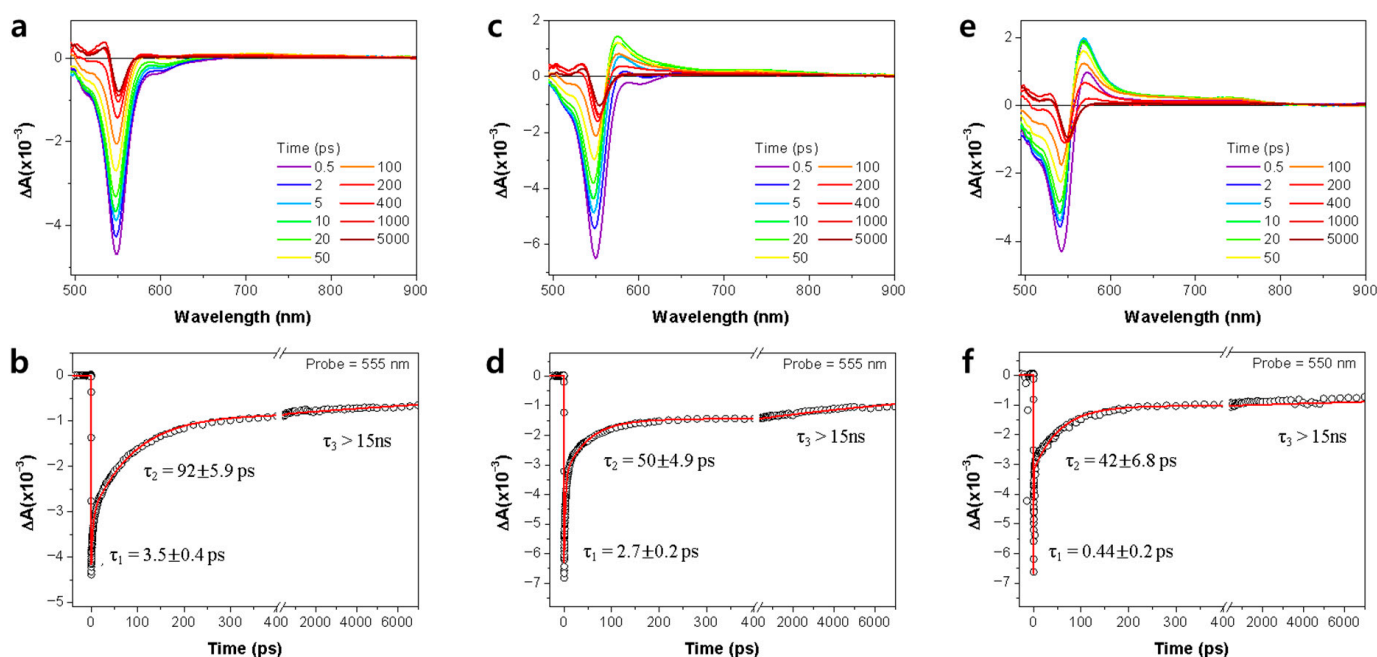


Figure 5. Femtosecond transient absorption spectra and decay profiles of **BI-Per** in (a,b) MCH/toluene (7:3) mixture, (c,d) toluene, and (e,f) DCM with a photoexcitation at 540 nm.

2.4. Electronic Structure Analyses

To gain a more precise understanding of the π -electronic structures of these compounds, TD-DFT calculations were performed with the CAM-B3LYP functional and def2-TZV basis set [42,43]. Consistent with the experimental observations, the calculations also reproduced the distinct behavior of **BI-Ant** and **BI-Pyr** relative to **BI-Per** (Figures 6 and S8–S10). For **BI-Ant** and **BI-Pyr**, both the HOMO and LUMO are primarily distributed over the BODIPY unit, and their lowest-energy electronic transitions are

mainly dominated by the HOMO-to-LUMO excitation (Figures S11 and S12), whereas the HOMO-1-to-LUMO excitations, which correspond to CT character, are estimated to be the second-lowest electronic transitions. These results are in good agreement with their fs-TA spectra in toluene, which are predominantly characterized by spectral evolution associated with the decay of the BODIPY-centered lowest singlet excited state and the subsequent formation of the triplet excited state (Figure 7a).

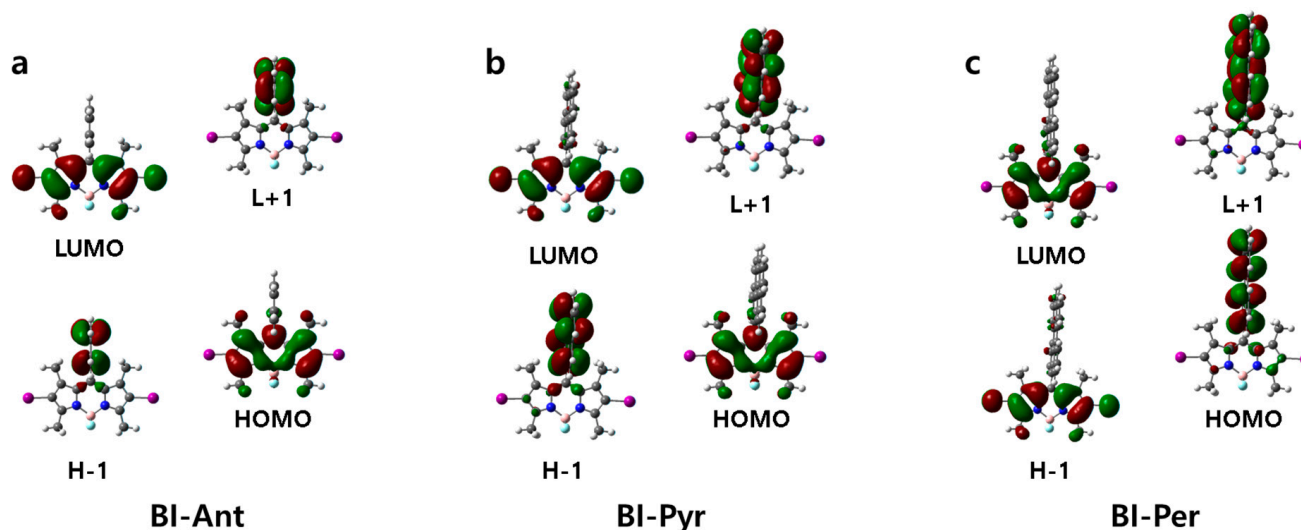


Figure 6. Frontier molecular orbitals of (a) BI-Ant, (b) BI-Pyr, and (c) BI-Per. The electron density is represented by red and green surfaces.

By contrast, in **BI-Per**, the HOMO and LUMO are predominantly localized on the perylene and BODIPY units, respectively. Although its lowest-energy transition appears at a similar wavelength to **BI-Ant** and **BI-Pyr**, it contains two major contributions, HOMO-to-LUMO and HOMO-1-to-LUMO transitions (Figure S13). Here, the HOMO-to-LUMO transition corresponds to electron-density transfer from the perylene unit to the BODIPY core, which clearly indicates its pronounced CT character. These computational results consistently explain both the polarity-dependent changes in its fluorescence measurements and the additional transient spectral evolution observed in the TA spectra (Figure 7b). Therefore, this well-defined CT character enhances SOCT-ISC and causes **BI-Per** to exhibit the most efficient ISC among the three systems.

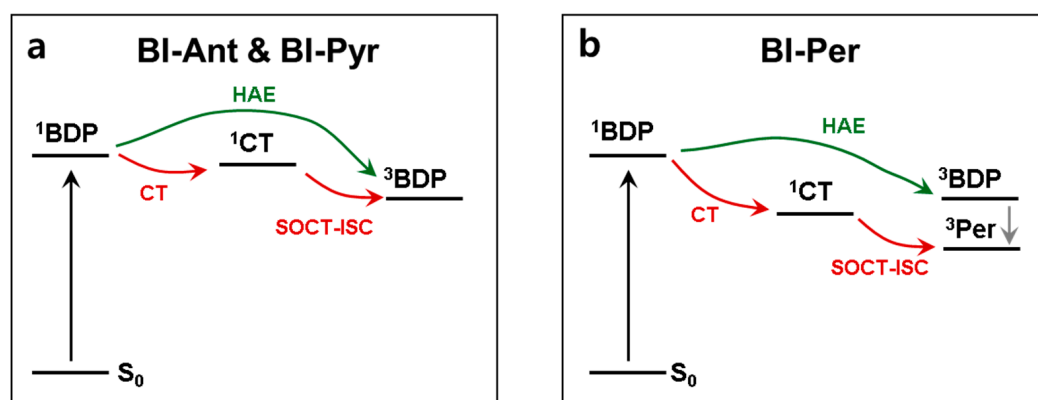


Figure 7. Jablonski diagram illustrating plausible photophysical pathways in (a) **BI-Ant** and **BI-Pyr** and (b) **BI-Per**. BDP and HAE denote BODIPY and the heavy-atom effect, respectively.

3. Materials and Methods

3.1. Sample Preparation

BI-Ant, **BI-Pyr**, and **BI-Per** were synthesized and characterized according to previously reported procedures [25].

3.2. UV-Vis Absorption, Fluorescence Emission, and $^1\text{O}_2$ Quantum Yield Measurements

Methylcyclohexane, toluene, and dichloromethane were purchased from Sigma-Aldrich. UV-vis absorption spectra were obtained with a UV-VIS spectrometer (V730, Jasco, Tokyo, Japan). Fluorescence emission spectra were measured with a UV-vis-NIR fluorometer (Fluoromax, Horiba, Kyoto, Japan). $^1\text{O}_2$ quantum yields were directly measured in toluene- d_8 via NIR $^1\text{O}_2$ emissions centered at 1270 nm with a reference dye, 2,6-Diiodo-1,3,5,7-tetramethyl-8-phenyl-BODIPY ($\Phi_\Delta = 0.83$ in toluene) [32]. All measurements were carried out using a 1 cm pathlength cuvette at concentrations of a few micromolars under room temperature.

3.3. Time-Resolved Spectroscopies

Photoluminescence decay was measured using a time-correlated single photon counting (TCSPC) system with a 1 cm pathlength cuvette at concentrations of a few micromolars under room temperature. A femtosecond oscillator with 1030 nm output (FLINT, Light Conversion, Vilnius, Lithuania) was used as an excitation light source, providing an ultrashort pulse with a high repetition rate (11 MHz), which was doubled with a second harmonic generator (Hiro, Light Conversion, Vilnius, Lithuania) (NFEC-2025-03-304293). Fluorescence was collected using a Picoquant TCSPC module (Picoquant, Berlin, Germany) (NFEC-2025-04-305380). To ensure measurement reliability, the experiment was performed in duplicate.

Femtosecond transient absorption (fs-TA) measurements (NFEC-2025-04-305649) were performed using a HARPIA-TA (Light Conversion) driven by a Yb:KGW laser system (Pharos, Light Conversion). The laser system provided 200 fs, 400 μJ pulses at 1030 nm with a 50 kHz repetition rate. The output beam was split into two parts; 90% of the output beam was seeded to an optical parametric amplifier (Orpheus, Light Conversion) to generate a pump pulse, and 10% of the output beam was seeded to a sapphire crystal to generate a white-light continuum (WLC) probe beam covering the spectral range from 490 nm to 910 nm. Following WLC generation, both the pump and probe beams were overlapped on the sample. After interacting with the sample, the pump beam was blocked by an iris aperture, and the transmitted probe beam was detected using a spectrograph (Kymera 193i, Andor, Belfast, United Kingdom). The TA signal was obtained by calculating the differential transmission ($\Delta T/T$) of the probe beam as a function of pump–probe delay and each data point was averaged 1500 times. All measurements were performed at room temperature using a 1 mm pathlength cuvette at concentrations in the tens of micromolar range. To ensure measurement reliability, the experiment was performed in duplicate.

The nanosecond transient absorption (ns-TA) data were measured with the commercial spectrometer (EOS, Ultrafast Systems, Sarasota, FL, USA), where each data point was averaged over 500 times. All measurements were performed at room temperature using a 1 mm pathlength cuvette at concentrations in the tens of micromolar range. To ensure measurement reliability, the experiment was performed in duplicate.

After every time-resolved measurement, the steady-state absorption was carefully checked to confirm no degradation of samples (Z-202312061408 at the Research Support Center for Bio-Bigdata Analysis and Utilization of Biological Resources).

3.4. Computational Methods

Quantum mechanical calculations were performed with the Gaussian 16 program suite (Gaussian, Wallingford, CT, USA). All calculations were carried out using the density functional theory (DFT) method with cam-B3LYP, employing the def2tzv basis set. To simulate the ground-state absorption spectra, we used TDDFT calculations with the same functional and basis set as used in the geometry optimization.

4. Conclusions

In summary, we demonstrated that iodine-substituted BODIPY photosensitizers bearing orthogonally arranged arene donors can achieve highly efficient triplet formation through the cooperative action of the heavy-atom effect and SOCT-ISC. **BI-Ant**, **BI-Pyr**, and **BI-Per** showed clear evidence of CT character, efficient singlet oxygen generation, and long-lived triplet populations. Time-resolved spectroscopic analyses revealed that **BI-Ant** and **BI-Pyr** mainly undergo BODIPY-centered ISC, whereas **BI-Per** exhibits a distinct intermediate strong CT state evolution and perylene-localized triplet formation, which leads to the fastest ISC in the series. The solvent-polarity dependence of the TA behavior further established that stabilization of the CT state enhances SOCT and accelerates the ISC process, indicating that the excited-state dynamics of these systems are not governed solely by iodine-induced spin–orbit coupling. Electronic structure calculations consistently supported the experimental observations and explained the especially strong CT character and superior ISC efficiency of **BI-Per**. Collectively, this work shows that integrating non-metal heavy-atom substitution with tailored donor–acceptor interactions is a powerful molecular design principle for overcoming the intrinsic fluorescence-dominated nature of BODIPY. More generally, our results suggest that metal-free triplet photosensitizers can be developed more efficiently by designing molecules that combine non-metal heavy-atom substitution with charge-transfer character arising from an orthogonal donor-acceptor geometry, which thereby enables the heavy-atom effect and SOCT to operate cooperatively and effectively accelerate ISC.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/app16094453/s1>: Figure S1: Optimized structures of (a) **BI-Ant**, (b) **BI-Pyr**, and (c) **BI-Per** in the side view. Figure S2: Singlet oxygen emission spectra of **BI-Ant** in (a) MCH/toluene (7:3) mixture, (b) toluene, and (c) DCM upon photoexcitation at 540 nm. Figure S3: Singlet oxygen emission spectra of **BI-Pyr** in (a) MCH/toluene (7:3) mixture, (b) toluene, and (c) DCM upon photoexcitation at 540 nm. Figure S4: Singlet oxygen emission spectra of **BI-Per** in (a) MCH/toluene (7:3) mixture, (b) toluene, and (c) DCM upon photoexcitation at 540 nm. Figure S5: Nanosecond transient absorption spectra of (a) **BI-Ant**, (b) **BI-Pyr**, and (c) **BI-Per** in toluene with a photoexcitation at 540 nm. Figure S6: Femtosecond transient absorption spectra and decay profiles of **BI-Ant** in (a,b) MCH/toluene (7:3) mixture, (c,d) toluene, and (e,f) DCM upon photoexcitation at 540 nm. Figure S7: Femtosecond transient absorption spectra and decay profiles of **BI-Pyr** in (a,b) MCH/toluene (7:3) mixture, (c,d) toluene, and (e,f) DCM upon photoexcitation at 540 nm. Figure S8: FMO diagram of **BI-Ant**. Figure S9: FMO diagram of **BI-Pyr**. Figure S10: FMO diagram of **BI-Per**. Figure S11: Calculated electronic transitions of **BI-Ant**. Figure S12: Calculated electronic transitions of **BI-Pyr**. Figure S13: Calculated electronic transitions of **BI-Per**; Table S1: $^1\text{O}_2$ quantum yields and ISC time constants; Cartesian coordinates of optimized structures of **BI-Ant**, **BI-Pyr**, and **BI-Per**.

Author Contributions: Conceptualization, J.O., T.H.K. and J.Y.; investigation, analyses and methodology, Y.N., K.M.L. and J.J.; writing—original draft preparation, Y.N. and J.O.; writing—review and editing, J.O., T.H.K. and J.Y. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available in article and Supplementary Materials.

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