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Letter

Outsourcing Intersystem Crossing without Heavy Atoms: Energy Transfer Dynamics in PyridoneBODIPY–C_{60} Complexes

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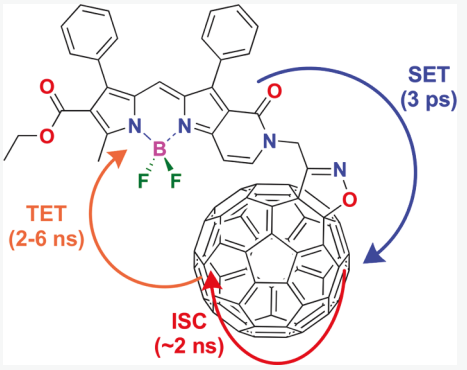
ABSTRACT: The excited state dynamics in two fully characterized pyridoneBODIPY–fullerene complexes were investigated using time-resolved spectroscopy. Photoexcitation was initially localized on the pyridoneBODIPY chromophore. The energy was rapidly transferred to the fullerene, which subsequently underwent ISC to form a triplet state and returned the energy to the pyridoneBODIPY via triplet–triplet energy transfer. This ping-pong energy transfer mechanism resulted in efficient (>85%) overall conversion of the excited state pyridoneBODIPY constituent despite a complete lack of ISC in the pyridoneBODIPY in the absence of the fullerene partner. The small difference in attachment chemistry for the fullerene did not impact the initial singlet energy transfer. However, the *N*-methylpyrrolidine bridge did slow both the triplet–triplet energy transfer and the ultimate relaxation rate of the final triplet state when compared to an isoxazole-based bridge. The rates of each step were quantified, and computational predictions were used to complement the proposed mechanism and energetics. The result demonstrated efficient triplet sensitization of a strong chromophore that lacks significant spin–orbit coupling.



Triplet photosensitizers combine strong light absorption that creates an excited singlet state and a mechanism for subsequent conversion to a triplet state that outcompetes other relaxation pathways. A common approach is to combine the two in a strong chromophore that incorporates a heavy atom to increase spin–orbit coupling (SOC) and enhance intersystem crossing (ISC). This approach can be very effective. However, structurally collocating the chromophore and SOC can limit design flexibility and the lifetime of the triplet state given that enhancing the SOC will also add to the rate of triplet to ground state relaxation. Outsourcing the ISC process to an adjacent molecular constituent has the potential to efficiently create a long-lived triplet state in a chromophore that lacks competitive ISC. The chromophore is relieved of any requirement for significant SOC, and the requirements for the absorption characteristics of the ISC constituent are relaxed. The process of triplet state formation on the chromophore involves two energy transfer steps. The excited singlet state of the chromophore transfers its energy to a partner that undergoes ISC and then returns the energy via triplet–triplet energy transfer. This has been termed a ping-pong mechanism.[1]

The dynamics of ping-pong energy transfer in inorganic complexes that use heavy atoms to promote ISC have been reported previously.[2−7] Fullerenes have been demonstrated as an efficient alternative to the heavy-atom effect for ISC. In a few reported complexes the final state of the system is the triplet localized on the chromophore with evidence for a ping-pong mechanism.[1,8−10] In this work, we investigated the energy transfer dynamics in two pyridoneBODIPY–C_{60} complexes (BODIPY is boron dipyrromethene). PyridoneBODIPYs are electron-deficient BODIPY platforms that have their first reduction potentials close to that of C_{60}.[11−13] To a large extent this precludes traditional photoinduced electron transfer with the formation of the $BODIPY^{+}$–C_{60}^{-} charge-separated state. Relatively low light absorption by the fullerene left the pump–probe signals dominated by the excited state dynamics of the pyridoneBODIPY chromophore, abbreviated PBDP. This facilitated direct probing of the singlet energy transfer to the fullerene, triplet energy return from the fullerene to PBDP, and the lifetime of the final PBDP triplet state. The two BODIPYs differ slightly in fullerene functionalization. Although this does not impact the initial singlet energy transfer rate, it does influence the rate of triplet energy transfer and the ultimate triplet lifetime. These dyads provide a detailed example of the dynamics involved when you outsource the ISC process from a chromophore to a bound fullerene and return the triplet with high efficiency.

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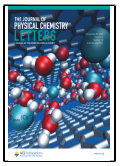

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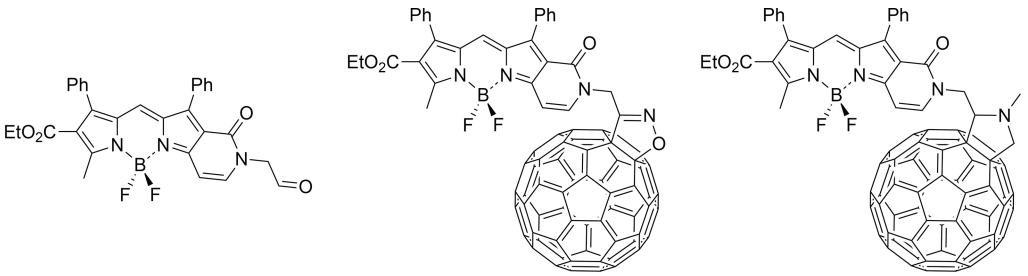

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Figure 1. Molecular structures and labels.

Figure 1 presents the structures of the PBDP reference, **3**, and the two dyads with the C_{60} bound to the pyridone via a CH_2 bridge and an isoxazole, **5**, and the *N*-methylpyrrolidine functionalization, **6**. Synthesis and characterization details are provided in the Supporting Information. The structures are numbered to remain consistent with the synthesis shown in Scheme S1. The absorption spectrum for each of the compounds, and the *N*-methylpyrrolidine C_{60} for comparison, is presented in Figure S16 and reproduced as the inverted dashed lines in Figure 2. We assign the excitation band at 575 nm to the strong $\pi \rightarrow \pi^*$ transitions delocalized over the PBDP as predicted by TD-DFT calculations (see the Supporting Information). The energy of this band was very similar for **3**, **5**, and **6**, which reflected the lack of the conjugation between the PBDP and C_{60} fragments. For comparison, the extinction coefficient for *N*-methylfulleropyrrolidine is less than 2% of that for **3** at 575 nm. Emission from the reference compound, **3**, was strong, and the emission spectrum is presented inverted with the dash-dotted line in the top panel of Figure 2. Addition of the fullerene was very effective at quenching the emission in **5** and **6**, leaving <1% of the emission from **3**.

Pump−broadband probe spectra pumped near the maximum of the PBDP absorption at 575 nm for **3**, **5**, and **6** dissolved in dichloromethane (DCM) are presented in Figure 2. Experimental details are available in the Supporting Information. The change in optical density (ΔOD) is a combination of the ground state bleach (GSB, negative ΔOD), stimulated emission (SE, negative ΔOD), and excited state absorption (ESA, positive ΔOD). The GSB mirrors the ground state absorption spectrum, and the SE mirrors the emission spectrum. Compound **3** is dominated by the GSB and SE between 520 and 700 nm, with ESA at shorter and longer wavelengths. The ΔOD spectrum appeared within the instrument time response and decayed exponentially in time with only small changes in spectral shape at early delay times. This is similar to pump−probe signals for other BODIPY derivatives following excitation to the first excited singlet state and subsequent relaxation to the ground state. The signals persisted beyond the maximum delay time of 3.5 ns.

Addition of the fullerene dramatically changed the measured dynamics. At the shortest time delays, for example, at 0.5 ps, the ΔOD spectra for **5** and **6** were very similar to that for **3**. This indicated that the initial excitation was analogous to that in **3**—excitation to an excited singlet state localized on the PBDP chromophore. However, in the case of **5** and **6** there was a much faster decay of the initial signals with a minimization of the entire ΔOD spectrum in ∼100 ps. This was followed by recovery of the signals dominated by the GSB, but without the SE and ESA at longer wavelengths and with an enhancement of the ESA at wavelengths shorter than 510 nm. The signals appeared to be continuing to increase beyond the maximum delay time measured of 3.5 ns. At long delay times the ΔOD spectra were consistent with the excited triplet state of the PBDP.[2,3,14,15]

To quantify the time constants associated with the observed dynamics, ΔOD at individual wavelengths were fitted as a function of time to a series of first-order events (see the Supporting Information for details). The resulting time constants are presented in Table 1. Figure 3 presents the ESA signals measured at 470 nm with an instrument response of 0.4 ns extending to a delay time of 2.5 μs. The data for reference compound **3** were well fitted by a single first-order decay with a time constant of $\tau_{lifetime}$ = 4.54 ± 0.04 ns. This excited state lifetime is similar to those reported for other BODIPY-based chromophores. Addition of the fullerene significantly changed the dynamics. For **5** and **6** there was an initial instrument limited rise followed by sub-10 ns rise, τ_{TER} in Table 1, and subsequent decay on a microsecond time scale, $\tau_{lifetime}$ in Table 1. There was ESA from both the singlet and triplet states of the PBDP 470 nm, with an increase in the absorption cross section for the triplet. Figure S26 presents the dynamics at 470 nm within the first 2 ns. The ESA decayed in the first few picoseconds with loss of the initially excited singlet state and then increased after 100 ps. The rise with τ_{TER} in Figure 3 was assigned to triplet energy return to the PBDP, and this assignment was corroborated by analysis of the GSB given below. The final decay was assigned to the lifetime of the PBDP triplet state, $\tau_{lifetime}$.

The changes in optical density at 640 and 540 nm, presented in Figure 4, were assigned to PBDP SE and GSB, respectively. The SE was used to measure loss of the initially excited singlet state, and the GSB measured loss and recovery of the ground state. The data for **3** were well fitted with a first-order decay using the previously determined time constant of $\tau_{lifetime}$ = 4.54 ns. The SE had a small initial increase that was assigned to excited state relaxation. The SE data for **5** and **6** were well fitted by two sequential first-order steps with the time constants $\tau_{SET,1}$ and $\tau_{SET,2}$ reported in Table 1. The time constants were similar in both cases with $\tau_{SET,1}$ = 300 fs and $\tau_{SET,2}$ a little over 3 ps. The first 30 ps of the GSB was well fitted using the same two time constants determined for the SE, shown with the solid lines on the bottom left of Figure 4. In contrast to the signals at 640 nm, the GSB signal started to recover at time delays longer than 50 ps. This recovery was well fitted using the time constants determined for the rise in ESA in Figure 3, τ_{TER} in Table 1, as shown by the solid lines in the bottom right of Figure 4.

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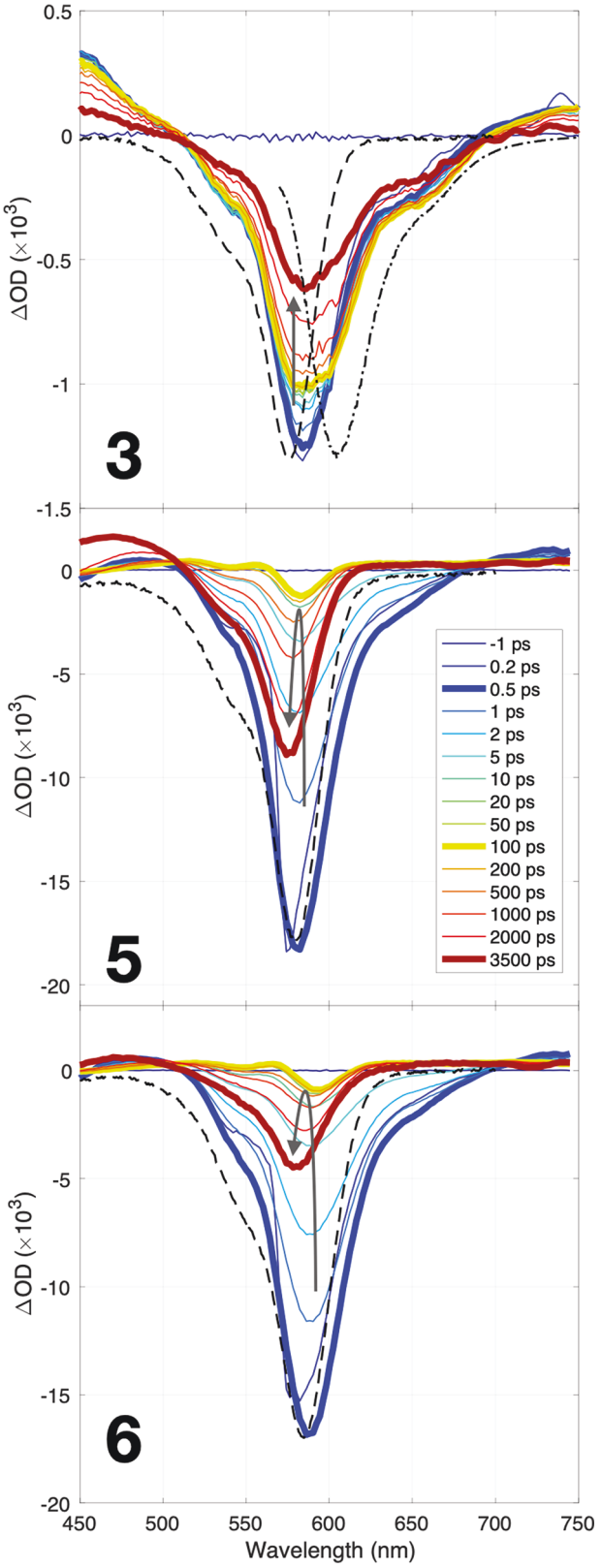

Figure 2. Pump−probe transient changes in optical density pumped at 575 nm for the structures in Figure 1 dissolved in DCM. The dashed lines are the absorption spectra inverted and scaled, and the dash-dotted line is the fluorescence spectrum inverted and scaled for reference.

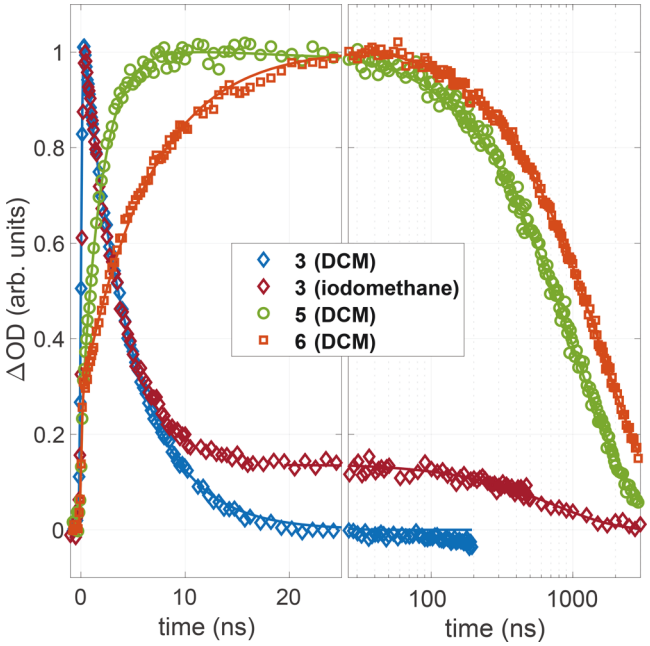

Figure 3. Pump−probe measurements on the structures in Figure 1 dissolved in the solvent indicated, pumped at 575 nm and probed at 470 nm ESA.

The correlated loss of the SE and GSB in the first 30 ps confirmed deactivation of the initial PBDP singlet to the ground state. Subsequent recovery of the GSB in the absence of correlated recovery of SE indicated the subsequent return of the PBDP to a state other than the ground state or the initial singlet excited state. We assigned the final state to the PBDP triplet based on the ΔOD spectra at long delay times (Figure 2). We cannot conclusively rule out the formation of an intermediate charge transfer state; however, there is no evidence for the PBDP cation radical or C_{60} anion radical in the ΔOD spectra. We concluded that the overall process was singlet energy transfer to the fullerene followed by ISC on the fullerene and triplet energy transfer back to the PBDP. This is illustrated in Figure 5.

The initial singlet energy transfer was fitted as a sequence of two first-order events. The two time constants were assigned to transfer from an initially prerelaxed excited state and transfer from the relaxed excited state. The time constant for the transfer from relaxed excited state is consistent with inductive (Förster) energy transfer[16−19] (see the Supporting Information for details). The time constant for triplet energy return to the PBDP was 1.8 ns for **5** and 6.7 ns for **6**. These are similar to the reported time constants for ISC in functionalized C_{60} of 1−2 ns.[20,21] For **5** we were not able to separate the rate of ISC from the rate of triplet energy transfer to the PBDP; however, the measured transfer rate places an upper limit on the time constant. In the case of **6**, 6.7 ns was slower than the reported time constant of 1.26 ns for ISC in the *N*-methylfulleropyrrolidine and thus reflected the subsequent return energy transfer step. A few nanoseconds is consistent with the slower Dexter-type mechanism for triplet energy transfer.[22,23] However, the reason for slower triplet energy transfer in **6** compared to **5** is not completely clear. The computational predictions do not indicate a notable difference in the donor−acceptor orbital overlap between the two complexes. The difference in rates may point to some measure of enhanced

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Table 1. First-Order Time Constants[a]

compound	solvent	$\tau_{SET,1}$ (ps)	$\tau_{SET,2}$ (ps)	τ_{TER} (ns)	$\tau_{lifetime}$ (ns)
3	CH_2Cl_2				4.54 ± 0.04
3	CH_3I				751 ± 32
5	CH_2Cl_2	0.298 ± 0.005	3.20 ± 0.05	1.83 ± 0.06	1008 ± 15
6	CH_2Cl_2	0.31 ± 0.01	3.42 ± 0.05	6.68 ± 0.07	1660 ± 27

[a]SET is singlet energy transfer, PBDP → C_{60}.TER is triplet energy return, C_{60} → PBDP.

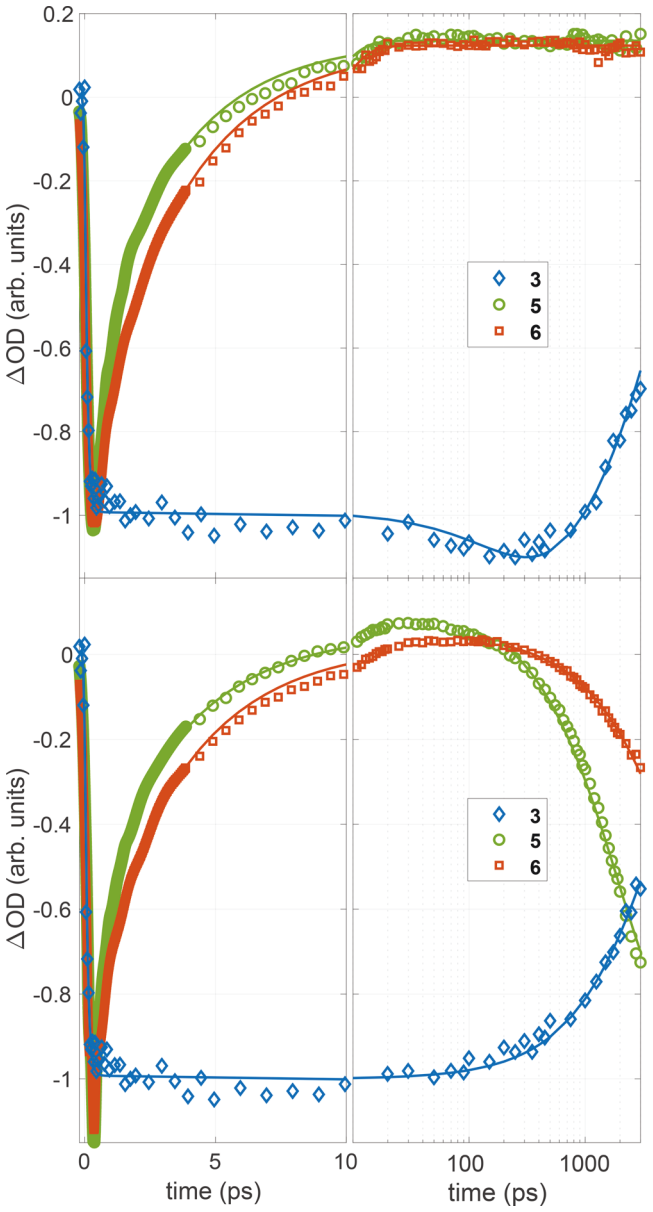

Figure 4. Pump−probe measurements on the structures in Figure 1 dissolved in DCM and pumped at 575 nm: (top) SE probed at 640 nm; (bottom) GSB probed at 540 nm.

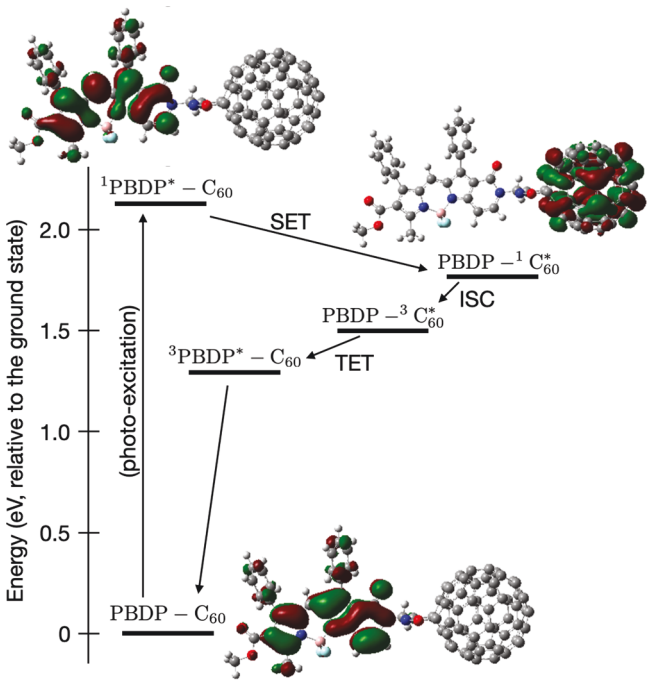

Figure 5. Relative energies and DFT orbital predictions for the singlet states for **5**. SET is singlet energy transfer, ISC is intersystem crossing, and TET is triplet energy transfer. Energy estimates are based on a combination of measurements and computation. The energetics for **6** are very similar; see the Supporting Information for details.

through-bond coupling in the case of the additional conjugation provided by the isoxazole linkage. Greater coupling in **5** could contribute to the shorter PBDP triplet lifetime in **5** compared to that in **6**. In addition, the TD-DFT calculations predict a smaller energy gap between the triplet localized on the C_{60} and on the PBDP for **5** (0.77 eV) compared to that for **6** (0.87 eV) (see Figure S20). The smaller energy gap may also contribute to the faster energy transfer in **5**.

For a comparison to directly inducing SOC and ISC in the PBDP chromophore rather than outsourcing it to the fullerene, transient absorption of **3** in iodomethane was measured and is presented in Figure 3. Compared to the measurement in DCM, a new longer lived state appeared with a lifetime of 750 ns (see Table 1). Accounting for the increase in the absorption coefficient at 470 nm upon going from singlet to triplet, less than 10% of the initially excited molecules underwent ISC to the triplet state. At the same time, the triplet lifetime for the PBDP in iodomethane was shorter than in the cases of **5** and **6**. There was very little SOC in the PBDP chromophore alone. DFT calculations predicted values of <0.6 cm^{-1} between the S1 and T1 states and between the S0 and T1 states (see the Supporting Information for details). In the case of using the heavy atom effect via the iodomethane to induce SOC in PBDP, SOC that was not strong enough to convert more than 10% of the excited singlets states to triplet states was still sufficient to enhance the rate of subsequent ISC mediated relaxation to the ground state. This illustrated the trade-offs that come with increasing SOC in a chromophore to access triplet states while simultaneously increasing the SOC that accelerates relaxation back to the ground singlet state. By

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locating the ISC on the adjacent moiety rather than the chromophore, SOC in the PBDP remains minimized, and the triplet state lifetime was extended.

The overall efficiency of triplet sensitization in **5** and **6** was estimated based on the individual rates. With the initial singlet energy transfer more than 3 orders of magnitude faster than the singlet lifetime of **3**, the first step proceeded with >99% efficiency. ISC in modified fullerenes was reported as >90%, and the triplet energy transfer step is about 30 times faster than lifetimes reported for the triplet state of functionalized fullerenes. This provides a lower bound of 85% of photoexcited PBDP chromophores converted to their triplet state. Although the ultimate triplet lifetimes were not particularly long compared to other BODIPY-based chromophores, the lifetimes were longer than the triplets on the same chromophore that were induced by the heavy atom effect in iodomethane solvent. These systems provided access to the details of outsourcing ISC to a fullerene, and the results demonstrated the ability to use this approach to efficiently access triplet states in chromophores that lack a competitive ISC mechanism.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c02388.

Experimental details, synthesis, characterization, DFT and TD-DFT calculations, pump−probe data and fits (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Schueppel, R.; Uhrich, C.; Pfeiffer, M.; Leo, K.; Brier, E.; Reinold, E.; Baeuerle, P. Enhanced Photogeneration of Triplet Excitons in an Oligothiophene−Fullerene Blend. *ChemPhysChem* **2007**, *8*, 1497−1503.

(2) Whited, M. T.; Djurovich, P. I.; Roberts, S. T.; Durrell, A. C.; Schlenker, C. W.; Bradforth, S. E.; Thompson, M. E. Singlet and Triplet Excitation Management in a Bichromophoric Near-Infrared-Phosphorescent BODIPY-Benzoporphyrin Platinum Complex. *J. Am. Chem. Soc.* **2011**, *133*, 88−96.

(3) Lazarides, T.; McCormick, T. M.; Wilson, K. C.; Lee, S.; Mccamant, D. W.; Eisenberg, R. Sensitizing the Sensitizer: The Synthesis and Photophysical Study of Bodipy-Pt(II)(diimine)(dithiolate) Conjugates. *J. Am. Chem. Soc.* **2011**, *133*, 350−364.

(4) Sabatini, R. P.; Zheng, B.; Fu, W.-F.; Mark, D. J.; Mark, M. F.; Hillenbrand, E. A.; Eisenberg, R.; McCamant, D. W. Deactivating Unproductive Pathways in Multichromophoric Sensitizers. *J. Phys. Chem. A* **2014**, *118*, 10663−10672.

(5) Tyson, D. S.; Luman, C. R.; Zhou, X.; Castellano, F. N. New Ru(II) Chromophores with Extended Excited-State Lifetimes. *Inorg. Chem.* **2001**, *40*, 4063−4071.

(6) Yarnell, J. E.; Deaton, J. C.; McCusker, C. E.; Castellano, F. N. Bidirectional "Ping-Pong" Energy Transfer and 3000-Fold Lifetime Enhancement in a Re(I) Charge Transfer Complex. *Inorg. Chem.* **2011**, *50*, 7820−7830.

(7) Jin, Z.; Qi, S.; Guo, X.; Tian, N.; Hou, Y.; Li, C.; Wang, X.; Zhou, Q. Smart use of "ping-pong" energy transfer to improve the two-photon photodynamic activity of an Ir complex. *Chem. Commun.* **2020**, *56*, 2845−2848.

(8) Ziessel, R.; Allen, B.; Rewinska, D.; Harriman, A. Selective Triplet-State Formation during Charge Recombination in a Fullerene/Bodipy Molecular Dyad (Bodipy = Borondipyrromethene). *Chem.—Eur. J.* **2009**, *15*, 7382−7393.

(9) Liu, Y.; Zhao, J. Visible light-harvesting perylenebisimide−fullerene (C60) dyads with bidirectional "ping-pong" energy transfer as triplet photosensitizers for photooxidation of 1,5-dihydroxynaphthalene. *Chem. Commun.* **2012**, *48*, 3751.

(10) Guo, S.; Sun, J.; Ma, L.; You, W.; Yang, P.; Zhao, J. Visible light-harvesting naphthalenediimide (NDI)-C60 dyads as heavy-atom-free organic triplet photosensitizers for triplet−triplet annihilation based upconversion. *Dyes Pigm.* **2013**, *96*, 449−458.

(11) Didukh, N. O.; Yakubovskyi, V. P.; Zatsikha, Y. V.; Rohde, G. T.; Nemykin, V. N.; Kovtun, Y. P. Flexible BODIPY Platform That Offers an Unexpected Regioselective Heterocyclization Reaction toward Preparation of 2-Pyridone[*a*]-Fused BODIPYs. *J. Org. Chem.* **2019**, *84*, 2133−2147.

(12) Zatsikha, Y. V.; Didukh, N. O.; Blesener, T.; Kayser, M. P.; Kovtun, Y. P.; Blank, D. A.; Nemykin, V. N. Preparation, Characterization, Redox, and Photoinduced Electron-Transfer Properties of the NIR-Absorbing *N* -Ferrocenyl-2-pyridone BODIPYs. *Eur. J. Inorg. Chem.* **2017**, *2017*, 318−324.

(13) Zatsikha, Y. V.; Swedin, R. K.; Healy, A. T.; Goff, P. C.; Didukh, N. O.; Blesener, T. S.; Kayser, M.; Kovtun, Y. P.; Blank, D. A.; Nemykin, V. N. Synthesis, Characterization, and Electron-Transfer Properties of Ferrocene−BODIPY−Fullerene Near-Infrared-Absorbing Triads: Are Catecholopyrrolidine-Linked Fullerenes a Good Architecture to Facilitate Electron-Transfer? *Chem.—Eur. J.* **2019**, *25*, 8401−8414.

(14) Sabatini, R. P.; McCormick, T. M.; Lazarides, T.; Wilson, K. C.; Eisenberg, R.; Mccamant, D. W. Intersystem Crossing in Halogenated Bodipy Chromophores Used for Solar Hydrogen Production. *J. Phys. Chem. Lett.* **2011**, *2*, 223−227.

(15) Lee, Y.; Malamakal, R. M.; Chenoweth, D. M.; Anna, J. M. Halogen Bonding Facilitates Intersystem Crossing in Iodo-BODIPY Chromophores. *J. Phys. Chem. Lett.* **2020**, *11*, 877−884.
(16) Förster, T. Experimentelle und theoretische Untersuchung des zwischenmolecularen Uebergangs von Electronenanregungsenergie. *Z. Naturforsch.* **1949**, *4a*, 321−327.
(17) Scholes, G. D. Long-range resonance energy transfer in molecular systems. *Annu. Rev. Phys. Chem.* **2003**, *54*, 57−87.
(18) Forster, T. Transfer Mechanisms of Electronic Excitation Energy. *Radiat. Res. Supp.* **1960**, *2*, 326−339.
(19) Förster, T. Zwischenmolekulare Energiewanderung und Fluoreszenz. *Ann. Phys. (Berlin, Ger.)* **1948**, *437*, 55−75.
(20) Guldi, D. M.; Prato, M. Excited-state properties of C60 fullerene derivatives. *Acc. Chem. Res.* **2000**, *33*, 695−703.
(21) Guldi, D. M.; Asmus, K.-D. Photophysical Properties of Mono- and Multiply-Functionalized Fullerene Derivatives. *J. Phys. Chem. A* **1997**, *101*, 1472−1481.
(22) Dexter, D. L. A. Theory of Sensitized Luminescence in Solids. *J. Chem. Phys.* **1953**, *21*, 836.
(23) Olaya-Castro, A.; Scholes, G. D. Energy transfer from Forster-Dexter theory to quantum coherent light-harvesting. *Int. Rev. Phys. Chem.* **2011**, *30*, 49−77.

https://doi.org/10.1021/acs.jpclett.2c02388
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