Homo- or Hetero- Triplet-Triplet Annihilation? A Case Study with Perylene-Bodipy Dyads/Triads

Xiaoneng Cui, Ahmed M. El-Zohry, Zhijia Wang, Jianzhang Zhao, and Omar F. Mohammed

J. Phys. Chem. C, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.7b05620 • Publication Date (Web): 06 Jul 2017

Downloaded from <http://pubs.acs.org> on July 12, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

Homo- or Hetero- Triplet-Triplet Annihilation? A Case Study with Perylene-Bodipy Dyads/Triads

Xiaoneng Cui,^{a¶} Ahmed M. El-Zohry,^{b¶} Zhijia Wang,^a Jianzhang Zhao ^{a} and Omar F.*

Mohammed ^{b}*

^a State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, E-208 West Campus, 2 Ling Gong Rd., Dalian 116024, P. R. China.

E-mail: zhaojzh@dlut.edu.cn

^b Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia.

E-mail: omar.abdelsaboor@kaust.edu.sa

¶ These authors contribute equally to this work.

Abstract: The photophysical processes of intramolecular ‘ping-pong’ energy transfers in the iodinated reference dyad **BDP-I₂-Py**, as well as the uniodinated dyad **BDP-Py** and triad **BDP-2Py**, were studied. For **BDP-I₂-Py**, a forward Förster resonance energy transfer (FRET) from the perylene (Py) unit to the diiodoBDP unit ($\tau = 7$ ps) and a backward triplet energy transfer (TTET, $\tau = 3$ ns) from the diiodoBDP unit to the Py unit were observed. For the **BDP-Py** and **BDP-2Py** systems, a FRET ($\tau = 5 \sim 8$ ps) and a photo-induced electron transfer (PET) ($\tau = 1 - 1.5$ ns) were observed in acetonitrile. The uniodinated dyad and triad were used as the triplet energy acceptor and emitter for a TTA upconversion with palladium tetraphenyltetrabenzoporphyrin as the triplet photosensitizer. A maximum upconversion quantum yield of 12.6 % was measured. Given that the dyad (**BDP-Py**) contains one BDP unit and one Py unit, while the triad (**BDP-2Py**) contains two Py units and one BDP unit, and based on the results from steady-state femtosecond and nanosecond transient optical spectroscopies, it is concluded that neither intramolecular *homo*-triplet-triplet annihilation (TTA) nor intramolecular *hetero*-TTA is possible during a TTA upconversion for those upconversion systems.

1. INTRODUCTION

Triplet-triplet annihilation (TTA) upconversion has attracted much attention due to its advantages of the strong absorption of excitation energy, low energy requirement, non-coherent excitation light and the high upconversion efficiency.¹⁻¹⁰ In a *supramolecular* upconversion scheme, a triplet photosensitizer is used to harvest excitation light energy, produce a triplet excited state, and then act as an energy donor for the crucial intermolecular triplet-triplet energy transfer (TTET).¹⁻⁶ A triplet energy acceptor is responsible for the TTA process and the production of the S₁ state (a 1/9 chance, according to the spin-statistic rule).^{1-6,11-13} The upconversion emits delayed fluorescence after cascade photo-harvesting, a promotion to the S₁

state, intersystem crossing (ISC), TTET and TTA.¹⁻⁶ Usually, the covalently linked triplet photosensitizers and acceptors perform a poor TTA upconversion, due to the backward, undesired singlet energy transfer from the triplet energy donor or emitter to the triplet photosensitizer.^{9,14-17}

Currently, the study of TTA upconversion focuses on the following topics. First, the design of a triplet photosensitizer and an efficient annihilator is still a major challenge.^{1-6,11,13,18-20} There are quite a few requirements for these molecules since the excited state energy levels must match, there must be intersystem crossing and the TTET must be efficient.¹⁻⁴ For a triplet energy acceptor, the fluorescence quantum yield must be high and the excited state energy level must be within the relation $2E_{T1} > E_{S1}$.^{1-6,11,13} In order to perform a TTA upconversion under aerobic conditions and in a solid matrix, TTA upconversion systems with a triplet photosensitizer and a triplet energy acceptor in molecular assemblies and microbeads have been studied.^{8,21-26} On the other hand, the application of TTA upconversion in photovoltaics,²⁷⁻³⁰ photocatalysis,³¹ and luminescence bioimaging is also promising.²⁴

In order to fully explore the potential applications of TTA upconversion, it is crucial to study the fundamental photophysical processes involved. For instance, in molecular assemblies or other rigid matrixes,^{8,25,32} the triplet energy acceptor and emitter are densely packed together. Therefore, the principle governing the TTA process will be interesting. Moreover, using dyads as the triplet acceptor has also been proposed, in order to optimize the energy levels to achieve a high TTET and TTA efficiency.^{11,13} Under these circumstances, is *intramolecular* TTA, whether *homo-* (homo-TTA) or *hetero-* (hetero-TTA) plausible? No study on this subject has been reported.^{11,13}

In a dyad triplet acceptor, two different chromophores simultaneously at the triplet excited state are involved in the TTA process. To unveil the possibility of an intramolecular hetero- or homo-TTA, herein we present a triad **BDP-2Py** as the triplet acceptor for a TTA upconversion (Scheme 1). There are two perylene units and one BDP unit in this molecule. Due to the lower energy level of the S_1 state, the BDP unit will be the triplet energy acceptor and emitter. On the other hand, perylene may act at the triplet energy acceptor for the intermolecular TTET.^{33–36} The questions will be, is there an intramolecular homo-TTA between the two perylene units? Or is there an intramolecular hetero-TTA between the perylene and the BDP units? We unveil the photophysical properties of **BDP-2Py** using steady state and time-resolved transient optical spectroscopies, as well as electrochemical studies. We observe a fast Förster resonance energy transfer (FRET) and intramolecular triplet-triplet energy transfer (TTET) processes, however, the intramolecular TTA is absent.

2. EXPERIMENTAL SECTION

2.1. General Methods. All the chemicals used in the synthesis were of analytical grade purity and used as received. Solvents were dried and distilled before being used for synthesis. Luminescence lifetimes were measured on an OB920 fluorescence/phosphorescence lifetime spectrometer.

2.2. Synthesis. *Compound BDP-Py.* In a 25 mL flask, compound **5** (56.7 mg, 0.15 mmol) and compound **3** (30.7 mg, 0.1 mmol) were dissolved in mixed solvent (10 mL, $\text{CHCl}_3/\text{CH}_3\text{OH}/\text{H}_2\text{O} = 8:1:1$, v/v) under N_2 , then $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (15.0 mg, 0.06 mmol) and L-ascorbic acid sodium salt (23.0 mg, 0.12 mmol) were added. The solution was stirred for 24 h at 25°C . The reaction mixture was diluted with CH_2Cl_2 (100 mL) and the organic phase was dried over Na_2SO_4 , then the solvent was removed under reduced pressure. The residue was purified

using column chromatography (silica gel, CH₂Cl₂/CH₃OH = 200:1, v/v) to produce an orange-red solid (20.0 mg, yield: 29%). ¹H NMR (CDCl₃, 500 MHz) δ 8.25–8.21 (m, 3H), 8.19 (d, 1H, *J* = 5.0 Hz), 7.78–7.73 (m, 3H), 7.55–7.46 (m, 5H), 7.11 (d, 2H, *J* = 10.0 Hz), 7.01 (d, 2H, *J* = 10.0 Hz), 5.95 (s, 2H), 5.87 (s, 2H), 5.19 (s, 2H), 2.51 (s, 6H), 1.30 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 158.7, 155.3, 144.0, 143.0, 141.5, 134.6, 133.2, 132.6, 132.2, 131.7, 130.7, 130.4, 129.2, 128.8, 128.7, 128.4, 127.7, 126.8, 126.7, 126.6, 122.5, 121.1, 121.0, 120.8, 119.5, 115.5, 62.2, 52.8, 29.7, 14.5, 14.4. MALDI-HRMS (TOF): calcd ([C₄₃H₃₄BF₂N₅O]⁺), *m/z* = 685.2824, found, *m/z* = 685.2850.

Compound BDP-I₂-Py. In a 25 mL flask, compound **6** (62.9 mg, 0.1 mmol) and compound **3** (30.7 mg, 0.1 mmol) were dissolved in mixed solvent (10 mL, CHCl₃/CH₃OH/H₂O=8:1:1, v/v) under N₂, then CuSO₄·5H₂O (15.0 mg, 0.06 mmol) and L-ascorbic acid sodium salt (23.0 mg, 0.12 mmol) were added. The solution was stirred for 24 h at 25°C. The reaction mixture was diluted with CH₂Cl₂ (100 mL) and the organic phase was dried over Na₂SO₄, then the solvent was removed under reduced pressure. The residue was purified using column chromatography (silica gel, CH₂Cl₂/CH₃OH = 100:1, v/v) to produce a red solid (22.0 mg, yield: 23%). ¹H NMR (CDCl₃, 400 MHz) δ 8.27–8.18 (m, 4H), 7.80–7.72 (m, 3H), 7.56–7.46 (m, 5H), 7.10 (q, 4H, *J* = 8.0 Hz), 5.96 (s, 2H), 5.19 (s, 2H), 2.62 (s, 6H), 1.36 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 156.9, 148.5, 148.4, 145.4, 140.6, 131.5, 128.1, 121.5, 115.6, 114.4, 85.6, 77.9, 77.8, 76.5, 76.4, 57.1, 56.8, 17.0, 16.0. MALDI-HRMS (TOF): calcd ([C₄₃H₃₂BF₂I₂N₅O]⁺), *m/z* = 937.0758, found, *m/z* = 937.0742.

Compound BDP-2Py. The produced sample is similar to the compound **BDP-Py**. In a 25 mL flask, compound **8** (43.0 mg, 0.1 mmol) and compound **3** (90.0 mg, 0.3 mmol) were dissolved in mixed solvent (10 mL, CHCl₃/CH₃OH/H₂O = 8:1:1, v/v) under N₂, then CuSO₄·5H₂O (30.0 mg,

0.12 mmol) and L-ascorbic acid sodium salt (46.0 mg, 0.24 mmol) were added. The solution was stirred for 24 h at 25°C. The reaction mixture was diluted with CH₂Cl₂ (100 mL) and the organic phase was dried over Na₂SO₄, then the solvent was removed under reduced pressure. The residue was purified using column chromatography (silica gel, CH₂Cl₂/CH₃OH = 100:1, v/v) to produce an orange-red solid (20.0 mg, yield: 19%). ¹H NMR (DMSO-*d*₆, 400 MHz): δ 8.37–8.27 (m, 8H), 8.19 (s, 1H), 8.15 (s, 1H), 8.00 (t, 2H, *J* = 8.0 Hz), 7.82 (d, 4H, *J* = 8.0 Hz), 7.59–7.50 (m, 6H), 7.40–7.35 (m, 2H), 7.18 (d, 1H, *J* = 8.0 Hz), 7.07 (s, 1H), 6.74 (d, 1H, *J* = 8.0 Hz), 6.02 (s, 2H), 5.96 (d, 4H, *J* = 4.0 Hz), 5.16 (d, 4H, *J* = 12.0 Hz), 2.33 (s, 6H), 1.15 (s, 6H). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 154.3, 148.3, 147.9, 142.7, 142.5, 141.6, 134.0, 131.9, 131.8, 131.2, 131.0, 130.8, 130.1, 129.9, 128.2, 128.1, 127.9, 127.5, 127.3, 126.8, 126.6, 124.9, 124.6, 123.1, 121.0, 120.9, 120.8, 120.1, 115.2, 113.5, 61.6, 61.3, 50.8, 50.7, 14.0, 13.6. MALDI-HRMS (TOF): calcd ([C₆₇H₄₉BF₂N₈O₂ + Na]⁺), *m/z* = 1069.3937, found, *m/z* = 1069.3931.

2.3. Electrochemical studies. Cyclic voltammetry was performed with a CHI610D electrochemical workstation (CHI instruments, Inc., Shanghai, China) at scan rate of 100 mV s⁻¹. The electrochemical measurements were performed with 0.1 M Bu₄N[PF₆] as the supporting electrolyte. The working electrode was a glassy carbon electrode, and the counter electrode was a platinum electrode. Ag/AgNO₃ (0.1 M in MeCN) couple as the reference electrode. CH₂Cl₂ was used as the solvent. The solution was purged with N₂ before measurement. Ferrocene was added as the internal reference.

2.4. Nanosecond Transient Absorption Spectra. The nanosecond time-resolved transient difference absorption spectra were measured with an LP920 laser flash-photolysis spectrometer (Edinburgh Instruments) and the signal was digitized with a Tektronix TDS 3012B oscilloscope. The samples were excited with a nanosecond pulsed laser (OPOLette 355II, tunable

wavelength within the range 410–2400 nm). The lifetimes were obtained with the LP900 software by monitoring the decay traces of the transients. All samples for the flash photolysis experiments were deaerated with N₂ for about 15 min before measurement, and the gas flow was maintained during the measurement.

2.5. TTA Upconversion. A diode-pumped solid-state (DPSS) continuous laser (635 nm) was used for the upconversion. The diameter of the 635 nm laser beam was about 6 mm. The power of the laser beam was measured with a VLP-2000 pyroelectric laser power meter. For the upconversion experiments, the mixed solution was degassed for at least 15 min with N₂ before measurement, and the gas flow was maintained during the measurement. The solution was then excited with the laser. The upconverted fluorescence was recorded with a RF 5301PC spectrofluorometer. In order to reduce the laser scattering, a black box was placed behind the fluorescent cuvette to dampen the laser beam.

The upconversion quantum yield (Φ_{UC}) was determined by the prompt luminescence of the sensitizer Pd-1 ($\Phi_L = 10.6\%$, in deaerated TL) as the inner standard. The upconversion quantum yields were calculated with the equation

$$\Phi_{UC} = 2\Phi_{std} \left(\frac{A_{std}}{A_{unk}} \right) \left(\frac{I_{unk}}{I_{std}} \right) \left(\frac{\eta_{unk}}{\eta_{std}} \right)^2 \quad (1)$$

where Φ_{UC} , A_{unk} , I_{unk} and η_{unk} respectively represent the photoluminescence quantum yield, the absorbance, the integrated photoluminescence intensity and the refractive index of the solvents (eq 1); standard is abbreviated as std, and unk stands for the samples to be measured.

2.8. fs TA Experimental Section. The TA experimental setup is detailed elsewhere.^{37,38} Briefly, the setup consisted of white-light continuum probe pulses generated in a 200 μm

CaF₂ nonlinear crystal, and spectrally tunable pump femtosecond pulses (370–550 nm; a few μ J pulse energy) were generated in an optical parametric amplifier (Coherent). The pump and probe pulses were overlapped spatially and temporally into a 1 mm thick cuvette cell containing the sample. Change in transient absorption was monitored by focusing the transmitted probe light through the solution onto a broadband UV-Vis detector.

3. RESULTS AND DISCUSSIONS

3.1. Design and Synthesis of the Compounds. Triad **BDP-2Py** is designed with two perylene units and one BDP unit (Scheme 1). The three units were covalently connected with a click reaction. With this triad, we want to answer two questions: (1) Is there an intramolecular homo-TTA between the two perylene units? (2) Is there an intramolecular hetero-TTA between the perylene and BDP units? Dyads **BDP-Py** and **BDP-I₂-Py** were designed as reference compounds to study the photophysical processes. **BDP-Py** contains only one perylene unit,^{11,13} thus we are able to study the difference between **BDP-2Py** and **BDP-Py** in TTA upconversion. **BDP-2Py** contains no heavy atom effect, so no triplet state can be produced upon photoexcitation. In order to study the intramolecular TTET with ultrafast transient absorption spectroscopy, we prepared the reference compound **BDP-I₂-Py**, in which the diiodoBDP unit is responsible for ISC.^{34,39–41} It should be pointed out that the intramolecular TTET of **BDP-2Py** cannot be studied with ultrafast time-resolved transient absorption; *intermolecular* photosensitizing must be used to produce the triplet state in **BDP-2Py**, due to the weak ISC of the BDP chromophore.^{42–46} This is an *intermolecular* TTET process, which is much slower than the intramolecular energy transfer. Therefore, the fast process (intramolecular TTET) cannot be monitored after the slow process (intermolecular TTET, i.e. the photosensitizing process) by femtosecond transient absorption spectra.

Scheme 1. The as-prepared compounds **BDP-Py**, **BDP-2Py** and reference compound **BDP-I₂-Py** studied in this paper (see Supporting Information in detail, Scheme S1).

3.2. UV-vis Absorption and Fluorescence Spectroscopy. As shown in Figure 1a, the UV-vis absorption wavelengths of **BDP-2Py** are similar to the component, and two distinct absorption bands are observed. Similar results are observed for **BDP-I₂-Py** (Figure 1b). These results indicate that there are no strong electronic interactions between the chromophores in the triad or the dyads.^{11,13,44,47,48}

The fluorescence emission spectra of the compounds are presented in Figure 1c. All the compounds were excited at the same wavelength ($\lambda_{\text{ex}} = 418 \text{ nm}$), where perylene shows strong fluorescence emission.^{49,50} For the dyads and the triad, the fluorescence emission of the perylene unit is almost completely quenched. Pristine BDP gives a very weak emission upon excitation at 418 nm.⁴³ For **BDP-2Py** and **BDP-Py**, a strong emission of the BDP moiety was observed, which indicates an efficient FRET process from perylene to BDP unit.^{44,51} For **BDP-I₂-Py**, only a weak emission was observed, which is due to an efficient ISC caused by the heavy atom effect of the iodine atom attached to the BDP unit.

Figure 1. (a) and (b) Absorption spectra and (c) fluorescence emission spectra for the investigated compounds, BDP and Py, where $\lambda_{\text{ex}} = 418 \text{ nm}$ and $c = 1.0 \times 10^{-5} \text{ M}$ in toluene (TL) at 20 °C.

The UV–vis absorption spectra and the fluorescence emission spectra of **BDP-Py** and **BDP-2Py** in different solvents were shown in Figure S1 (Supporting Information). The UV–vis absorption spectra slightly change among the different solvents, but the fluorescence of both the dyad and the triad is significantly quenched in polar solvents (with the excitation at the perylene absorption band). We propose that this quenching effect was caused by the faster photo-induced electron transfer (PET) between the perylene and BDP units in the dyad and triad;¹³ see later section on the calculation of the Gibbs free energy changes of the hypothetical PET process, as well as the femtosecond transient absorption spectroscopic studies. It was previously reported that the excimer fluorescence emission of a perylene excimer occurs at 640 nm.^{52,53} In its crystalline state, the excimer emission of perylene was reported at 550 nm.⁵⁴ Based on the emission profile of **BDP-2Py**, we propose that there is no significant excimer emission due to the perylene moiety.^{54,55}

The fluorescence excitation spectra of **BDP-Py** and **BDP-2Py** are compared to study the intramolecular energy transfer (Figure S2). Previously, the quenching of the fluorescence of a singlet energy donor was used to evaluate the singlet energy transfer efficiency. However, this is not a convincing method, because the photo-induced electron transfer (PET) may also contribute to the fluorescence quenching of the singlet energy donor. The comparison of the fluorescence excitation spectra with the UV-vis absorption spectra is more reliable when evaluating the singlet energy transfer efficiency, and the results indicate that the energy transfer efficiency is close to unity in toluene. Similar results are observed in acetonitrile (Figure S3 in Supporting Information). This result is interesting since our previous fluorescence study demonstrated that the fluorescence of the BDP unit in **BDP-Py** and **BDP-2Py** is completely quenched, which is unambiguously indicated by the photo-induced electron transfer.¹³ The explanation is that the PET process occurs after the FRET process, and the S_1 state on the BDP unit, not the perylene unit, drives the PET process. Given that the perylene S_1 state drives the PET, and the PET then competes with the FRET, a quantitative singlet energy transfer will not be observed. The perfect superposition of the fluorescence excitation spectrum on the UV-vis absorption spectrum was demonstrated in Figure S2.

The photophysical properties of the compounds are summarized in Table 1. The fluorescence quantum yields of **BDP-Py** and **BDP-2Py** are comparable to that of BDP. High fluorescence quantum yields are desirable for a triplet acceptor/emitter. The fluorescence lifetimes of **BDP-Py** and **BDP-2Py** in polar solvents, such as acetonitrile, are much shorter than in toluene, indicating the quenching of the excited state in polar solvents, most probably by PET.

Table 1. Photophysical Parameters of the Compounds ^a

	λ_{abs} (nm) ^a	ϵ ^b	λ_{em} (nm) ^c	Φ_{F} (%) ^d	τ_{F} (ns) ^e
BDP	504	8.40	526	72 ^g	3.8
Py	412/439	2.90/3.79	455/482/514	98 ^g	4.1
BDP-Py	418/445/503	2.52/3.50/8.05	516	79	4.4/1.4 ^f
BDP-2Py	418/445/504	4.92/6.28/8.17	516	77	5.6/1.2 ^f
BDP-I₂-Py	418/445/535	3.29/3.62/8.94	553	4.2	1.2

^a In toluene (1.0×10^{-5} M), at 20 °C. ^b Molar absorption coefficient at the absorption maxima. ϵ : $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. ^c Emission wavelength, $\lambda_{\text{ex}} = 418 \text{ nm}$. ^d Fluorescence quantum yields in toluene, with BDP ($\Phi_{\text{F}} = 0.72$, in THF) as the standard. ^e Fluorescence lifetimes in toluene. ^f Measured in CH_3CN . ^g Literature value.

3.3. Electrochemical Characterization and the Gibbs Free Energy Changes of the Photo-Induced Electron Transfer. In order to study the thermodynamics of the PET process, the electrochemical characterization (cyclic voltammetry, CV) was performed. The CV curves of the compound BDP has a reversible oxidation wave at +0.75 V (Figure S4a, Supporting Information). In the cathode region, a reversible reduction wave was observed at -1.70 V. For perylene (Figure S4b), however, only a pseudo-reversible oxidation wave at +0.56 V was observed; no wave was observed in the reduction region. The CV of **BDP-Py** is identical to the sum of the CV curves of BDP and perylene (Figure 2a). The oxidation waves become irreversible. Similar results were observed for **BDP-2Py** (Figure 2b). These results indicate that there is no electronic interaction between the perylene and BDP units at the ground state, and the perylene unit will act as an electron donor and the BDP unit as an electron acceptor.

Figure 2. Cyclic voltammogram of the compounds (a) **BDP-Py** and (b) **BDP-2Py**. Ferrocene (Fc) was used as the reference. In deaerated CH₂Cl₂, 0.10M Bu₄N[PF₆] is the supporting electrolyte and Ag/AgNO₃ is the reference electrode; scan rates: 100 mV/s at 20 °C.

Table 2. Electrochemical Data of Compounds. The Anodic and Cathodic Wave Potentials, the Free-Energy Changes (ΔG_{CS}^0) and the Charge Separated States (E_{CS} . With the Py Unit as the Electron Donor and the BDP Unit as the Electron Acceptor)

a

	$E_{(OX)} / V$	$E_{(RED)} / V$	$\Delta G_{CS}^0 (eV)$	$E_{CTS} (eV)$
			Toluene/ THF/MeCN	Toluene/ THF/MeCN
BDP	+0.75	-1.70	- ^b	- ^b
Py	+0.56	- ^b	- ^b	- ^b
BDP-Py	+0.60/+0.74	-1.70	+0.66 / -0.14 / -0.45	2.99 / 2.29 / 1.87
BDP-2Py	+0.52/+0.73	-1.70	+0.55 / -0.23 / -0.53	2.89 / 2.20 / 1.96

^a Cyclic voltammetry in Ar-saturated CH₂Cl₂, containing a 0.10 M Bu₄NPF₆ supporting electrolyte; Counter electrode is Pt electrode; Working electrode is glassy carbon electrode; Ag/AgNO₃ couple as the reference electrode; Electrochemical potentials versus Fc(+/-0). c[Ag⁺] = 0.1 M; ^b No reduction potential or $\Delta G_{CS}(eV)$ values; The singlet excited state of BDP (2.40 eV) as E_{00} .

According to the Weller equation (eqs 1 and 2), the Gibbs free energy changes (ΔG_{CS}) of the hypothetical PET processes in different solvents are calculated from Eq 2 to Eq 4⁵⁶⁻⁶²

$$\Delta G_{CS}^0 = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_S \quad (2)$$

$$\Delta G_S = -\frac{e^2}{4\pi\epsilon_S\epsilon_0 R_{CC}} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{R_D} + \frac{1}{R_A} \right) \left(\frac{1}{\epsilon_{REF}} - \frac{1}{\epsilon_S} \right) \quad (3)$$

$$\Delta G_{CR} = -(\Delta G_{CS} + E_{00}) \quad (4)$$

where ΔG_S is the static Coulombic energy described by eq 2, e = electronic charge, E_{OX} = half-wave potential for one-electron 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 fluorescence emission (for the singlet excited state), ϵ_S = static dielectric constant of the solvent, R_{CC} = center-to-center separation distance between the electron donor and electron acceptor as determined by DFT optimization of the geometry, R_D is the radius of the electron donor, R_A is the radius of the electron acceptor, ϵ_{REF} is the static dielectric constant of the solvent used for the electrochemical studies and ϵ_0 is the permittivity of the free space. The solvents used in the calculation of free energy of the electron transfer are toluene (TL) ($\epsilon_S = 2.4$), tetrahydrofuran ($\epsilon_S = 7.58$) and acetonitrile ($\epsilon_S = 37.5$).

The results show that the values are negative in polar solvents, which means the PET is thermodynamically allowed. In less polar solvents, however, the value is positive and the PET is thermodynamically prohibited. These results are in full agreement with the fluorescence emissions in different solvents. Furthermore, the energy levels of the charge separated state (CSS) were also calculated. The results show that the CTS energy level decreases in polar solvents.⁶¹

This information is useful for the construction of a photophysical diagram of BDP-Py and BDP-2Py (see Scheme 2 and 3).

3.4. Femtosecond Transient Absorption (fs-TA) Spectra: Intramolecular Singlet and Triplet Energy Transfer (Ping-Pong Energy Transfer). First, diiodoBDP (**BDP-I₂**) was measured by fs-TA in MeCN and TL using 400 nm as the excitation wavelength. Figure S5 shows the fs-TA spectra of **BDP-I₂** at 350 fs and 2.5 ns, where the negative absorption is attributed to the ground state bleach (GSB) at ~530 nm. It is also interesting to observe the narrowing of the transient bands over time, which is attributed to the disappearance of the stimulated emission (SE) due to ISC and the triplet state population at this timescale. This has been further confirmed by extracting the triplet state spectra and observing a difference between 2.5 ns and 350 fs (Figure S5a). Also, the extracted kinetic traces at 550 nm (SE) reflect the conversion from a singlet to a triplet state in 100 ps in MeCN and ca. 300 ps in toluene.⁶² On the other hand, the kinetic traces at 500 nm (GSB) seem to remain constant within the same time frame (Figure S5b).

For the dyad **BDP-I₂-Py**, using 400 nm as the excitation wavelength would excite the Py moiety rather than the BDP-I₂ moiety, due to the difference between the molar absorptivities of the two chromophores (Figure 1b). Unlike **BDP-I₂**, the GSB for the BDP moiety in **BDP-I₂-Py** increases in intensity between 400 fs and 30 ps, then starts to decrease again until 2.5 ns, with the appearance of positive features after 30 ps (Figure 3a). These two processes can be attributed to FRET from the singlet state of the Py moiety to the **BDP-I₂** moiety, and to TTET from the triplet state of the **BDP-I₂** moiety to the Py moiety (the triplet state energy of the diiodoBDP unit and the Py unit is 1.69 eV and 1.53 eV, respectively). The extracted lifetimes for the FRET process are fitted to be about 7 ps in MeCN and 9 ps in TL. The ISC in **BDP-I₂** is faster than the TTET to

the Py moiety, and this makes the later process to be the limiting one for such a consecutive cascade process, this can be confirmed by the decrease of GSB in **BDP-I₂** after the FRET process. However, to extract the TTET lifetime, nanosecond excitation pulses were used with an excitation wavelength of 530 nm (to avoid exciting the Py moiety), in which the GSB of the Py moiety at around 430 nm starts to be populated after 1 ns of exciting the **BDP-I₂** (Figure S6a). Such an increase in the GSB of the Py moiety would not appear unless TTET had already occurred, as the FRET from a **BDP-I₂** singlet state to a Py unit is not thermodynamically possible. Interestingly, the TTET lifetime is strongly dependent on the solvent used, as the lifetime is around 3.0 ns in MeCN but 9.0 ns in TL (Figure S6b). The variation of the TTET kinetics may be due to the change of the molecular geometry in different solvents. It is known that TTET is via Dexter mechanism, close contact of the molecular orbitals is normally required.

Figure 3. (a) fs-TA for **BDP-I₂-Py** in MeCN, using 400 nm as the excitation wavelength; the SSA (steady state absorption) and SSE (steady state emission) are overlapped with the TA data to determine the nature of each band. (b) Kinetic traces extracted at 440 and 520 nm, with their respective fitting lines.

Figure 4. fs-TA for (a) **BDP-Py** and (c) **BDP-2Py** in MeCN, using 400 nm as the excitation wavelength; the SSA and SSE are overlapped with the TA data to determine the nature of each band. Kinetic traces extracted at 500 nm for (b) **BDP-Py** and (d) **BDP-2Py** in MeCN with their fitting line.

For **BDP-Py**, without an iodine atom, the fs-TA shows an increase in the GSB of BDP between 9 and 13 ps in TL and MeCN, by exciting with 400 nm (Figure S7 and Figure 4). However, no positive features appear after the FRET process as shown in **BDP-I₂-Py** (Figure 3a) but rather the GSB of BDP diminishes with time, in addition to developing weak positive features that appear at 550 nm in MeCN (Figure 4a). From the thermodynamic parameters, these observations have been attributed to the PET process from the Py to the BDP unit, which is reflected in the appearance of a Py GSB at 430 nm, and the weak positive features at 550 nm from the negatively charged BDP moiety (radical anion).⁶³ The estimated lifetime for the PET

process is around 1 ns, as shown in Figure 4b. Confirming the earlier statements about the inhibition of the PET process in non-polar solvents, only the FRET process was observed for **BDP-Py** in TL at 400 nm excitation. This is verified by the detected kinetic plateau for **BDP-Py** in TL after the FRET process (see Figure S7).

With **BDP-2Py**, we found that by increasing the number of Py moieties, the rate of the FRET process from the Py moiety to the BDP moieties is slightly enhanced to reach 6 ps in MeCN and 10 ps in TL upon 400 nm excitation (Figure 4c). The PET process for **BDP-2Py** in MeCN was fitted to ~1.2 ns, slower than in **BDP-Py**, which matches with the charge separation energy state values calculated in Table 2. Also, the results indicate that there is no significant production of a triplet state by the charge recombination process.

3.5. Nanosecond Transient Absorption Spectra: Intramolecular Triplet-Triplet Energy Transfer (TTET) and Localization of the Triplet Excited State. In order to study the triplet excited states of the dyads and the triad in detail, nanosecond transient absorption spectroscopy of the compounds were studied, especially the long-lived triplet state (Figure 5), which is different from that of Figure S6. In Figure S6, we observed a change in kinetics due to the expected TTET from the **BDP-I₂** to the Py moiety, thus, we expect to follow the triplet state of Py in this section. However, we first study the properties of **BDP-I₂-Py**, because the diiodoBDP unit in this dyad is able to undertake ISC,³⁴ whereas **BDP-Py** and **BDP-2Py** lack this ability.⁴³

The dyad was excited at 532 nm (Figure 5a), thus selectively exciting the diiodoBDP unit. Interestingly, the transient absorption spectra is not typical of diiodoBDP spectra, because the expected bleaching band at 500 nm is missing.^{34,41} The excited state absorption (ESA) bands are also different from those of a BDP moiety. We propose that the transient absorption spectra can

Figure 5. Nanosecond time-resolved transient difference absorption spectra of **BDP-I₂-Py**, (a) and (c) excited with 532 nm nanosecond pulsed laser, decay trace at 470 nm; and (b) and d) excited with 445 nm nanosecond pulsed laser, decay trace at 470 nm. $c = 1.0 \times 10^{-5}$ M, in deaerated toluene at 20 °C.

be attributed to the triplet state of perylene.¹³ This postulation is supported by the appearance of a bleaching band at 450 nm, where perylene produces the GSB. The triplet state lifetime was 272 μs (Figure 5c). This result is interesting because the diiodoBDP unit is selectively excited, but the triplet state is localized on the perylene unit. Note that perylene moiety itself is without any ISC capability and perylene is known for its high fluorescence quantum yield (Table 1).⁴⁸ Thus the conclusion is that there is TTET from the BDP to the perylene unit, which was estimated in

the previous section to be around 9.0 ns in TL. This fast *intramolecular* TTET from the diiodoBDP unit to the perylene unit suggests that *intermolecular* TTA between the BDP and perylene (or BDP in another molecule) moieties is *unlikely*, because the assumed intermolecular process (TTA) is diffusion-controlled, and it is on the μs scale.³³ The results in Figure 5a also indicate that there is no back triplet energy transfer from the perylene unit to the diiodoBDP unit, otherwise the growth of the bleaching band at diiodoBDP will be observed after the initial decrease.

Alternatively, the dyad **BDP-I₂-Py** was excited at 445 nm, where perylene is the absorbant (Figure 5b). However, strong ESA bands similar to those in Figure 5a were observed, indicated that the perylene-localized triplet state was populated again. This is an interesting result because perylene has a very weak ISC ability.⁵⁰ Preliminary analysis of the excited state energy levels indicate that a ping-pong energy transfer is involved, i.e. selective excitation of the perylene moiety is followed by a FRET to the diiodoBDP unit, as in the previous section. The ISC of the diiodoBDP unit is then followed by a backward triplet energy transfer to the perylene unit. The sum of these ping-pong energy transfer processes (forward singlet energy transfer from the perylene unit to the diiodoBDP unit, then the ISC and the backward triplet energy transfer to the perylene unit) take less than 10 ns (Figure S6). This is confirmed by the femtosecond and nanosecond transient absorption spectra (Figure 3 and S6).

The triplet state property of **BDP-2Py** is shown in Figure 6. For this triad, however, there is no ISC unit, so we used a sensitizing method to produce the triplet state. We probe the properties of the triad, in terms of localization of the triplet state and the triplet state lifetimes. The properties of BDP-Py were studied using a mixture of BDP-Py/DiiodoBDP. Upon pulsed laser excitation, the bleaching band of the diiodoBDP diminished sharply at the same time the TA spectra of

Figure 6. Nanosecond time-resolved transient absorption spectra of mixtures of **BDP-I₂** with **BDP-Py** or **BDP-2Py** mixed together, with 532 nm nanosecond pulsed laser. (a) and (b) $c[\text{BDP-I}_2]/c[\text{BDP-Py}] = 1:2$ (molar ratio), decay trace at 490 nm. (c) and (d) $c[\text{BDP-I}_2]/c[\text{BDP-2Py}] = 1:1$ (molar ratio), decay trace at 490 nm. $c[\text{BDP-I}_2] = 1.0 \times 10^{-5}$ M, in deaerated toluene at 20 °C.

perylene developed. This change indicates an intermolecular TTET between the diiodoBDP and perylene units in **BDP-Py**. The lack of a GSB band from the BDP unit in **BDP-Py** indicates that either the BDP unit in **BDP-Py** is not a good triplet acceptor, or there is a fast intramolecular TTET to the perylene unit (Figure S6). The intermolecular TTET process can be clearly followed by monitoring the transient signal at 490 nm, where perylene shows an ESA band. Firstly there is negative signal, which is due to the instant production of the diiodoBDP triplet state upon photoexcitation. Then the transient absorption changes sharply to a positive value (at 5.5 μs).

This is the TTET through diffusion process, which is followed by the production of the perylene triplet state. Therefore, the last kinetic decay is attributed to the decay of the perylene triplet state. The triplet state lifetime is determined to be 100 μ s (Figure 6b). These results indicate that the triplet state in **BDP-Py** tends to be localized on perylene.

The triplet property of **BDP-2Py** (Figure 6c) is similar to that of **BDP-Py** (Figure 6a). The kinetic study shows that the intermolecular TTET takes about 14 μ s, and the decay of the perylene triplet state takes about 233 μ s. The important issues here are the O.D. value of the transient signal of **BDP-2Py** is similar to that of **BDP-Py**, and the triplet state lifetime of **BDP-2Py** (233 μ s) is longer than that of **BDP-Py**. These results strongly suggest that there is no intramolecular TTA in **BDP-2Py** under the experimental conditions, otherwise the triplet state lifetime of **BDP-2Py** would be much shorter than that of **BDP-Py** (will be reduced to ns or ps time scale). For example, the TTA of Ru(bpy)₃ appended on a polystyryl chain (2 – 3 Å distance between the chromophores) takes only 3 ps.⁶⁴ Intrachain TTA of the triplet state of 9,10-diphenylanthracene takes less than 1 ns (1 ns was the time-resolution limit of the spectrometer; exact kinetics were not determined).⁶⁵ Therefore, for **BDP-2Py**, these results suggest that neither an intramolecular hetero-TTA between the BDP and the perylene moieties, nor an intramolecular homo-TTA between the two perylene moieties, is possible.

The photophysical processes of triad **BDP-I₂-Py** and **BDP-2Py** are summarized in Scheme 2 and Scheme 3, respectively. As discussed previously, a ‘ping-pong’ energy transfer was observed upon selective photoexcitation of the perylene unit. All kinetics were studied with femtosecond and nanosecond transient absorption spectroscopy. For **BDP-2Py** (Scheme 3), FRET and photo-induced charge separation were observed.

Scheme 2. Photophysical Processes Involved in BDP-I₂-Py (in toluene). Keys: FRET stands for Förster resonance energy transfer, ISC stands for intersystem crossing. TTET stands for triplet-to-triplet energy transfer. The localization of the excited state in dyads is designated by red text. The number of the superscript designates the spin multiplicity. Radiative transitions are shown with solid arrows and the non-radiative transitions are shown with dotted arrows.

Scheme 3. Photophysical Processes Involved in BDP-2Py Upon Photoexcitation, in CH₃CN. Keys: CSS stands for charge-separated state. CS stands for charge separation and CR stands for charge recombination. The localization of the excited state in dyads is designated by

red text. The number of the superscript designates the spin multiplicity. Radiative transitions are shown with solid arrows and the non-radiative transitions are shown with dotted arrows.

3.6. Triplet-Triplet Annihilation (TTA) Upconversion. The dyad **BDP-Py** and triad **BDP-2Py** were used as the triplet acceptor and emitter for TTA upconversion (Figure 7a). Red light-excitable Pd-1 (Palladium tetraphenyltetrabenzoporphyrin), was used as the triplet photosensitizer.^{66–68} The photophysical processes involved in the TTA upconversion are shown in Scheme 4.

Figure 7. (a) Upconversions with photosensitizer **Pd-1**. Excited with 635 nm laser (4.8 mW, 17.0 mW cm⁻²). c [**Pd-1**] = 2.0×10^{-6} M; c [**BDP-Py**] = 4.0×10^{-5} M; c [**BDP-2Py**] = 2.0×10^{-5} M; c [**BDP**] = c [**Py**] = 4.0×10^{-5} M; (b) Stern-Volmer plot of the quenching of the triplet state of PdTPTBP with triplet acceptors BDP, Py, **BDP-Py** and **BDP-2Py**; c [triplet photosensitizer] = 2.0×10^{-6} M, in deaerated TL, 20 °C. (c) Photographs of the emission of the sensitizer alone and the

TTA upconversion; (d) CIE diagram of the emission of the upconversion; excited with 635 nm laser.

Scheme 4. Qualitative Jablonski Diagram Illustrating the Sensitized TTA Upconversion Process between the Sensitizer and the Annihilator. Key: E is energy. GS is ground state (S_0). $^1\text{MLCT}^*$ is the metal-to-ligand-charge-transfer singlet excited state of the photosensitizer Pd-1. ISC is intersystem crossing. $^3\text{MLCT}^*$ is the metal-to-ligand-charge-transfer triplet excited state. TTET is triplet-triplet energy transfer. $^3\text{Perylene}^*$ is the triplet excited state of annihilator. TTA is triplet-triplet annihilation. $^1\text{Perylene}^*$ is the singlet excited state of annihilator (initially the hot or the vibrationally excited S_1 state will be populated). The emission bands observed for the photosensitizer alone is the $^3\text{MLCT}$ emissive excited state. The emission bands observed in the TTA experiment are the $^1\text{perylene}^*$ emissions (fluorescence).

With pristine perylene as the triplet acceptor and emitter, an upconverted emission was observed at 446 nm with an upconversion quantum yield of 7.2%. With **BDP-Py** as the triplet acceptor and emitter, the upconverted fluorescence was observed at 518 nm, the time difference

being due to the emission of the BDP unit in the dyad.^{11,13} The upconversion quantum yield was 12.6% (Table 3), which is much higher than that of pristine perylene (7.2%). This triplet-state quenching study indicates that the TTET between perylene and **Pd-1** and the TTET between **BDP-Py** and Pd-1 are similar, thus the higher upconversion quantum yield for **BDP-Py** is most likely due to the better matched E₁/S₁ energy levels in **BDP-Py**, compared to those of perylene. All of the upconversion measurements were performed in TL, so the PET process between the excited BDP and Py moiety is not a limiting process here, unlike before in the transient absorption measurements.

The upconversion emission wavelength of **BDP-2Py** is similar to that of **BDP-Py**. However, the upconversion quantum yield decreased to 8.9%, from the 12.6% of BDP-Py. In order to quantitatively study the intermolecular triplet-triplet energy transfer (TTET), the quenching of the triplet state of Pd-1 by perylene, **BDP-Py**, **BDP-2Py** and BDP was studied (Figure 7b). Perylene, **BDP-Py** and **BDP-2Py** are more efficient triplet energy acceptors (quenchers) than BDP. The Stern-Volmer curves show that a hetero-TTA between the perylene and the BDP units is unlikely due to the poor performance of the BDP unit as a triplet energy acceptor. The quenching ability was quantitatively evaluated by calculating the K_{SV} values (Table 3).

Table 3. Stern–Volmer Quenching Constant (K_{SV}) and Bimolecular Quenching Constant (k_q) of the Triplet Energy Acceptors.

	K_{SV} (10^3 M^{-1}) ^a	k_q ($10^9 \text{ M}^{-1}\text{s}^{-1}$) ^b	k_0 ($10^9 \text{ M}^{-1}\text{s}^{-1}$) ^c	f (%) ^d	Φ_{UC} (%) ^e
BDP	54.2	0.47	12.0	3.8	0.6
Py	256.6	2.25	12.1	15.7	7.2
BDP-Py	263.6	2.31	11.2	17.1	12.6
BDP-2Py	185.6	1.63	11.3	12.6	8.9

^a Stern–Volmer quenching constant (K_{SV}), measured by transient absorption in deaerated toluene with **Pd-1** as photosensitizer, $c = 2.0 \times 10^{-6}$ M, decay trace at 440 nm, excited with 635 nm. ^b Bimolecular quenching constants (k_q). ^c Diffusion-controlled bimolecular quenching rate constants. ^d Quenching efficiency. ^e TTA upconversion quantum yields in deaerated toluene. See more detailed information in SI.

The TTA upconversion is visible to the naked eye using a 635 nm laser as the excitation light. (Figure 7c). Without a triplet acceptor or emitter, red emission was observed, owing to the phosphorescence emission of the photosensitizer **Pd-1**. With perylene, blue emission was observed from the upconversion. In the presence of **BDP-Py** or **BDP-2Py**, strong green emission was observed. The emission color changes were quantized using the CIE coordinates (Figure 7d).

4. CONCLUSIONS

In summary, we prepared the dyad (**BDP-Py**) containing a BODIPY unit (BDP) and a perylene (Py) unit, and the triad (**BDP-2Py**) containing two Py units and one BDP unit. A reference dyad **BDP-I₂-Py**, in which the BDP unit is iodinated, was also prepared in order to study its photophysical properties. A ping-pong energy transfer, i.e. the forward Förster resonance energy transfer (FRET), from the Py unit to the diiodoBDP unit (7 ~ 9 ps) and a backward triplet energy transfer from the diiodoBDP unit to the Py unit (2 ~ 7 ns) were observed in **BDP-I₂-Py**. FRET and photo-induced electron transfer (PET) were observed in **BDP-Py** and **BDP-2Py** in MeCN, but only FRET was observed in TL. Based on the steady state and time-resolved transient optical spectroscopy results, we conclude that neither intramolecular hetero-TTA nor intramolecular homo-TTA is likely in either the dyads or the triad, i.e. no intramolecular TTA can occur between the two Py units or between the Py and BDP units. The dyad and the triad were tested as the triplet energy acceptor and emitter for the TTA upconversion with **Pd-1** as the triplet photosensitizer. Upconversion quantum yield up to 12.6% was observed.

ASSOCIATED CONTENT

S Supporting Information

Experimental procedures, molecular structure characterization, additional spectra, and details of the calculations for the electrochemical study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

ACKNOWLEDGMENT

We thank the NSFC (21473020, 21673031, 21273028, 21421005 and 21603021), Program for Changjiang Scholars and Innovative Research Team in University [IRT_13R06], the Fundamental Research Funds for the Central Universities (DUT16TD25, DUT15ZD224, DUT2016TB12) for financial support. We would like to thank Dr. Manas Parida for his useful contribution to this project and King Abdullah University of Science and Technology (KAUST) for the financial support.

REFERENCES

- (1) Singh-Rachford, T. N.; Castellano, F. N. Photon Upconversion Based on Sensitized Triplet–Triplet Annihilation. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
- (2) Zhao, J.; Ji, S.; Guo, H. Triplet–Triplet Annihilation Based Upconversion: from Triplet Sensitizers and Triplet Acceptors to Upconversion Quantum Yields. *RSC Adv.* **2011**, *1*, 937–950.
- (3) Monguzzi, A.; Tubino, R.; Hoseinkhani, S.; Campione, M.; Meinardi, F. Low Power, Non-Coherent Sensitized Photon Up-Conversion: Modelling and Perspectives. *Phys. Chem. Chem. Phys.* **2012**, *14*, 4322–4332.

- (4) Ceroni, P. Energy Up-Conversion by Low-Power Excitation: New Applications of an Old Concept. *Chem.–Eur. J.* **2011**, *17*, 9560–9564.
- (5) Amemori, S.; Sasaki, Y.; Yanai, N.; Kimizuka, N. Near-Infrared-to-Visible Photon Upconversion Sensitized by a Metal Complex with Spin-Forbidden yet Strong S_0 – T_1 Absorption. *J. Am. Chem. Soc.* **2016**, *138*, 8702–8705.
- (6) Huang, Z.; Li, X.; Mahboub, M.; Hanson, K. M.; Nichols, V. M.; Le, H.; Tang, M. L.; Bardeen, C. J. Hybrid Molecule–Nanocrystal Photon Upconversion Across the Visible and Near-Infrared. *Nano Lett.* **2015**, *15*, 5552–5557.
- (7) Peng, J.; Jiang, X.; Guo, X.; Zhao, D.; Ma, Y. Sensitizer Design for Efficient Triplet–Triplet Annihilation Upconversion: Annihilator-Appended Tris-Cyclometalated Ir(III) Complexes. *Chem. Commun.* **2014**, *50*, 7828–7830.
- (8) Duan, P.; Yanai, N.; Nagatomi, H.; Kimizuka, N. Photon Upconversion in Supramolecular Gel Matrixes: Spontaneous Accumulation of Light-Harvesting Donor–Acceptor Arrays in Nanofibers and Acquired Air Stability. *J. Am. Chem. Soc.* **2015**, *137*, 1887–1894.
- (9) Yu, S.; Zeng, Y.; Chen, J.; Yu, T.; Zhang, X.; Yang, G.; Li, Y. Intramolecular Triplet–Triplet Energy Transfer Enhanced Triplet–Triplet Annihilation Upconversion with a Short-Lived Triplet State Platinum(II) Terpyridyl Acetylide Photosensitizer. *RSC Adv.* **2015**, *5*, 70640–70648.
- (10) Wang, B.; Sun, B.; Wang, X.; Ye, C.; Ding, P.; Liang, Z.; Chen, Z.; Tao, X.; Wu, L. Efficient Triplet Sensitizers of Palladium(II) Tetraphenylporphyrins for Upconversion-Powered Photoelectrochemistry. *J. Phys. Chem. C* **2014**, *118*, 1417–1425.

- (11) Turshatov, A.; Busko, D.; Avlasevich, Y.; Miteva, T.; Landfester, K.; Balushev, S. Synergetic Effect in Triplet–Triplet Annihilation Upconversion: Highly Efficient Multi-Chromophore Emitter. *ChemPhysChem* **2012**, *13*, 3112–3115.
- (12) Gray, V.; Dzebo, D.; Lundin, A.; Alborzpour, J. P.; Abrahamsson, M.; Bo, A.; Moth-Poulsen, K. Photophysical Characterization of the 9,10-Disubstituted Anthracene Chromophore and its Applications in Triplet–Triplet Annihilation Photon Upconversion. *J. Mater. Chem. C* **2015**, *3*, 11111–11121.
- (13) Cui, X.; Charafeddin, A.; Wang, J.; Guennic, B. L.; Zhao, J.; Jacquemin, D. Perylene-Derived Triplet Acceptors with Optimized Excited State Energy Levels for Triplet–Triplet Annihilation Assisted Upconversion. *J. Org. Chem.* **2014**, *79*, 2038–2048.
- (14) Kozlov, D. V.; Castellano, F. N. Anti-Stokes Delayed Fluorescence from Metal–Organic Bichromophores. *Chem. Commun.* **2004**, 2860–2861.
- (15) Fan, C.; Wu, W.; Chruma, J. J.; Zhao, J.; Yang, C. Enhanced Triplet–Triplet Energy Transfer and Upconversion Fluorescence through Host–Guest Complexation. *J. Am. Chem. Soc.* **2016**, *138*, 15405–15412.
- (16) Jiang, J.; Alsam, A. A.; Wang, S.; Aly, S. M.; Pan, Z.; Mohammed, O. F.; Schanze, K. S. Effect of Conjugation Length on Photoinduced Charge-Transfer in π -Conjugated Oligomer-Acceptor Dyads. *J. Phys. Chem. A* **2017**, DOI: 10.1021/acs.jpca.7b03547, in press.
- (17) Alsulami, Q. A.; Aly, S. M.; Goswami, S.; Alarousu, E.; Usman, A.; Schanze, K. S.; Mohammed, O. F. Ultrafast Excited-State Dynamics of Diketopyrrolopyrrole (DPP)-Based Materials: Static Versus Diffusion-Controlled Electron Transfer Process. *J. Phys. Chem. C* **2015**, *119*, 15919–15925.

- (18) Zhao, J.; Wu, W.; Sun, J.; Guo, S. Triplet Photosensitizers: from Molecular Design to Applications. *Chem. Soc. Rev.* **2013**, *42*, 5323–5351.
- (19) Zhao, J.; Xu, K.; Yang, W.; Wang, Z.; Zhong, F. The Triplet Excited State of Bodipy: Formation, Modulation and Application. *Chem. Soc. Rev.* **2015**, *44*, 8904–8939.
- (20) Haefele, A.; Blumhoff, J.; Khnayzer, R. S.; Castellano, F. N. Getting to the (Square) Root of the Problem: How to Make Noncoherent Pumped Upconversion Linear. *J. Phys. Chem. Lett.* **2012**, *3*, 299–303.
- (21) Kang, J. H.; Reichmanis, E. Low-Threshold Photon Upconversion Capsules Obtained by Photoinduced Interfacial Polymerization. *Angew. Chem. Int. Ed.* **2012**, *51*, 11841–11844.
- (22) Kim, J. H.; Deng, F.; Castellano, F. N.; Kim, J. H. Red-to-Blue/Cyan/Green Upconverting Microcapsules for Aqueous- and Dry-Phase Color Tuning and Magnetic Sorting. *ACS Photonics* **2014**, *1*, 382–388.
- (23) Wohnhaas, C.; Filatov, M. A.; Busko, D.; Avlasevich, Y.; Balushev, S.; Miteva, T.; Landfester, K.; Turshatov, A. Triplet–Triplet Annihilation Upconversion Based Nanocapsules for Bioimaging Under Excitation by Red and Deep-Red Light *Macromol. Biosci.* **2013**, *13*, 1422–1430.
- (24) Liu, Q.; Yang, T.; Feng, W.; Li, F. Blue-Emissive Upconversion Nanoparticles for Low-Power-Excited Bioimaging in Vivo. *J. Am. Chem. Soc.* **2012**, *134*, 5390–5397.
- (25) Yanai, N.; Kimizuka, N. Recent Emergence of Photon Upconversion Based on Triplet Energy Migration in Molecular Assemblies. *Chem. Commun.* **2016**, *52*, 5354–5370.
- (26) Vadrucchi, R.; Weder, C.; Simon, Y. S. Low-Power Photon Upconversion in Organic Glasses. *J. Mater. Chem. C* **2014**, *2*, 2837–2841.

(27) Schulze, T. F.; Czolk, J.; Cheng, Y. Y.; Fückel, B.; Macqueen, R. W.; Khoury, T.; Crossley, M. J.; Stannowski, B.; Lips, K.; Lemmer, U. Efficiency Enhancement of Organic and Thin-Film Silicon Solar Cells with Photochemical Upconversion. *J. Phys. Chem. C* **2012**, *116*, 22794–22801.

(28) Nattestad, A.; Cheng, Y. Y.; Macqueen, R. W.; Schulze, T. F.; Thompson, F. W.; Mozer, A. J.; Fückel, B.; Khoury, T.; Crossley, M. J.; Lips, K. Dye-Sensitized Solar Cell with Integrated Triplet–Triplet Annihilation Upconversion System. *J. Phys. Chem. Lett.* **2013**, *4*, 2073–2078.

(29) Monguzzi, A.; Braga, D.; Gandini, M.; Holmberg, V. C.; Kim, D. K.; Sahu, A.; Norris, D. J.; Meinardi, F. Broadband Up-Conversion at Subsolar Irradiance: Triplet–Triplet Annihilation Boosted by Fluorescent Semiconductor Nanocrystals. *Nano Lett.* **2014**, *14*, 6644–6650.

(30) Cheng, Y. Y.; Fückel, B.; MacQueen, R. W.; Khoury, T.; Clady, R. G. C. R.; Schulze, T. F.; Ekins-Daukes, N. J.; Crossley, M. J.; Stannowski, B.; Lips, K.; et al. Improving the Light-Harvesting of Amorphous Silicon Solar Cells with Photochemical Upconversion. *Energy Environ. Sci.* **2012**, *5*, 6953–6959.

(31) Khnayzer, R. S.; Blumhoff, J.; Harrington, J. A.; Haefele, A.; Deng, F.; Castellano, F. N. Upconversion-Powered Photoelectrochemistry. *Chem. Commun.* **2012**, *48*, 209–211.

(32) Duan, P.; Yanai, N.; Kimizuka, N. Photon Upconverting Liquids: Matrix-Free Molecular Upconversion Systems Functioning in Air. *J. Am. Chem. Soc.* **2013**, *135*, 19056–19059.

(33) Singhrachford, T. N.; Castellano, F. N. Triplet Sensitized Red-to-Blue Photon Upconversion. *J. Phys. Chem. Lett.* **2009**, *1*, 195–200.

(34) Wu, W.; Guo, H.; Wu, W.; Ji, S.; Zhao, J. Organic Triplet Sensitizer Library Derived from a Single Chromophore (BODIPY) with Long-Lived Triplet Excited State for Triplet–Triplet Annihilation Based Upconversion. *J. Org. Chem.* **2011**, *76*, 7056–7064.

(35) Wu, W.; Zhao, J.; Sun, J.; Song, G. Light-Harvesting Fullerene Dyads as Organic Triplet Photosensitizers for Triplet–Triplet Annihilation Upconversions. *J. Org. Chem.* **2012**, *77*, 5305–5312.

(36) Murakami, Y.; Kikuchi, H.; Kawai, A. Kinetics of Photon Upconversion in Ionic Liquids: Energy Transfer between Sensitizer and Emitter Molecules. *J. Phys. Chem. B* **2013**, *117*, 2487–2494.

(37) Aly, S. M.; Parida, M. R.; Alarousu, E.; Mohammed, O. F. Ultrafast Electron Injection at the Cationic Porphyrin–Graphene Interface Assisted by Molecular Flattening. *Chem. Commun.* **2014**, *50*, 10452–10455.

(38) Aly, S. M.; Goswami, S.; Alsulami, Q. A.; Schanze, K. S.; Mohammed, O. F. Ultrafast Photoinduced Electron Transfer in a π -Conjugated Oligomer/Porphyrin Complex. *J. Phys. Chem. Lett.* **2014**, *5*, 3386–3390.

(39) Yogo, T.; Urano, Y.; Ishitsuka, Y.; Maniwa, F.; Nagano, T. Highly Efficient and Photostable Photosensitizer Based on BODIPY Chromophore. *J. Am. Chem. Soc.* **2005**, *127*, 12162–12163.

(40) Zhang, X. F.; Yang, X. Singlet Oxygen Generation and Triplet Excited-State Spectra of Brominated BODIPY. *J. Phys. Chem. B* **2013**, *117*, 5533–5539.

(41) 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.

(42) Loudet, A.; Burgess, K. BODIPY Dyes and Their Derivatives: Syntheses and Spectroscopic Properties. *Chem. Rev.* **2007**, *107*, 4891–4932.

(43) Ulrich, G.; Ziessel, R.; Harriman, A. The Chemistry of Fluorescent Bodipy Dyes: Versatility Unsurpassed. *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201.

(44) Ziessel, R.; Harriman, A. Artificial Light-Harvesting Antennae: Electronic Energy Transfer by Way of Molecular Funnels. *Chem. Commun.* **2011**, *47*, 611–631.

(45) Awuah, S. G.; You, Y. Boron Dipyrromethene (BODIPY)-Based Photosensitizers for Photodynamic Therapy. *RSC Adv.* **2012**, *2*, 11169–11183.

(46) Lu, H.; Mack, J.; Yang, Y.; Shen, Z. Structural Modification Strategies for the Rational Design of Red/NIR Region BODIPYs. *Chem. Soc. Rev.* **2014**, *43*, 4778–4823.

(47) Alamiry, M. A. H.; Benniston, A. C.; Copley, G.; Harriman, A.; Howgego, D. Intramolecular Excimer Formation for Covalently Linked Boron Dipyrromethene Dyes. *J. Phys. Chem. A* **2011**, *115*, 12111–12119.

(48) Guliyev, R.; Coskun, A.; Akkaya, E. U. Design Strategies for Ratiometric Chemosensors: Modulation of Excitation Energy Transfer at the Energy Donor Site. *J. Am. Chem. Soc.* **2009**, *131*, 9007–9013.

(49) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Principles of Molecular Photochemistry : An Introduction*; University Science Books, **2009**.

(50) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy, 2nd ed.*; Kluwer Academic: New York, **1999**.

(51) Kostereli, Z.; Ozdemir, T.; Buyukcakil, O.; Akkaya, E. U. Tetrastyril-BODIPY-Based Dendritic Light Harvester and Estimation of Energy Transfer Efficiency. *Org. Lett.* **2012**, *14*, 3636–3639.

(52) Katoh, R.; Sinha, S.; Murata, S.; Tachiya, M. Origin of the Stabilization Energy of Perylene Excimer as Studied by Fluorescence and Near-IR Transient Absorption Spectroscopy. *J. Photochem. Photobio. A* **2001**, *145*, 23–34.

(53) Nakagawa, K.; Numata, Y.; Ishino, H.; Tanaka, D.; Kobayashi, T.; Tokunaga, E. Excimer Luminescence From Nonresonantly Excited Pyrene and Perylene Molecules in Solution. *J. Phys. Chem. A* **2013**, *117*, 11449–11455.

(54) Seko, T.; Ogura, K.; Kawakami, Y.; Sugino, H.; Toyotama, H.; Tanaka, J. Excimer Emission of Anthracene, Perylene, Coronene and Pyrene Microcrystals Dispersed in Water. *Chem. Phys. Lett.* **1998**, *291*, 438–444.

(55) Johnson, P. C.; Offen, H. W. Perylene Excimer Fluorescence in Cyclohexane. *Chem. Phys. Lett.* **1973**, *18*, 258–260.

(56) Jones, G.; Kumar, S.; Klueva, O.; Pacheco, D. Photoinduced Electron Transfer for Pyrromethene Dyes. *J. Phys. Chem. A* **2003**, *107*, 8429–8434.

(57) Bandi, V.; Gobeze, H. B.; Lakshmi, V.; Ravikanth, M.; D'Souza, F. Vectorial Charge Separation and Selective Triplet-State Formation during Charge Recombination in a Pyrrolyl-Bridged BODIPY–Fullerene Dyad. *J. Phys. Chem. C* **2015**, *119*, 8095–8102.

(58) Shi, W. J.; El-Khouly, M. E.; Ohkubo, K.; Fukuzumi, S.; Ng, D. K. Photosynthetic Antenna-Reaction Center Mimicry with a Covalently Linked Monostyryl Boron-Dipyrromethene-Aza-Boron-Dipyrromethene-C60 Triad. *Chem.–Eur. J.* **2013**, *19*, 11332–11341.

(59) Hankache, J.; Wenger, O. S. Large Increase of the Lifetime of a Charge-Separated State in a Molecular Triad Induced by Hydrogen-Bonding Solvent. *Chem.–Eur. J.* **2012**, *18*, 6443–6447.

(60) Kc, C. B.; Lim, G. N.; Nesterov, V. N.; Karr, P. A.; D'Souza, F. Phenothiazine–BODIPY–Fullerene Triads as Photosynthetic Reaction Center Models: Substitution and Solvent Polarity Effects on Photoinduced Charge Separation and Recombination. *Chem.–Eur. J.* **2014**, *20*, 17100–17112.

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

(62) 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.

(63) Hattori, S.; Ohkubo, K.; Urano, Y.; Sunahara, H.; Nagano, T.; Wada, Y.; Tkachenko, N. V.; Lemmetyinen, H.; Fukuzumi, S. Charge Separation in a Nonfluorescent Donor–Acceptor Dyad Derived from Boron Dipyrromethene Dye, Leading to Photocurrent Generation. *J. Phys. Chem. B* **2005**, *109*, 15368–15375.

(64) Shaw, G. B.; Papanikolas, J. M., Triplet–Triplet Annihilation of Excited States of Polypyridyl Ru(II) Complexes Bound to Polystyrene. *J. Phys. Chem. B* **2002**, *106*, 6156–6162.

(65) Tilley, A. J.; Robotham, B. E.; Steer, R. P.; Ghiggino, K. P. Sensitized Non-Coherent Photon Upconversion by Intramolecular Triplet–Triplet Annihilation in a Diphenylanthracene Pendant Polymer. *Chem. Phys. Lett.* **2015**, *618*, 198–202.

(66) Askes, S. H.; Bahreman, A.; Bonnet, S. Activation of a Photodissociative Ruthenium Complex by Triplet–Triplet Annihilation Upconversion in Liposomes. *Angew. Chem. Int. Ed.* **2014**, *53*, 1029–1033.

- (67) Murakami, Y.; Kikuchi, H.; Kawai, A. Kinetics of Photon Upconversion in Ionic Liquids: Time-Resolved Analysis of Delayed Fluorescence. *J. Phys. Chem. B* **2013**, *117*, 5180–5187.
- (68) Singhrachford, T. N.; Haebele, A.; Ziessel, R.; Castellano, F. N. Boron Dipyrromethene Chromophores: Next Generation Triplet Acceptors/Annihilators for Low Power Upconversion Schemes. *J. Am. Chem. Soc.* **2008**, *130*, 16164–16165.

TOC Graphic: