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The triplet excited state of Bodipy: formation, modulation and application

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Boron dipyrromethene (Bodipy) is one of the most extensively investigated organic chromophores. Most of the investigations are focused on the singlet excited state of Bodipy, such as fluorescence. In stark contrast, the study of the triplet excited state of Bodipy is limited, but it is an emerging area, since the triplet state of Bodipy is tremendously important for several areas, such as the fundamental photochemistry study, photodynamic therapy (PDT), photocatalysis and triplet–triplet annihilation (TTA) upconversion. The recent developments in the study of the production, modulation and application of the triplet excited state of Bodipy are discussed in this review article. The formation of the triplet state of Bodipy upon photoexcitation, *via* the well known approach such as the heavy atom effect (including I, Br, Ru, Ir, etc.), and the new methods, such as using a spin converter (e.g. C₆₀), charge recombination, exciton coupling and the doubly substituted excited state, are summarized. All the Bodipy-based triplet photosensitizers show strong absorption of visible or near IR light and the long-lived triplet excited state, which are important for the application of the triplet excited state in PDT or photocatalysis. Moreover, the methods for switching (or modulation) of the triplet excited state of Bodipy were discussed, such as those based on the photo-induced electron transfer (PET), by controlling the competing Förster-resonance-energy-transfer (FRET), or the intermolecular charge transfer (ICT). Controlling the triplet excited state will give functional molecules such as activatable PDT reagents or molecular devices. It is worth noting that switching of the singlet excited state and the triplet state of Bodipy may follow different principles. Application of the triplet excited state of Bodipy in PDT, hydrogen (H₂) production, photoredox catalytic organic reactions and TTA upconversion were discussed. The challenges and the opportunities in these areas were briefly discussed.

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(thus $S_0 \rightarrow S_n$ transition), intersystem crossing (ISC), exciton coupling,¹¹ charge recombination,¹² etc. On the other hand, application of the triplet excited state covers vast areas such as electroluminescence,^{13–18} photocatalysis,^{19,20} photodynamic therapy (PDT),^{4,21–24} photovoltaics,^{25–29} luminescence bioimaging and sensing,^{30–39} and recently the triplet-triplet annihilation (TTA) upconversion.^{40–45}

Triplet photosensitizers are compounds that produce the triplet excited state efficiently upon photoexcitation.^{4,21,22,46} The development of new triplet photosensitizers is retarded to a large extent, due to the difficulties of molecular structural designing.⁴⁷ The mechanism of the ISC of organic compounds is elusive, especially for those without any heavy atoms.^{1,48} The conventional triplet photosensitizers are limited to aromatic ketones⁴⁹ and porphyrin derivatives.³³ Transition metal complexes with precious metal atoms were also used as triplet photosensitizers.^{4,20,32,50} However, new metal-free organic triplet photosensitizers are rarely reported.^{21,33,47,51,52}

On the other hand, the selection of suitable chromophores for the preparation of organic triplet photosensitizers is also crucial, e.g. for the sake of easy derivatization and photostability. Concerning this aspect, boron-dipyrromethene (Bodipy) is of particular interest, due to its robust photophysical properties, such as strong absorption of visible light, high fluorescence quantum yield (suppressed non-radiative decay), good photostability and



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feasible derivatization.^{53–56} Bodipy was extensively used in singlet excited state-related studies, such as fluorescent molecular probes,^{57–65} light-harvesting arrays,^{66,67} molecular logic gates,^{68,69} dye-sensitized solar cells and photovoltaics.^{70–75} The study of the triplet excited state of Bodipy is still in the early stage.^{21,46,76,77} This review will summarize the recent developments of the study of triplet excited states of Bodipy, including the formation, modulation (controlling) and the applications of the triplet states.

One of the fascinating properties of the Bodipy chromophore is the feasible derivatization.^{53–56} It is easy to introduce substituents into Bodipy to tune the photophysical properties, such as the absorption/emission wavelength,⁵⁶ the hydrophilicity,^{78–80} or the redox property.^{47,80,81} The feasible derivatization makes it an ideal candidate for the preparation of a new triplet photosensitizer, and it is perhaps the most investigated chromophore for triplet state production than any other chromophore, except the conventional porphyrin derivatives.⁴⁷ Bodipy has been used in the triplet excited state studies.^{82–85} New organic triplet photosensitizers based on Bodipy have been used in photocatalysis,^{86,87} PDT,^{21,46,88,89} and TTA upconversion.^{85,90–92}

Different from the fluorescence ($S_1 \rightarrow S_0$ radiative decay),¹ the triplet excited state property is more complicated. The most straightforward pathway for the generation of the triplet state is the $S_1 \rightarrow T_1$ non-radiative transition. However, $S_1 \rightarrow T_n$ ISC is also normal, such as for the ISC of anthracene.^{93,94} Besides the well known heavy atom-effect, the exciton coupling¹¹ and the population of the double substituted excited state^{95,96} were also reported to be responsible for the formation of the triplet excited state upon photoexcitation. Moreover, some illusive mechanisms, such as the matching of the S_1/T_n state energy level, may contribute significantly to the formation of the triplet excited state.^{1,97} Charge recombination (CR) was also reported to be able to produce the triplet excited state upon excitation.^{12,98} All these drastically varied mechanisms make it difficult to design new organic triplet photosensitizers. For example, it is not a trivial task for an organic chemist to prepare organic chromophores with matched S_1/T_2 energy levels for efficient ISC. Actually, the molecular structure– T_1 state energy level



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relationship of organic chromophores is not as clear as the relationship between the S_1 state energy level and the molecular structure.

It should be pointed out that the spectroscopies used for the study of the triplet excited state are also different from that of the singlet excited state (usually fluorescence) of Bodipy. Most of the triplet photosensitizers do not phosphoresce in fluid solution at room temperature, thus the triplet excited state was very often studied by nanosecond transient absorption spectroscopy.⁹⁹ A complimentary method is the time-resolved photo-acoustic spectroscopy method, or laser induced optoacoustic spectroscopy, which is based on the photothermal effect. These methods have been used for the study of the lifetime as well as the triplet state quantum yield.^{100–102}

2. Formation of the triplet excited state of Bodipy

2.1. Heavy atom effect (I, Pt, Ir, Ru, Br, S, etc.)

The heavy atom effect for enhancing spin-orbit coupling is the most popular method to facilitate the ISC of organic compounds. This is also true for Bodipy.^{85,88,103–105}

In 2005, Nagano prepared 2,6-diiodoBodipy **1** as the PDT reagent (Fig. 1).⁸⁸ The compound gives strong visible light absorption (molar absorption coefficients $\varepsilon = 110\,000\text{ M}^{-1}\text{ cm}^{-1}$ at 535 nm), and a low fluorescence quantum yield ($\Phi_F = 0.02$ in MeOH, Table 1). The low fluorescence quantum yield is a prerequisite for efficient ISC.

However, the triplet state property of 2,6-diiodoBodipy was not studied by nanosecond transient absorption spectroscopy.⁸⁸ Instead, the singlet oxygen ($^1\text{O}_2$) photosensitizing ability of **1** was studied with 1,3-diphenylisobenzofuran (DPBF) as the singlet oxygen ($^1\text{O}_2$) scavenger.¹⁰⁶ The $^1\text{O}_2$ photosensitizing ability of 2,6-diiodoBodipy is 1.6-fold that of Rose Bengal (RB) (in methanol). Electrochemical studies show that 2,6-diiodoBodipy is more difficult to be oxidized ($E_{\text{ox}} = 1.13\text{ V vs. SCE}$) than RB (0.89 V vs. SCE), thus 2,6-diiodoBodipy is more stable toward $^1\text{O}_2$ (strong oxidant) than RB. The PDT effect on living HeLa cells was studied, and it was found that the cells were killed by photoirradiation after incubation with 2,6-diiodoBodipy **1**.⁸⁸

Normal Bodipys exhibits absorption in the green spectra range (*ca.* 500 nm), which is not ideal for *in vivo* PDT.²³ Instead, near IR absorption is desired for *in vivo* PDT because deeper penetration can be achieved with near IR light. O'Shea *et al.* prepared brominated azaBodipy.⁸⁹ AzaBodipy absorbs at 680 nm,^{76,103,107} which is red-shifted by *ca.* 180 nm as compared with that of



Fig. 1 2,6-DiiodoBodipy as the organic triplet photosensitizer.⁸⁸

Table 1 Photophysical properties of compounds **1–17**^a

	$\lambda_{\text{abs}}^b/\text{nm}$	ε^c	$\lambda_{\text{em}}^d/\text{nm}$	Φ_F^e	Φ_Δ^f	$\tau_T^g/\mu\text{s}$	Ref.
1	535	110 000		0.02	—	—	88
2a	650	79 000	673	0.01	—	—	89
2b	679	75 000	714	0.1	—	—	89
2c	653	80 000	679	<0.01	—	—	89
3	666	69 900	694		0.70 ± 0.03	1.5	109
4	731	201 000	754	0.37	—	—	112
5	720	89 000	754	0.45	—	—	112
6	503	82 000	515	71.2 ± 0.4	—	0.02	85
7	510	88 000	532	3.6 ± 0.3	—	66.3	85
8	529	89 000	552	2.7 ± 0.3	—	57.1	85
9	629	72 800	706	9.5 ± 0.1	—	4.0	85
10	539	75 400	563	7.8 ± 0.4	—	57.2	85
11	557	59 400	631	4.6 ± 0.2	—	54.6	85
12	576	180 000	623	10.5 ± 0.2	—	26.9	85
13	575/618	90 900/89 500	646	9.3 ± 0.2	—	47.0	85
14	505	—	527	0.69	—	—	224
15	526	—	543	0.105	—	—	119
16	532	—	551	0.011	—	—	119
17a	501	—	522	0.044	0	—	104
17b	521	—	543	0.071	0.39	43	104
17c	540	—	565	0.053	0.45	39	104
17d	559	—	576	0.065	0.49	36	104
17e	556	—	569	0.014	0.64	26	104

^a For detailed information, please refer to the main text and the references.

^b Absorption wavelengths at the maxima. ^c Molar absorption coefficient in $\text{M}^{-1}\text{ cm}^{-1}$. ^d Emission wavelength. ^e Fluorescence quantum yield.

^f Singlet oxygen quantum yield. ^g Triplet state lifetime.

normal Bodipy.^{53,54} The ε value of the azaBodipy derivatives are up to $80\,000\text{ M}^{-1}\text{ cm}^{-1}$. Upon bromination, the fluorescence quantum yields (Φ_F) of the compounds decreased from 20–30% to less than 1% (Fig. 2). Reduced fluorescence quantum yield upon bromination is an indication of ISC, facilitated by the heavy atom effect.

The triplet state property of bromo-azaBodipy **2** was not studied by nanosecond (ns) transient absorption (TA) spectroscopy (Fig. 2).⁸⁹ The $^1\text{O}_2$ photosensitizing ability was studied by comparison with that of hematoporphyrin, a known PDT reagent. BromoazaBodipy is 4-times more efficient than hematoporphyrin to produce $^1\text{O}_2$. However, the $^1\text{O}_2$ quantum yields (Φ_Δ) of the compounds were not determined, and thus the apparent fast $^1\text{O}_2$ production may be also due to the stronger absorption of bromoazaBodipy than hematoporphyrin in the visible spectral region. It was found that the $^1\text{O}_2$ photosensitizing ability was greatly reduced when the bromo atoms were attached onto the

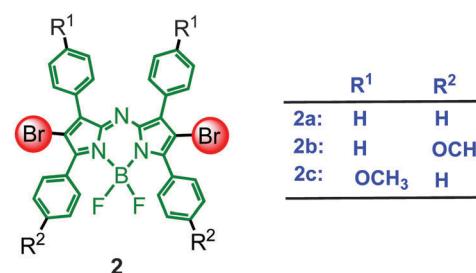


Fig. 2 Bromo azaBodipy as the organic triplet photosensitizer showing near IR absorption.⁸⁹

peripheral phenyl moieties and not on the π -conjugation framework of the azaBodipy. This is within expectation because the electrons in the frontier molecular orbitals must be in the immediate proximity of the heavy atoms in order to maximize the ISC. The PDT effect of the near-IR absorbing compounds was studied with HeLa cervical carcinoma cells. In a separate study, TDDFT computations give the T_1 state energy level of 0.79–0.87 eV for the brominated azaBodipy, slightly higher than that of $^1\text{O}_2$, and thus photozessitizing $^1\text{O}_2$ is rationalized.¹⁰⁸

Ramaiah reported iodinated azaBodipy **3** as a triplet photosensitizer (Fig. 3).^{76,109} The compound shows absorption at 666 nm, with a molar absorption coefficient of $69\,900\text{ M}^{-1}\text{ cm}^{-1}$.

The triplet state lifetime of the compound was determined to be $1.6\text{ }\mu\text{s}$ by ns TA spectroscopy, which is much shorter than 2,6-diiodoBodipy ($>50\text{ }\mu\text{s}$).⁸⁵ The Φ_T value was determined to be 0.78 ± 0.02 . The Φ_Δ value of the compound was determined to be 0.70 ± 0.03 . In comparison MB gives a Φ_Δ value of 0.52 (Table 1).

The triplet excited state lifetime (τ_T) of the triplet photosensitizers, among the other photophysical parameters, is crucial for efficient PDT. The reason is that the hypoxia micro-environment of the tumor tissues makes the PDT difficult, due to the low O_2 concentration in the tumor tissue. Thus, only the triplet photosensitizers with a long triplet excited state lifetime (*ca.* 100 μs , for example) are highly sensitive to sensitize $^1\text{O}_2$ even at low O_2 concentration, and they are more efficient $^1\text{O}_2$ photosensitizers as compared with that of the photosensitizers with a shorter triplet state lifetime (few μs). This postulations have been confirmed using Ru(II) complexes.¹¹⁰ The triplet-triplet-energy-transfer (TTET) efficiency between the photosensitizer and O_2 is highly dependent on the triplet state lifetime of the former.¹¹¹

Thienyl-fused Bodipys **4** and **5** were also reported as organic triplet photosensitizers (Fig. 4).¹¹² With the thiophene moiety fused into the π -conjugation framework of Bodipy, the absorption wavelength was dramatically red-shifted to 730 nm. The ϵ value is from $89\,000\text{--}200\,000\text{ M}^{-1}\text{ cm}^{-1}$ (Table 1).

With DPBF as the $^1\text{O}_2$ scavenger, the $^1\text{O}_2$ photosensitizing of compounds was studied. Compound **5** shows $^1\text{O}_2$ photosensitizing ability. But no $^1\text{O}_2$ quantum yields were reported.¹¹² The triplet state of the compound was not studied by ns TA spectroscopy. Recent studies demonstrated that heavy atoms, such as iodine or bromine, are not required for similar thienyl-fused Bodipy to attain ISC ability (compound **4**, Fig. 4).^{113,114}

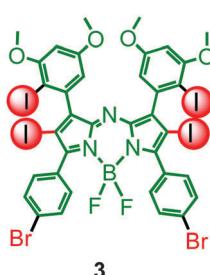


Fig. 3 Iodinated azaBodipy as the triplet photosensitizer.¹⁰⁹

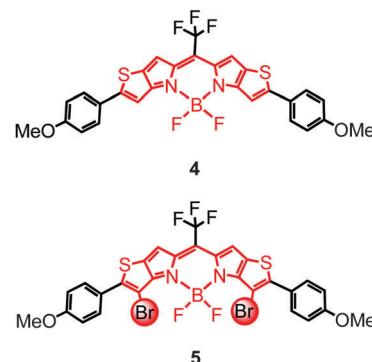


Fig. 4 Bromo thienyl-fused Bodipy **5** as the triplet photosensitizer.¹¹²

Inspired by the feasible derivatization of the Bodipy chromophore (thus the feasible absorption wavelength tuning), and the effective heavy atom effect with iodine atoms attached at the π -conjugation framework, Zhao prepared a small library of iodobodipy derivatives as triplet photosensitizers (**7**–**13**, Fig. 5), and the triplet excited state lifetimes were studied using ns TA spectra (Table 1).⁸⁵

With the introduction of different conjugation moieties onto the π -core of Bodipy, the absorption wavelength of the derivatives can be tuned from 515 nm to 706 nm.⁸⁵ On the other hand, the iodine atoms were directly attached onto the π -conjugation framework, and thus the heavy atom effect was maximized. With homo- and hetero-coupling reaction, the Bodipy dimers **12** and **13** were prepared (Fig. 5). Derivatives with a significant intramolecular charge transfer (ICT) feature were also prepared (such as **9**, Fig. 5). It should be pointed out that for **14**, the production of the triplet state is negligible, because the iodine atom is not attached onto the π -core of Bodipy.

With the introduction of iodine atoms on the π -conjugation framework of the compounds, the fluorescence quantum yields

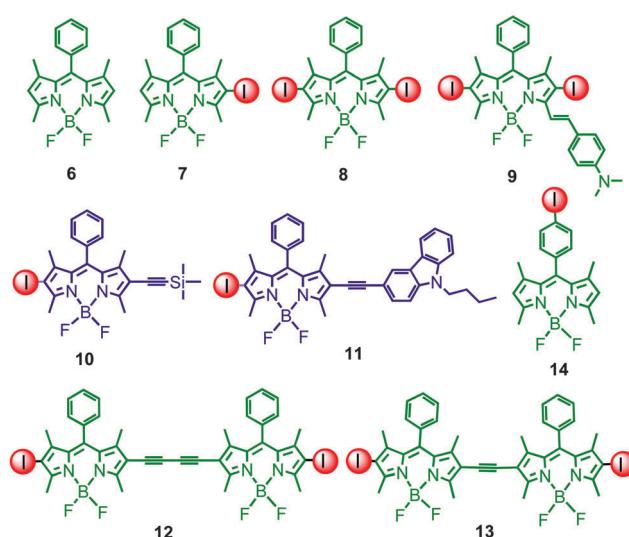


Fig. 5 Bodipy-derived organic triplet photosensitizer library with variable absorption wavelength.⁸⁵ Compound **14** was used as reference.

of the compounds ($\Phi_F < 10\%$) were decreased as compared with that of the unsubstituted Bodipy ($\Phi_F = 71\%$). This is the indication of the probable ISC in the iodinated compounds.⁸⁵

The triplet excited state property of the compounds was studied by the ns TA spectroscopy.⁸⁵ For compound **8**, a bleaching band at 520 nm was observed upon 532 nm nanosecond pulsed laser excitation (Fig. 6). This bleaching is due to the ground state depletion upon photoexcitation (a portion of the molecules were promoted to the long-lived triplet state). Excited state absorption (ESA) bands in the range of 450 nm, 550–750 nm were observed, which are attributed to the $T_1 \rightarrow T_n$ transitions. The triplet state lifetime was determined to be 57.1 μs . The triplet state lifetime (τ_T), especially for the compounds with a long-lived triplet state lifetime, is highly dependent on the concentration of the compounds, and even more, the excitation laser power. Highly populated triplet excited states will suffer from severe self-quenching, and the triplet state lifetime will become shorter. This is in stark contrast to the fluorescence lifetime measurement, which is much less sensitive to the concentration and the laser power.² Moreover, caution should be taken for interpretation of the ESA bands, especially to evaluate the bleaching band quantitatively (the molar absorption coefficient of the excited state), because very often the ESA overlaps with the bleaching bands (Fig. 6).

The reliable triplet state lifetime can be determined by concentration extrapolation into indefinitely diluted solution. Later we determined the triplet state lifetime of diiodoBodipy to be 228.9 μs .¹¹⁵ These triplet excited state lifetimes are generally much longer than the normal $^3\text{MLCT}$ excited state of the transition metal complexes, which are usually less than 10 μs .^{4,7,8,50} Similar long-lived triplet excited states were observed for the other Bodipy-derived triplet photosensitizers.⁴⁷ Notably the triplet state lifetime of **9** ($\tau_T = 4.0 \mu\text{s}$) is much shorter than the others. These lifetimes are generally much longer than the triplet state lifetime of bromo or iodo azabodipy (1.6 μs).^{76,109}

The triplet state energy level is one of the crucial parameters for triplet photosensitizers.^{116,117} For the non-phosphorescent compounds, it is not a trivial task to derive the T_1 triplet state energy level. TDDFT computations do not always give reliable estimation, especially for the Bodipy chromophores.¹¹⁸

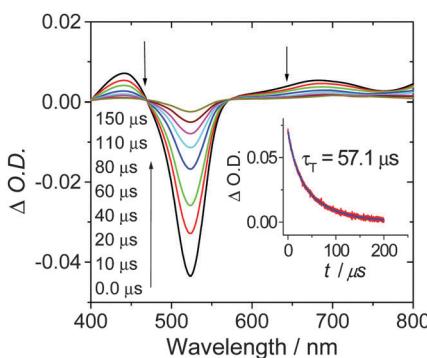


Fig. 6 Nanosecond TA spectra of compound **8** in deaerated CH_3CN after pulsed laser excitation ($\lambda_{\text{ex}} = 532 \text{ nm}$). Inset: Decay trace of compound **8** at 525 nm; $1.5 \times 10^{-5} \text{ M}$; 20°C . Reproduced with permission from Wu et al.⁸⁵

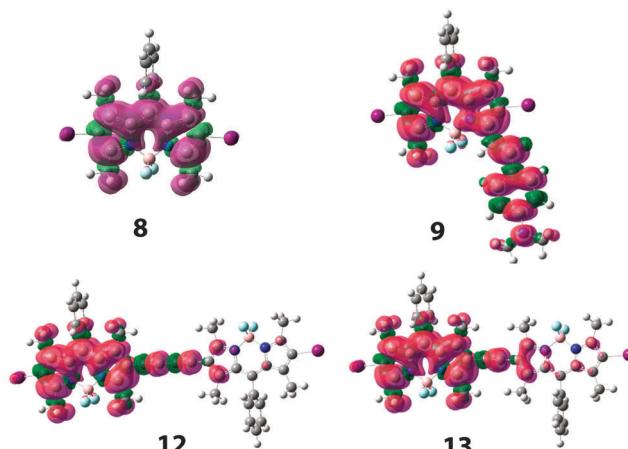


Fig. 7 Isosurfaces of spin density of Bodipy triplet photosensitizers and the model compound **8** at the optimized triplet state geometries. Calculation was performed at the B3LYP/6-31G(d)/LanL2DZ level using Gaussian 09W. Reproduced with permission from Wu et al.⁸⁵

Unfortunately, the relationship between the molecular structure and the triplet state energy level in normal organic compounds is unclear, and even worse, the relationship may be different from that of the fluorescence (singlet excited states). This situation is demonstrated with **12** and **13** (Fig. 5). These Bodipy dimers show much red-shifted absorption than **8** (0.33 eV of difference). However, the application of the triplet photosensitizers in TTA upconversion show that the T_1 state energy level of **12** and **13** does not decrease significantly as compared with that of **8**, although the S_1 state energy level decreased by *ca.* 0.28 eV.⁸⁵ Concerning this aspect, the spin density surface of the compounds gives a clue in that the spin density surface of **12** and **13** is distributed on one of the two Bodipy moieties in the dimers (Fig. 7), and thus the triplet state energy level of these Bodipy dimers does not decrease as the singlet excited state does.

The ISC rate constants of the halogenated Bodipy (Fig. 8) were studied by femtosecond (fs) TA spectroscopy (Fig. 9).¹¹⁹ Upon femtosecond photoexcitation, the ESA band at 340 nm decreases (Fig. 9), and a new band at 440 nm grows in at the same time (Fig. 9). The latter was attributed to the ESA of the triplet excited state of Bodipy. The rate constant of the growth was determined to be 131 ps, which was assigned to the inter-system crossing (ISC) process.¹¹⁹ This process is much faster than the fluorescence of Bodipy chromophores (a few ns),

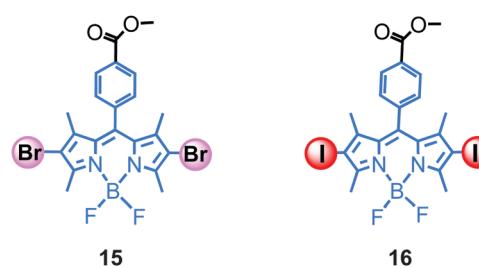


Fig. 8 Bromo- and iodinated Bodipy derivatives with ISC rate constants determined.¹¹⁹

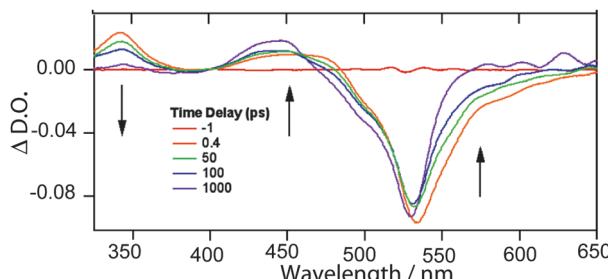


Fig. 9 Femtosecond transient absorption spectra of Bodipy **16** in acetonitrile. Arrows indicate spectral changes as time progresses. Reproduced with permission from ref. 119.

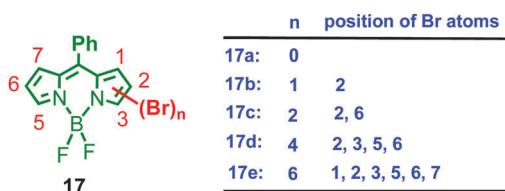


Fig. 10 Polybrominated Bodipy derivatives as triplet photosensitizers.¹⁰⁴

and thus iodination is an efficient approach for the Bodipy chromophore to form a triplet excited state.

The $^1\text{O}_2$ generation and the triplet excited state quantum yield (Φ_T) of polybrominated Bodipy were studied (Fig. 10).^{104,120} The Φ_T value increased to 0.66 for hexabromoBodipy. The corresponding Φ_Δ value is 0.64.

2.2. Bodipy-containing transition metal complexes

The heavy atom effect is not limited to bromine or iodine atoms. Precious metal atoms, such as Ru, Pt, Ir, and Re, were also widely used for the heavy atom effect, such as in the phosphorescent materials.^{3,7,8,36,50,121,122} The photophysical properties of the transient metal complexes with Bodipy as the ligand were also studied.

Bodipy-containing Ru(II) complexes were prepared (Fig. 11).⁸² In order to avoid π -conjugation between the Bodipy units and

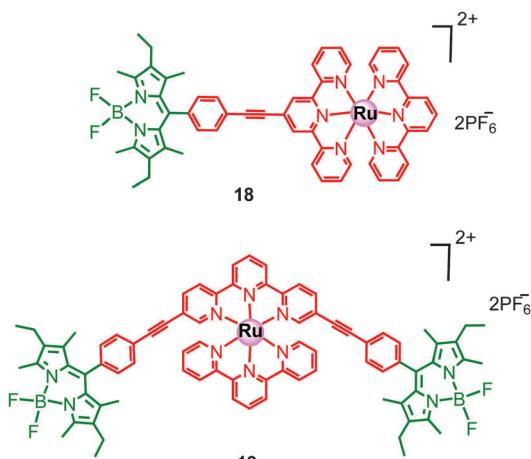


Fig. 11 Bodipy-containing Ru(II) terpyridine complexes **18** and **19**.⁸²

the Ru(II) coordination center, the acetylidy linkers were attached onto the *meso*-phenyl moieties in Bodipy, which takes a perpendicular geometry toward the dipyrromethene core of Bodipy. Both complexes **18** and **19** give strong absorption at 523 nm, which is attributed to the Bodipy moiety. The absorption band of the Ru(II) terpyridine coordination center was buried in the intense absorption band of the Bodipy ligand. Interestingly, neither the fluorescence of the Bodipy ligand nor the phosphorescence of the Ru(II) coordination center was observed.

At 77 K (in a butyronitrile solid matrix), the fluorescence of the Bodipy ligand (536 nm) and an emission band in the near IR range (774 nm) were observed.⁸² The emission at 774 nm was attributed to the phosphorescence of the Bodipy ligand (Table 2). This is the first time that the phosphorescence of the Bodipy chromophore was observed (at 77 K). The proof for the phosphorescence assignment is the long-lifetime of the emission band at 774 nm (50 ms) and the large Stokes shift.

Nanosecond TA spectroscopy showed that a ground state bleaching band at 530 nm was observed, as well as the ESA bands in the range of 550–700 nm. Thus, it was concluded that the T_1 state of the complexes was localized on the Bodipy ligand, and not on the Ru(II) coordination center. The triplet state lifetimes of complexes **18** and **19** were determined to be 8 μ s and 30 μ s, respectively. In comparison, the Ru(II) terpyridine coordination center, without the Bodipy moiety, gives a much shorter triplet state lifetime (a few hundred ps).^{6,123,124}

Based on the electrochemical studies and the calculation of the Gibbs free energy changes (ΔG_{CS}) of the photoinduced electron transfer (PET), it was proposed that a charge separation (CS) state lies below the $^1\pi-\pi^*$ state of the Bodipy ligand, which is responsible for the quenching of the fluorescence of the Bodipy ligand (although quenching of the Bodipy fluorescence by ISC, or a $^1\text{Bodipy}^* \rightarrow ^1\text{MLCT}^*$ singlet energy transfer, cannot be excluded) (Fig. 12). Charge recombination (CR) may produce the triplet state localized on the Bodipy ligand. Down hill triplet energy transfer from the $^3\text{MLCT}$ state will also produce the Bodipy-localized $^3\pi-\pi^*$ state. Both paths give the T_1 state localized on the Bodipy ligand. The evidence for the above postulation is the partial recovery of the fluorescence of the Bodipy ligand at low temperature, and it is known that CT will be inhibited at low temperature due to the lack of the solvation effect (stabilization of the CT state, so that the PET is exoenergetic, *i.e.* thermodynamically allowed).

Table 2 Photophysical properties of **18–23**^a

	$\lambda_{\text{abs}}/\text{nm}$	ϵ	$\lambda_{\text{em}}/\text{nm}$	Φ_Δ	$\tau_T, \mu\text{s}$	τ_p	Ref.
18	523	66 100	536/774 (77 K)	—	8	50 ms	82
19	523	89 600	540/774 (77 K)	—	30	50 ms	82
20	523	61 340	536 (77 K)	—	—	5 ns	83
21	523	86 700	535 (77 K)	—	—	6 ns	83
22	528	65 200	748/741 (77 K)	0.93	279.7	33.9 ms	125
23	499	76 700	513/510 (77 K)	0.64	246.6	4.4 μs	125

^a For detailed information, please refer to the main text and the references.

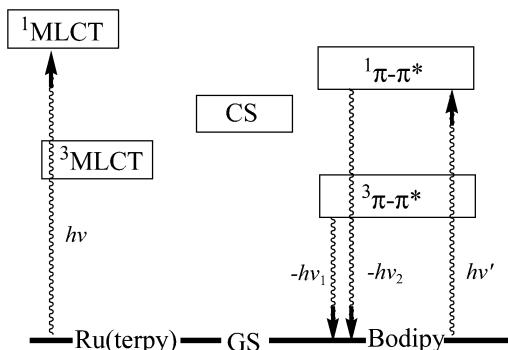


Fig. 12 Excited state levels of the Ru(terpy)-Bodipy dyads **18** and **19**. GS stands for the ground state, CS stands for the charge-separated state. Reproduced with permission from ref. 82.

Similar photophysical properties were observed using the Ru(bpy)₃-Bodipy complexes (Fig. 13).⁸³ Ultrafast TA spectroscopy shows that the intramolecular singlet energy transfer from the ¹MLCT state to the ¹π-π* state takes within 1 ps. Then the CS occurs, which takes about 3–15 ps. The CR process takes about 30–200 ps, which produces the triplet state localized on the Bodipy ligands.

Different from the complexes in Fig. 11 and 13, we investigated another molecular structural motif for the Bodipy-Ru(bpy)₃ dyads, *i.e.* the Bodipy chromophore is fully π-conjugated with the Ru(bpy)₃ coordination center (**22**, **23** is reference without the conjugation between the Bodipy and the Ru(II) coordination center, Fig. 14).¹²⁵ In **22**, an ethynyl linker was attached onto the bpy ligand and the 2-position of the Bodipy chromophore. Thus π-conjugation between the two moieties was established. The molecular structural motif of **23** is similar to that reported previously (Fig. 11 and 13).⁸³

The designing rational for **22** is that the π-conjugation between the Bodipy chromophore and the coordination center may facilitate the ISC, and thus the harvested photoexcitation energy of the complex can be efficiently funneled to the triplet excited state manifold. Non π-conjugated chromophores and coordination centers may render a situation that strong absorption

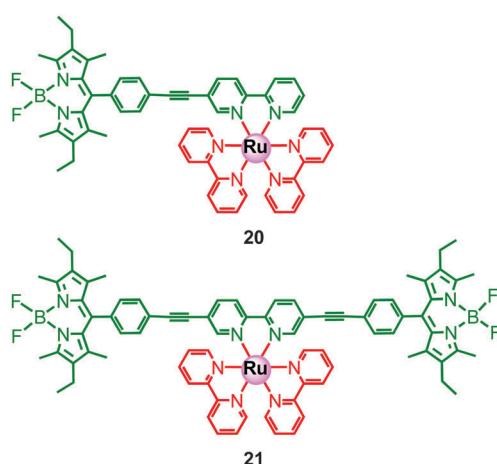


Fig. 13 Bodipy-containing Ru(II)(bpy)₃ complexes **20** and **21**.⁸³

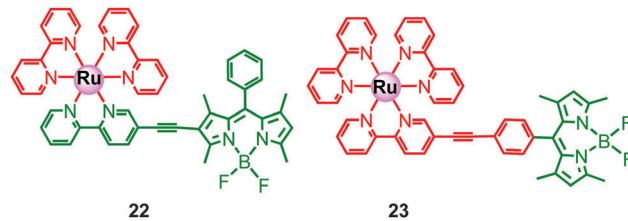


Fig. 14 Bodipy-containing Ru(II)(bpy)₃ complexes **22** and **23**. In **22**, π-conjugation between the Bodipy chromophore and the Ru(II) coordination centre was established.¹²⁵

of visible light is observed, but the absorbed photoexcitation energy is unable to be efficiently funneled to the triplet excited state manifold, *i.e.* it is trapped onto the light-harvesting ligand.

The absorption of **22** (528 nm) is slightly red-shifted as compared with that of **23** (499 nm). Both complexes show strong absorption ($\varepsilon = 65\,200\text{ M}^{-1}\text{ cm}^{-1}$ and $76\,700\text{ M}^{-1}\text{ cm}^{-1}$, respectively). The fluorescence of the Bodipy ligand was not observed in **22**, whereas in **23**, the residual Bodipy ligand fluorescence was observed at 513 nm ($\Phi_F = 1\%$) (Table 2). Interestingly, an emission band at 750 nm was observed for **22** at room temperature. Based on the emission wavelength (large Stokes shift), the band was attributed to the phosphorescence of the Bodipy ligand. To the best of our knowledge, this is the first time that the phosphorescence of the Bodipy chromophore was observed with Ru(II) complexes at room temperature. At 77 K, a sharp emission band at 741 nm was observed for **22**. The small thermally induced Stokes shift indicates that the emission band is due to an ³IL state, not an ³MLCT state. The charge transfer emissive state, such as the ³MLCT state, usually gives a much larger thermally induced Stokes shift.

Nanosecond TA spectroscopy was used to study the triplet state property of the complexes.¹²⁵ The feature of the TA spectra is similar to that of the Bodipy chromophore. Moreover, the bleaching bands also support that the T₁ state of the complexes was localized on the Bodipy ligand, not on the Ru(II) coordination center. Spin density surfaces of the complexes calculated with DFT support this conclusion. Interestingly, the triplet state lifetimes of **22** and **23** were determined to be 279.7 μs and 246.6 μs, respectively (at room temperature). These long triplet excited state lifetimes are unprecedented for the Bodipy-containing Ru(II) complexes.

The Φ_Δ values of **22** and **23** were determined. The Φ_Δ value of **22** (0.93) is higher than **23** (0.64). The higher Φ_Δ value of **22** than that of **23** indicates efficient ISC in **22** than **23**, although the contribution from other factors, such as CT and CR, are unable to be excluded. The complexes were used as triplet photosensitizers for TTA upconversion, and **22** ($\Phi_{UC} = 1.2\%$) is more efficient than **23** ($\Phi_{UC} = 0.7\%$).

Based on the results in literature and those from our own group, we propose it is a general rule to use bulky ligands to achieve a long-lived triplet excited state, due to the reduced heavy atom effect (SOC) for these ³π-π* triplet states. In other words, the reduced heavy atom effect is sufficient for efficient

$S_1 \rightarrow T_1$ ISC (quantum yield is high), but it is not sufficient for the $T_1 \rightarrow S_0$ ISC, because with larger $\Delta E_{T_1/S_0}$, the $T_1 \rightarrow S_0$ ISC requires much stronger SOC (eqn (1)).¹²⁶

$$k_{\text{isc}} \propto \frac{\langle T_1 | H_{\text{SO}} | S_1 \rangle^2}{(\Delta E_{S_1-T_1})^2} \quad (1)$$

This postulation is supported by the photophysics of the well known complex $\text{Ru}(\text{bpy})_3\text{Cl}_2$. Note that the heavy atom effect is sufficient to ensure efficient $S_1 \rightarrow T_1$ intersystem crossing, but it does not result in a fast $T_1 \rightarrow S_0$ decay. The ${}^1\text{MLCT} \rightarrow {}^3\text{MLCT}$ ISC of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ takes less than 1 ps, yet the ${}^3\text{MLCT} \rightarrow S_0$ decay takes hundreds of ns.⁷ These results infer that the effect of the same heavy atom on the ${}^1\text{MLCT} \rightarrow {}^3\text{MLCT}$ and ${}^3\text{MLCT} \rightarrow S_0$ processes is different.

To us it is always in doubt whether non-conjugated linking of a chromophore to the coordination center will induce efficient ISC, because such a molecular structural motif is not beneficial for maximizing the heavy atom effect (the frontier molecular orbital usually does not spread to the heavy atom). No reliable conclusion can be made from the previous study of the Bodipy-containing complexes due to the lack of quantitative data. A study on the following Bodipy-containing Pt(II) complexes clarified the above question to a large extent.

In $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$ Pt(II) acetylide complex 24 (Fig. 15), the Bodipy moiety and the Pt(II)-coordination center are not in π -conjugation due to the *meso*-phenyl moiety of the Bodipy chromophore. The Φ_F value of the Bodipy ligand in 24 is 27%, as compared to that of the uncoordinated ligands ($\Phi_F = 92\%$) (Table 3). Thus, the ISC is non-efficient upon photoexcitation into the Bodipy chromophore in 24.¹²⁷ The phosphorescence of the Pt(II)

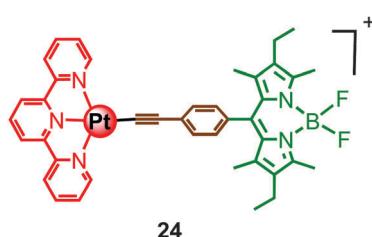


Fig. 15 Bodipy-containing $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$ Pt(II) acetylide complex 24.¹²⁷

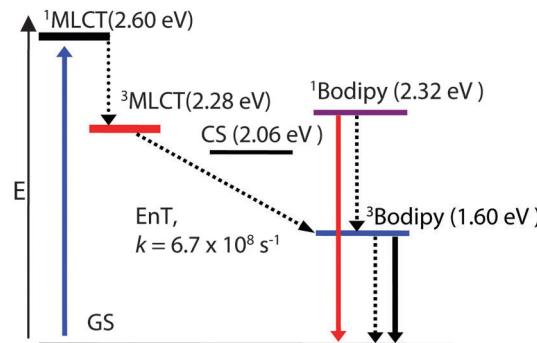


Fig. 16 The photophysical processes in 24 upon photoexcitation.¹²⁷ Reproduced with permission from ref. 127.

coordination center (to be centered at 635 nm) was not observed in 24.

UV-vis absorption spectra and the electrochemical studies indicate that the components in 24 are in supramolecular state, *i.e.* there is no electronic interaction between the components in ground state. Fluorescence lifetime of 24 and the reference Bodipy ligands indicate that there is no significant fluorescence quenching at low temperature (77 K). Electrochemical studies indicate the presence of the CS state, lying between the ${}^3\text{MLCT}$ state and the ${}^3\text{Bodipy}$ state (Fig. 16). Due to the ultrafast ISC in the Ru(II) coordination center (>1 ps), excitation into the ${}^1\text{MLCT}$ state does not contribute to the fluorescence of the Bodipy moiety, which requires ${}^1\text{MLCT} \rightarrow {}^1\text{Bodipy}$ singlet energy transfer, a slower process than the ISC of the Ru(II) coordination centre. Based on the molecular structural motif, the authors argued that the CS is non-efficient. The ${}^3\text{Bodipy}$ state is populated mainly from the ISC (${}^1\text{Bodipy} \rightarrow {}^3\text{Bodipy}$). At low temperature (77 K), the phosphorescence from the Bodipy moiety is not significant, an indication of non-efficient ISC.¹²⁷ Similar photophysical properties were also observed with the $\text{C}^{\wedge}\text{N}$ Pt(II) acac complex (acac = acetyl-acetonate. Fig. 17),¹²⁸ *i.e.* non-efficient ISC of the Bodipy chromophore.

In order to maximize the heavy atom effect in Bodipy-containing Pt(II) complexes, we proposed a new molecular structural motif (26, Fig. 18).¹²⁹ In 26, the Pt(II) atoms are directly coordinated with the π -conjugation framework of the

Table 3 Photophysical properties of 24–35^a

	$\lambda_{\text{abs}}/\text{nm}$	ε	$\lambda_{\text{em}}/\text{nm}$	Φ_F	$\tau_T, \mu\text{s}$	τ_p	Ref.
24	523	54 610	536/535 (77 K)	0.27	—	6 ns	127
25	650	126 000	670/665 (77 K)	0.45	—	3.90 ns	128
26	406/574	33 900/53 800	660/770	0.035 (Φ_p)	125.8	1.5 ms	129
27	561	72 000	631/792	0.003/0.0006 (Φ_p)	35.9	—	130
28	503	153 000	521	0.0188	162.1	—	130
29	537	53 000	590	0.33	—	—	131
30	536/597	60 200/8300	—	—	—	—	131
31	524/568	107 700/11 800	—	—	—	—	131
32	522/612	—	—	—	—	—	132
33	522/600	—	—	—	—	—	132
34	514/619	—	628/772/764 (77 K)	<0.001/0.26 (Φ_p)	95	67 μs /92 μs (77 K)	134
35	425/620	—	—	—	—	30 μs	134

^a For detailed information, please refer to the main text and the references.

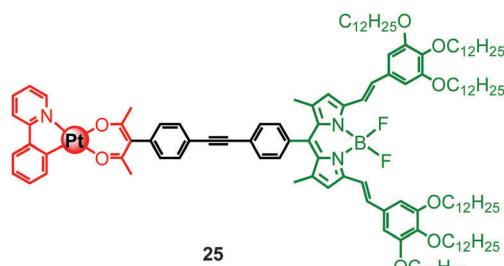


Fig. 17 The styrylBodipy-containing Pt(II) (acac) complex **25**.¹²⁸

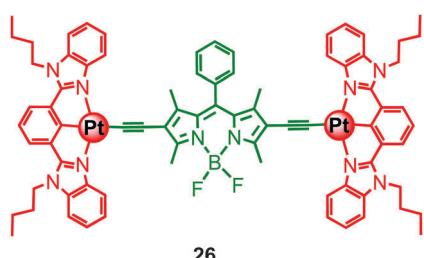


Fig. 18 Bodipy-containing Pt(II) complex **26** with the π -conjugation framework of Bodipy linked to Pt(II) atoms.¹²⁹

Bodipy chromophore, thus the heavy atom effect, and the ISC is maximized, because the electrons in the frontier molecular orbital is able to move to the vicinity of Pt(II) atoms. Strong absorption of visible light and efficient production of the triplet excited state are envisioned.¹²⁹

Complex **26** shows a drastically different absorption profile as compared to that of the free ethynylBodipy ligand, indicating substantial perturbation on the π -conjugation framework of the Bodipy chromophore upon coordination with Pt(II) atoms.¹²⁹ This observation is different from that of the Bodipy-containing transition metal complexes, in which the Bodipy chromophore is not directly linked to the coordination centers *via* π -conjugation (complexes **24** and **25**, Fig. 15 and 17). The absorption maximum of **26** is at 574 nm ($\epsilon = 53\,800\,M^{-1}\,cm^{-1}$). The absorption band is broader than the free ligand (centered at 543 nm, $\epsilon = 85\,800\,M^{-1}\,cm^{-1}$).

An intense emission band at 770 nm was observed for **26** at room temperature in fluid solution ($\Phi_P = 3.5\%$) (Table 3). The luminescence lifetime of this near IR emission band was determined to be 128.4 μ s. Thus based on the long luminescence lifetime and the large Stokes shift, the emission was attributed to the phosphorescence of the coordinated Bodipy ligand. To the best of our knowledge, this is the first observation of the RT phosphorescence of the Bodipy chromophore with Pt(II) complexes.¹²⁹ Room temperature phosphorescence of the Bodipy chromophore indicated the efficient ISC of the 1 Bodipy excited state, as well as the 3 Bodipy $\rightarrow S_0$ ISC. An emission band at 660 nm was also observed, which was assigned to an 3 MLCT emission. Note that the triplet state lifetime of **26** is much longer than that of the normal N⁺N Pt(II) acetylalide complexes (usually the emissive state is in the 3 MLCT/ 3 L feature and the lifetime is shorter than 10 μ s).⁸ This is due to

the $^3\pi-\pi^*$ feature of the triplet state of **26**, *i.e.* the less contribution of the Pt(II) atoms to the triplet excited state.

Only the emission at 775 nm was observed at 77 K. The thermally induced Stokes shift is very small, only 84 cm⁻¹, which indicates the 3 IL feature of the emissive triplet excited state.¹²⁹ With ns TA spectroscopy, we conclude that the triplet state is localized on the Bodipy chromophore of the complex. The triplet state lifetime was determined to be 125.8 μ s (Table 3). The complex was used as a triplet photosensitizer for TTA upconversion, and an upconversion quantum yield of 5.2% was observed.

The molecular structural designing rational that connection of the Bodipy chromophore with the metal coordination center *via* π -conjugation to enhance the ISC was also demonstrated by the preparation of N⁺N Pt(II) bisacetylalide complexes **27** and **28** (Fig. 19).¹³⁰ The difference of the two complex lies in the linker between the Bodipy chromophore and the Pt(II) coordination center. **27** and **28** show drastically different absorption profiles (Fig. 20). The spectra show that the π -conjugation framework of the Bodipy moiety in **27** is drastically perturbed.

For **28**, the residual fluorescence of the Bodipy ligand was observed. The phosphorescence of the Pt(II) coordination center (at 567 nm for the N⁺N Pt(II) bisphenylacetylalide complex, $\Phi_P = 16\%$) was not observed, which is attributed to the triplet-triplet energy transfer (TTET) from the 3 MLCT state to the 3 Bodipy state. For **27**, however, two emission bands at 631 nm and 792 nm were observed, the luminescence lifetime of 0.9 ns and the phosphorescence lifetime of 35.9 μ s were observed, respectively.

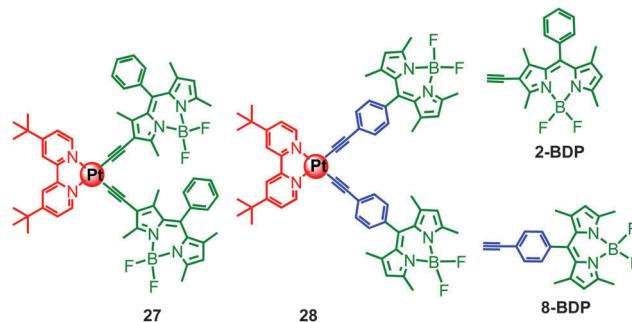


Fig. 19 N⁺N Pt(II) bisacetylalide complexes **27** and **28** with Bodipy ligands.¹³⁰

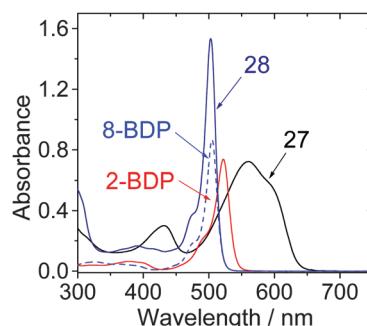


Fig. 20 UV-vis absorption of free ligands 2-BDP, 8-BDP and the complexes **27** and **28**.¹³⁰

Thus the two emission bands can be attributed to the fluorescence and phosphorescence, respectively. The triplet state lifetime of **27** was determined to be 37.9 μ s by ns TA spectroscopy. On the other hand, the triplet state lifetime of **28** was determined to be 162.1 μ s. Our later study shows that the Φ_T value of **27** is *ca.* 2-fold that of **28**. These results indicate that direct metalation of the Bodipy chromophore is an effective approach to attain efficient ISC. These lifetimes are much longer than the triplet state lifetime of the normal Pt(II) complexes.⁸

Eisenberg used the Bodipy ligand for the preparation of Pt(II) diimide(dithiolate) complexes, with the intention of sensitizing the sensitizer, *i.e.* to enhance the visible light-harvesting ability of the Pt(II) triplet photosensitizer (Fig. 21).¹³¹ The Bodipy chromophore is attached onto either the bipyridine ligand (**29** and **30**), or the dithiolate ligand (**31**).¹³¹ Note that in this case the Bodipy chromophore is not linked to the Pt(II) center with the π -conjugation framework. Both the UV-vis absorption and the electrochemical data infer that the spectral properties of dyads **30** and **31** are the sum of the components of the dyads, and thus there is no significant electronic interaction between the components in the dyads in the ground state. Similar to some of the previously reported Bodipy-containing Ru(II) or Pt(II) complexes, both the mixed-metal-ligand-to-ligand' charge transfer (MMLL'CT) emission of the Pt(II) coordination center and the Bodipy fluorescence were quenched, which indicated either energy transfer or electron transfer.

Femtosecond TA spectra of **30** were recorded to reveal the photophysical processes.¹³¹ Upon selective excitation into the Bodipy ligand (530 nm), the ground state bleaching of the Bodipy moiety at 530 nm was observed, as well as the stimulated emission (SE) band at *ca.* 600 nm. The ground state bleaching decreases significantly within 2 ps, with a decrease of the excited state absorption (ESA) at 350 nm. This process is attributed to the $^1\text{Bodipy} \rightarrow ^1\text{MMLL}'\text{CT}$ singlet energy transfer. The bleaching band did not change during the following 2–6 ps, during which the $^1\text{MMLL}'\text{CT} \rightarrow ^3\text{MMLL}'\text{CT}$ ISC occurred. Then the bleaching band of the Bodipy moiety increased again, with the increase of the ESA band at 425 nm (the featured ESA of the Bodipy triplet state), and this process takes 6–8 ps, which is the $^3\text{MMLL}'\text{CT} \rightarrow ^3\text{Bodipy}$ intramolecular TTET.

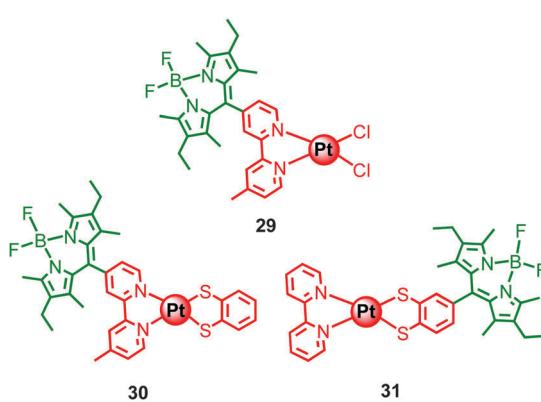


Fig. 21 Bodipy–Pt(II)(diimine)(dithiolate) dyads (**29–31**) showing strong absorption of visible light.¹³¹

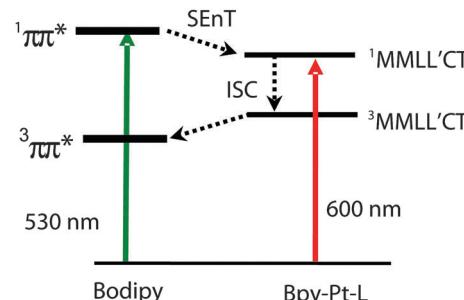


Fig. 22 Energy level diagram relevant to the photochemistry of complexes **30** and **31**. Reproduced with permission from ref. 131.

The photophysical processes of **30** are summarized in Fig. 22.¹³¹ Upon selective photoexcitation, the $^1\text{Bodipy}$ singlet excited state was produced, and then the singlet energy transfer took (SEnT) place, giving the MMLL'CT singlet excited state. The ultrafast ISC (<1 ps) of the Pt(II) coordination center produced the triplet excited state ($^3\text{MMLL}'\text{CT}$). Then intramolecular TTET produced the triplet excited state of Bodipy. Thus, both the fluorescence of the Bodipy moiety and the phosphorescence of the Pt(II) coordination center should be quenched.

The poor spectral overlap and the unfavorable dipole moment orientation in dyad **30** predict slow singlet energy transfer (calculated as $1/k_{\text{EnT}} = 710$ ps), provided the energy transfer is *via* the Förster mechanism (FRET). However, the experimental singlet energy transfer time is $1/k_{\text{EnT}} = 0.6$ ps. Thus it was proposed that the electron exchange is responsible for the ultrafast singlet energy transfer in **30**, not the Förster mechanism.² The triplet excited state lifetimes of the complexes **30** and **31** were not reported.¹³¹

For dyads **30** and **31**, the triplet excited state is no longer localized on the Pt(II) coordination center.¹³¹ The triplet state is localized on the Bodipy ligand (confirmed by the fs TA spectra); this may change the redox property and it is probably detrimental to the application in photocatalysis. To address this problem, Eisenberg modified the molecular structures, and electron withdrawing groups were attached onto the bpy ligand (complexes **32** and **33**, Fig. 23); thus the energy level of the $^3\text{MMLL}'\text{CT}$ state becomes lower than that of the Bodipy triplet state, and thus the T₁ state of the dyads **32** and **33** is localized on the Pt(II) coordination center, not on the Bodipy antenna (Fig. 23).¹³²

It should be pointed out that direct attachment of an organic chromophore to the Pt(II) center does not guarantee the long-lived

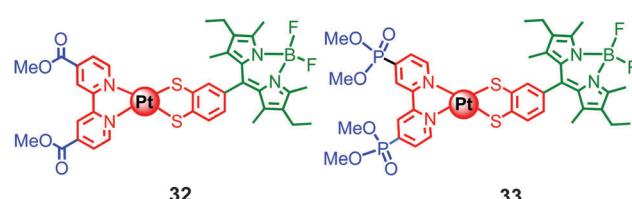


Fig. 23 Pt(II) diimine dithiolate complexes **32** and **33** containing the Bodipy antenna.¹³²

triplet excited state, rather, the lifetime of the triplet state is dependent on the molecular structure of the chromophore to a large extent. For example, with perylenebisimide (PBI) attached to the Pt(II) center in a N^NN Pt(II) bisacetylidyne complex, a short triplet state lifetime was observed (246 ns).¹³³ Complicated mechanisms may dictate the photophysical processes, such as the symmetry of either the ligand or the molecular orbitals. These features may also dictate the ISC.⁴⁸

Thompson reported the Bodipy-tetraphenyltetrabenzo-porphyrin (TPBP) Pt(II) bichromophoric complex (**34**) (Fig. 24).¹³⁴ The goal is to prepare a broadband visible light-absorbing triplet photosensitizer, based on the energy transfer between the Bodipy antenna and the benzoporphyrin-Pt(II) coordination center. However, a fast non-radiative decay channel exists for the specific Bodipy chromophore used in the conjugates (Fig. 24). Note that there are no methyl groups at the 1,7-position of the Bodipy, and thus the rotation of the *meso*-phenyl moiety dissipates the energy of the S₁ state. This property was later employed to develop fluorescent viscosity molecular probes.^{135,136} However, this fast decay channel does not necessarily mean an inhibition of FRET, provided the FRET process is faster.

The Bodipy moiety shows strong absorption at 514 nm. Thus with four Bodipy antennae, **34** shows an intense absorption band at 514 nm, which is comparable to the Soret band of **35** at *ca.* 425 nm. Phosphorescence at 772 nm was observed for **34**, which is attributed to the Pt(II) coordination center. The phosphorescence excitation spectrum demonstrated the efficient singlet energy transfer from the Bodipy moiety to the Pt(II) coordination center. The phosphorescence lifetime is 67 μs, which is much longer than the complex **35** which is without the Bodipy moieties ($\tau_p = 30 \mu\text{s}$). Thus the Bodipy chromophore exerted a substantial influence on the excited state of the complex **35** (Table 3).

The ultrafast TA spectra of the complex were recorded upon selective photoexcitation into the Bodipy part. Singlet energy transfer in complex **34** was confirmed, on a time scale of $1/k_{\text{EnT}} = 1.29 \pm 0.11 \text{ ps}$. The transient spectrum indicated the backward TTET from the Pt(TPBP) coordination center to the Bodipy moiety. The rate constant is $k_{\text{TTET}} = 1.0 \times 10^{10} \text{ s}^{-1}$. It should be pointed out that this kind of ping-pong energy transfer, *i.e.* forward singlet energy transfer and the backward triplet energy transfer, was not observed with the FRET molecules.²

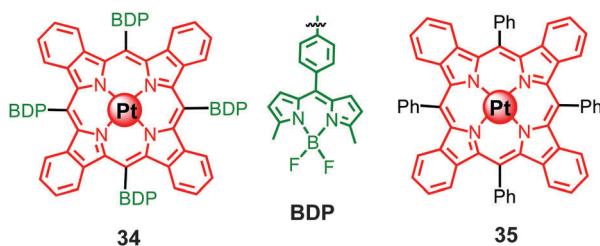


Fig. 24 The broadband visible light-harvesting Bodipy-tetraphenyltetrabenzporphyrin complex (**34**). The Bodipy chromophore (BDP) and the unsubstituted Pt(TPBP) complex (**35**) are also presented.¹³⁴

The ns TA spectroscopy of **34** was studied. Three bleaching bands at 430 nm, 515 nm, and 620 nm were observed promptly upon nanosecond pulsed laser excitation. Thus the triplet state is delocalized on Bodipy and Pt(TBTP) moieties. All the transient signals decay with the same kinetics, indicating an equilibrium between the triplet state of the Bodipy and the Pt(TBTP) moiety (fast forward and backward energy transfer). The triplet state lifetime (and the phosphorescence lifetime) is 67 μs, which is much longer than the 30 μs lifetime of the unsubstituted complex **35**. This extension of the triplet state lifetime is attributed to the energy reservoir effect of the Bodipy chromophore.¹³⁴

Castellano reported the Bodipy-containing Ir(III) complex **36** (Fig. 25).⁸⁴ Since the π-conjugation framework of the Bodipy chromophore is isolated from the Ir(III) coordination center, thus the dyad is in supramolecular state and the components of the dyad show their respective absorption and electrochemical properties.

The phosphorescence of the Ir(III) coordination center was quantitatively quenched in complex **36**, due to the triplet-triplet energy transfer (TTET) to the Bodipy moiety, which is at the lower triplet state energy level ($E_{T_1} = 1.69 \text{ eV}$) than the Ir(III) coordination center ($E_{T_1} = 1.97\text{--}2.10 \text{ eV}$). The formation of the ³Bodipy* triplet excited state was confirmed by the ns TA spectrum. The triplet state lifetime is 25 μs (Table 4). The phosphorescence of the Bodipy moiety was observed at 77 K, as well as the residual fluorescence of the Bodipy ligand.

The photophysics of **36** is summarized in Fig. 26. The quenching of the ³MLCT emission and the fluorescence of the Bodipy ligand can be rationalized. However, as discussed above, the quantum yield of the ISC of ¹Bodipy → ³Bodipy is unclear. No residual fluorescence quantum yields, or triplet state quantum yields are available.⁸⁴

In order to clarify the effect of different linkers between the Bodipy chromophore and the Ir(III) coordination center, *i.e.* either

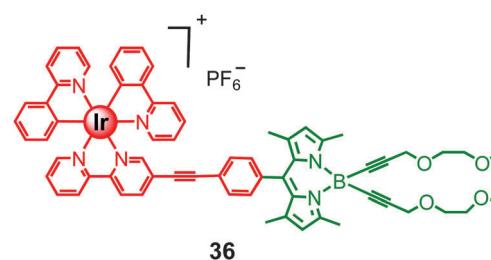
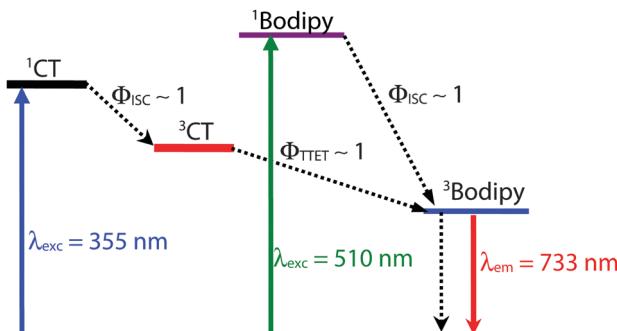


Fig. 25 Bodipy-containing Ir(III) complex **36**.⁸⁴

Table 4 Photophysical properties of compounds **36**–**40**^a

	λ_{abs} , nm	ϵ	λ_{em} /nm	Φ_F	Φ_Δ	τ_T , μs	τ_p	Ref.
36	501	83 600	730 (77 K)	—	—	25	—	84
37	499	71 400	514	1.8	0.52	23.7	—	137
38	527	83 000	553/742	0.3/0.03	0.97	87.2	4.5 ms (77 K)	137
39	536	91 700	556/742	0.0013	0.88	104.0	—	147
40	574	64 600	647	0.171	0.06	127.2	—	147

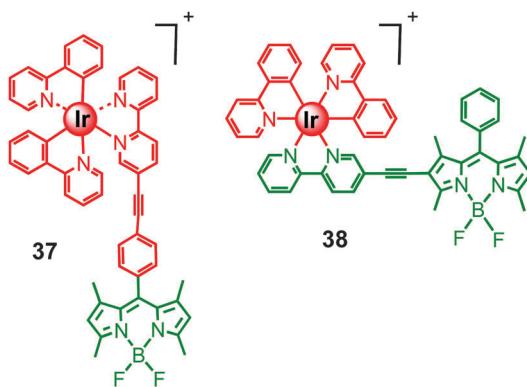
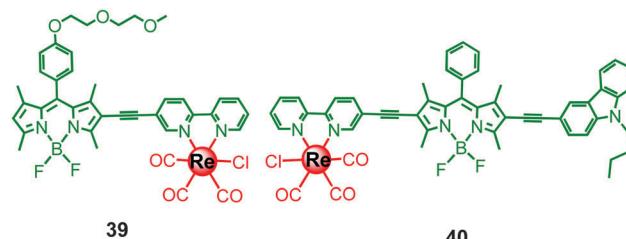
^a For detailed information, please refer to the main text and the references.

Fig. 26 The photophysical processes of Bodipy-containing Ir(III) complex **36**.⁸⁴

in π -conjugation or not in π -conjugation linkage, on the triplet state quantum yield of the light-harvesting antenna, we prepared the Ir(III) complexes **37** and **38** (Fig. 27).¹³⁷ In **37**, the Bodipy moiety is not in π -conjugation with the Ir(III) coordination center, whereas in **38** the Bodipy chromophore is in π -conjugation with the Ir(III) coordination center.

The absorption of **38** is slightly red-shifted as compared with **37**. The residual fluorescence of the Bodipy moiety was observed in both **37** and **38**. The residual Bodipy fluorescence in **38** is only 16% of that of **37**, and thus the ISC is more efficient in **38**. As a support to this postulation, room temperature phosphorescence of the Bodipy moiety at 742 nm was observed with **38**, but not with **37**.¹³⁷ The triplet state lifetimes of **37** and **38** were determined to be 23.7 μ s and 87.2 μ s, respectively. As further proof for the efficient ISC in **38** but not in **37**, the Φ_{Δ} values were determined to be 52% and 97% for **37** and **38**, respectively (Table 4). Thus, we can draw a conclusion that π -conjugated linkage of a visible light-harvesting chromophore to the metal atom of the coordination center is crucial to attain efficient ISC.⁴⁷ This property can be employed to design transition metal complexes showing effective strong absorption of visible light, yet a long-lived triplet excited state. We prepared series of complexes to verify this postulation.⁴⁷

Re(I) complexes have attracted much attention due to the applications in luminescent bioimaging,^{31,34,138–142} photo-voltaics,¹⁴³ and triplet photosensitizers for photocatalysis.^{144–146} However, most of these complexes show weak absorption in the

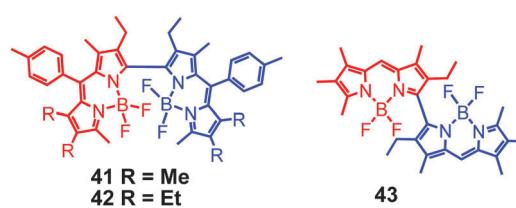
Fig. 27 Bodipy-containing Ir(III) complexes **37** and **38**.¹³⁷Fig. 28 Bodipy-containing Re(I) tricarbonyl chloride complexes **39** and **40**.¹⁴⁷

visible spectra region, and thus we studied the preparation of Re(I) complexes with Bodipy ligands. Based on the aforementioned studies on the Pt(II) and Ru(II) complexes, we used the π -conjugation linker motif to prepare the Re(I) complexes **39** and **40** (Fig. 28).¹⁴⁷

Different Bodipy ligands were used in **39** and **40** to tune the absorption wavelength. **39** shows intensive absorption at 536 nm ($\epsilon = 91\,700\text{ M}^{-1}\text{ cm}^{-1}$), whereas **40** shows absorption at 574 nm ($\epsilon = 64\,600\text{ M}^{-1}\text{ cm}^{-1}$). For both complexes, the residual Bodipy ligand fluorescence was observed, and the fluorescence quantum yields of **39** and **40** were determined to be 0.13% and 17.1%, respectively. Thus we propose that ISC in **40** is non-efficient, which is probably due to the bulky antenna and thus the reduced heavy atom effect (electrons in the large delocalized molecular orbitals may be less likely to ‘feel’ the heavy atom effect of Re). Using ns TA spectroscopy, the triplet state lifetimes of **39** and **40** were determined to be 104.0 μ s and 127.2 μ s, respectively. The singlet oxygen quantum yields (Φ_{Δ}) of **39** and **40** were determined to be 88% and 6%, respectively. Therefore, we propose that with a bulky light-harvesting ligand, the ISC efficiency may decrease drastically. This result may be useful for future designing of the Bodipy-containing transition metal complexes.

2.3. Bodipy dimers showing exciton couplings

It is known that ISC is not only dependent on the heavy atom effect. With two identical chromophores connected in close vicinity, but without π -conjugation, the exciton coupling, *i.e.* the interaction of the transition dipole moments of the chromophores, leads to two delocalized excited states. If the lower singlet exciton state is closer in energy to the triplet state of the chromophore, then ISC can be enhanced.¹¹ Bodipy-dimers **41–43** were reported to show the exciton coupling effect (Fig. 29),¹¹ with a clear indication that the absorption band of the monomer was split into two different absorption bands in the dimer (Fig. 30). **42** shows a Φ_F value of 0.69. Similar Bodipy dimers

Fig. 29 Bodipy dimers **41–43** show the exciton coupling effect.^{11,148}

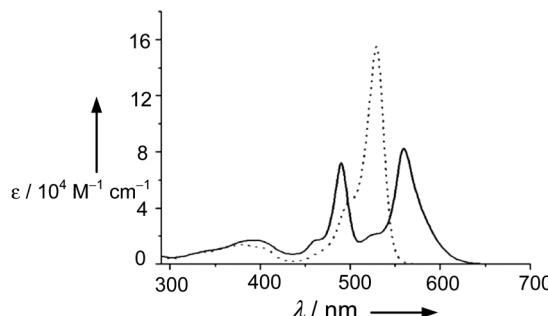


Fig. 30 The spectroscopic properties of **42** (solid line) and the monomer (dot line) in toluene. Reproduced with permission from ref. 148.

Table 5 Photophysical properties of compounds **41–54^a**

	λ_{abs} , nm	ϵ	λ_{em} , nm	Φ_F	Φ_Δ	τ_T , μs	τ_p	Ref.
41	489/558	67 100/77 100	638	0.67	—	—	—	11
42	490/559	72 000/82 600	638	0.69	—	—	—	11
43	3492/565	64 400/73 600	648	0.71	—	0.4	—	148
44	514	—	527	0.03	0.51	—	—	95
45	515	—	588	0.31	0.46	—	—	95
46	542	—	605	0.49	0.21	—	—	95
47	688	211 000	695	0.39	0.47	—	—	113
48	698	146 000	705	0.38	0.20	—	—	113
49	709	287 000	712	0.67	—	—	—	113
50	688	120 000	700	0.22	0.42	—	—	113
51	731	185 000	755	0.38	—	—	—	113
52	738	160 000	763	0.10	—	—	—	113
53	571	83 500	582	0.040	0.581	170.5	—	114
54	529	56 500	608	0.112	0.0493	389.9	—	114

^a For detailed information, please refer to the main text and the references.

showing the exciton coupling effect were reported (**43**, Fig. 42).¹⁴⁸ The dimers show Φ_F values of 0.67–0.76. The Φ_Δ value for **43** was determined to be 0.4 (with TPP as standard, $\Phi_\Delta = 0.70$ in aerated toluene) (Table 5). Thus the ISC in these Bodipy dimers is far from efficient. However, no new progress in this area has been made in recent years.

2.4. Orthogonal Bodipy dimers showing the double substituted excited state

Recently Bodipy dimers based on different structural motifs from that in Fig. 29 were reported (Fig. 31).⁹⁵ The dimers **44–46** (Fig. 31) show no splitting of the UV-vis absorption bands thus the exciton coupling mechanism is excluded. The ISC in these Bodipy dimers is attributed to the closely lying or degenerated

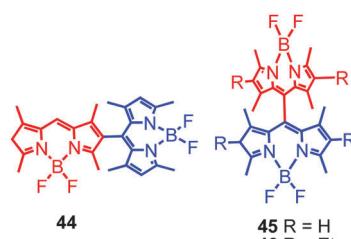


Fig. 31 Bodipy dimmers **44–46** that show ISC.⁹⁵

S_1 states of the two isolated yet identical chromophores in the molecule. The Φ_Δ values of the dimers **44–46** are 0.51, 0.46 and 0.21, respectively (Table 5). A later study shows that this approach is no longer effective with chromophores showing a red-shifted absorption wavelength.⁹⁶ We demonstrated that the triplet state yield of these Bodipy dimers is high and is useful in TTA upconversion.¹⁴⁹

2.5. Heavy atom-free Bodipy-derived triplet photosensitizers

Recently heavy atom free thienyl-fused Bodipy derivatives were reported to show efficient ISC (Fig. 32).¹¹³ Compound **47** shows strong absorption of visible light at 688 nm ($\epsilon = 211 000 \text{ M}^{-1} \text{ cm}^{-1}$), the fluorescence quantum yield (Φ_F) is 22%, and the singlet oxygen quantum yield (Φ_Δ) is 42%.¹¹³ Femtosecond TA spectroscopy was used for the study of the singlet excited state, but no detailed information such as the intersystem crossing rate constant was reported.

Recently Ji *et al.* demonstrated that fused thiophene is crucial for the efficient ISC (Fig. 33).¹¹⁴ For example, **53** shows a triplet state quantum yield (Φ_T) of 63.7%, whereas for **54**, the triplet state quantum yield (Φ_T) is only 6.1%.¹¹⁴ The fluorescence quantum yields of **53** and **54** are 4.0% and 11.2% (Table 5), respectively. Thus it is not reliable to judge the ISC efficiency (not readily available) based on the fluorescence quantum yield. The singlet oxygen quantum yields (Φ_Δ) of the compounds (58.1% and 4.9%, respectively) are in agreement with the triplet state quantum yields (Φ_T). Using nanosecond TA spectroscopy, the triplet state lifetimes of **53** and **54** were determined to be 170.5 μs and 389.9 μs , respectively.

TDDFT computation indicates that the S_1/T_2 energy gap for **53** is small (0.24 eV), and thus $S_1 \rightarrow T_2$ may be the main ISC channel. Moreover, the spin orbit coupling (SOC) is 1.3 cm^{-1} . For **54**, however, the S_1/T_1 energy gap is much larger (0.56 eV), and the SOC is much weaker (0.4 cm^{-1}). Thus the efficient ISC in **53** can be rationalized by the small S_1/T_2 energy gap and the large SOC.¹¹⁴ Unfortunately, it is difficult to implement



Fig. 32 Thieno-pyrrole fused Bodipy dyes showing ISC upon photo-excitation.¹¹³

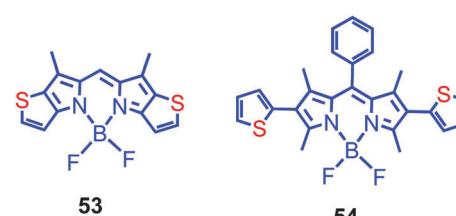


Fig. 33 Thieno-fused Bodipy **53** and the **54** with a dangled thiophene moiety.¹¹⁴

these results to molecular structure designing, since the S₁/T₂ energy gap is not readily available. TDDFT computations may be helpful.

Concerning the formation of the triplet excited state of Bodipy without the heavy atom effect, a C₆₀-Bodipy dyad is an important molecular structure motif for the formation of the Bodipy triplet excited state upon photoexcitation.¹²

Ziessel studied the photophysics of a C₆₀-Bodipy dyad 55 in detail (Fig. 34).¹⁵⁰ It was found that the solvent polarity dictates the photophysical processes of the C₆₀-Bodipy dyad. In a non-polar solvent, such as toluene, no photoinduced charge separation occurred, and this is a general rule that the Gibb free energy change (ΔG°) of PET in a non-polar solvent is less negative than that in polar solvents.^{151–154} Instead, singlet energy transfer from Bodipy to the C₆₀ moiety was predicated. The ISC of the C₆₀ moiety produces the triplet excited state,¹⁵⁵ which is localized firstly on the C₆₀ unit. All these processes were confirmed by ultrafast TA spectra. Although there is a modest driving force for photoinduced electron transfer from the Bodipy moiety to the C₆₀ moiety ($\Delta G^\circ = -0.18$ eV), no C₆₀ π -radical anion was detected using the fs TA spectra (the featured absorption band of C₆₀ radical anion is at 1000 nm), upon selective photoexcitation into the Bodipy moiety by 490 nm excitation (Table 6). FRET may not be the main mechanism for energy transfer, due to the poor spectral overlap of the energy donor and the energy acceptor, as well as the weak absorption of C₆₀ (forbidden S₀ \rightarrow S₁ transition for C₆₀, the singlet energy acceptor).

Using ns TA spectroscopy, equilibrium between the C₆₀ triplet state and the Bodipy triplet state was observed, although most of the triplet state is localized on the C₆₀ moiety. These results are interesting, since it is shown that heavy atom-free

organic triplet photosensitizers can be developed with visible light-harvesting antennae and C₆₀, with C₆₀ as the spin converter.⁴⁷

In polar solvents such as benzonitrile, upon photoexcitation into the C₆₀ part, the S₁ state is populated and it decays within 125 ps, and the CTS formed, indicated by the C₆₀ π -radical anion absorption at 1000 nm and the bleaching band of the Bodipy moiety. The CTS decays with a lifetime of 440 ps. The energy level of CTS is positioned slightly below the triplet states of both the C₆₀ and the Bodipy moieties, and thus no triplet state was produced by charge recombination (CR), instead the ground state (S₀) was produced by CR. Photoexcitation into the Bodipy moiety gives similar photophysical processes.

In less polar solvents such as CH₂Cl₂ and methyltetrahydrofuran, photoexcitation into the Bodipy or the C₆₀ units also lead to the formation of CTS. The CTS is higher in energy than the triplet state, and thus CR produces the triplet state of C₆₀. These conclusions are based on the TA spectral data.

Using different Bodipy antennae for the dyad may change the photophysics. For example, with styrylBodipy as the antenna, no singlet energy transfer from the styrylBodipy antenna to the C₆₀ unit was observed, and only CTS was observed upon excitation, followed by CR giving the triplet state localized on the styrylBodipy unit (56, Fig. 35).¹⁵² This result is in stark contrast to the previous study on the Bodipy-C₆₀ dyad (dyad 55 in Fig. 34), for which the CR selectively gives the C₆₀-localized triplet excited state.

The fluorescence of the styrylBodipy antenna in dyad 56 was dramatically quenched, but no enhancement of the C₆₀ emission was observed, and thus it is proposed that the photoinduced charge separation is responsible for the fluorescence quenching. Electrochemical studies show that the formation of charge transfer state (CTS) is favorable in either PhCN or toluene, with $\Delta G_{\text{CS}} = -0.68$ eV and -0.40 eV, respectively.¹⁵²

Femtosecond TA spectra indicated the formation of a C₆₀ radical anion, which shows absorption at 1000 nm, as well as the absorption of the radical cation of the styrylBodipy moiety at 767 nm. The rate constant of the charge separation is $3.1 \times 10^{10} \text{ s}^{-1}$, and the CR rate constant is $2.1 \times 10^9 \text{ s}^{-1}$. Nanosecond TA spectra show that the styrylBodipy triplet excited state was produced upon photoexcitation, and the triplet state lifetime was determined to be 476 μ s. The photophysical processes are summarized in Fig. 36.

AzaBodipy is interesting due to its absorption in the red/near IR region (600–700 nm).^{89,107} Note that the normal Bodipy

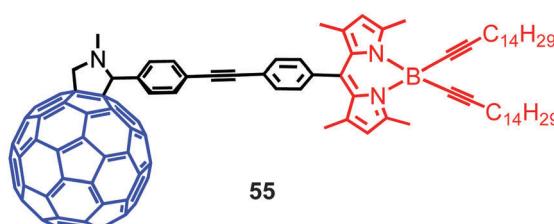


Fig. 34 Bodipy-C₆₀ dyad 55.¹⁵⁰

Table 6 Photophysical properties of compounds 55–60^a

	λ_{abs} , nm	ε	λ_{em} , nm	Φ_F	τ_T , μ s	Ref.
55	335/501/693	—	516/720	—	—	150
56	375/648	—	592/662	—	—	152
57	312/479/640	—	682	—	—	156
58	515	70 400	710	—	33.3	90
59	590	82 500	627	0.017	35.2	90
60	645	56 800	662	0.01	105.6	157
61	331	51 000	—	—	—	158
62	505	102 000	517	—	—	158
63	630	115 000	642	—	—	158
64	593	106 000	611	—	—	158
65	535	—	610	0.005	2.0 ± 0.5	160

^a For detailed information, please refer to the main text and the references.

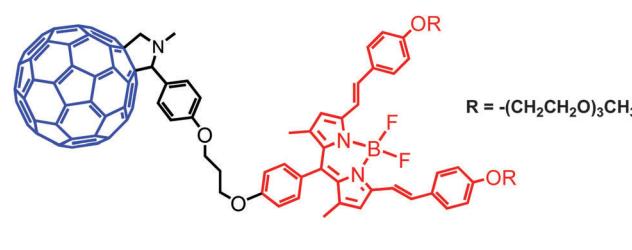


Fig. 35 StyrylBodipy-C₆₀ dyad 56 with triplet state formation.¹⁵²

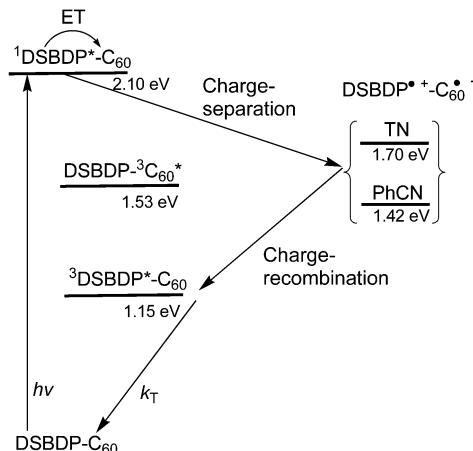


Fig. 36 The photophysical processes involved in styrylBodipy–C₆₀ dyad 56. Reproduced with permission from ref. 152.

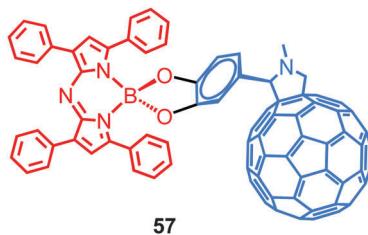


Fig. 37 AzaBodipy–C₆₀ dyad.¹⁵⁶

gives absorption at about 500 nm.⁵³ AzaBodipy was used for preparation of dyad 57 (Fig. 37).¹⁵⁶

The fluorescence of the azaBodipy antenna was significantly quenched in dyad 57, which is attributed to electron transfer. This postulation was confirmed by the observation of the near IR absorption of the C₆₀ radical anion at 1000 nm in the fs TA spectra. By following the kinetics at this wavelength, the rate constant of the charge separation (CS) was determined to be $1.0 \times 10^{12} \text{ s}^{-1}$, and the CR process occurs with a rate constant of $5.0 \times 10^9 \text{ s}^{-1}$. The T₁ state energy level of the azaBodipy (0.79–0.87 eV),¹⁰⁸ which is much lower than that of C₆₀ (1.62 eV).¹⁵⁵ Thus the CR may produce the triplet state of the azaBodipy moiety. The formation of the azaBodipy triplet state was confirmed by ns TA spectra. The triplet state lifetime was determined to be 83.3 μs .

Our group prepared Bodipy–C₆₀ dyads 58 and 59 (Fig. 38).⁹⁰ For 58, the absorption band is centered at 515 nm ($\epsilon = 70\,400 \text{ M}^{-1} \text{ cm}^{-1}$). For 59, the absorption wavelength is red-shifted to 590 nm ($\epsilon = 82\,500 \text{ M}^{-1} \text{ cm}^{-1}$). The fluorescence of the antenna was significantly quenched in the dyads, indicating singlet energy transfer, although CS can't be excluded, especially in polar solvents. ns TA spectra show that for both dyads, the triplet states localized on the C₆₀ moieties were produced upon photo-excitation, indicated by the ESA band of the T₁ state of C₆₀ at 720 nm (Fig. 39). The triplet state lifetimes of 58 and 59 were determined to be 33.3 μs and 35.2 μs , respectively, which are close to the intrinsic triplet state lifetime of C₆₀ ($40 \pm 4 \mu\text{s}$).¹⁵⁵

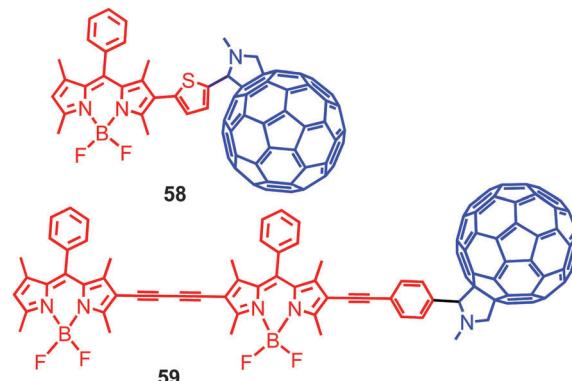


Fig. 38 Bodipy–C₆₀ dyads 58 and 59 with variable visible light absorption.⁹⁰

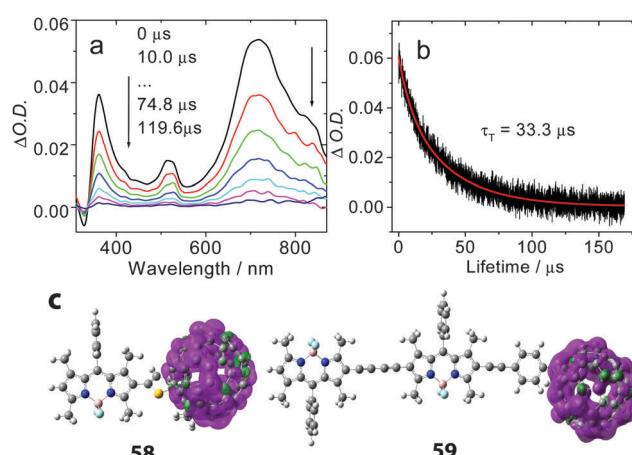


Fig. 39 (a) Nanosecond transient absorption spectra of 58 ($\lambda_{\text{ex}} = 532 \text{ nm}$) and (b) the decay trace at 720 nm. In deaerated toluene, 25 °C. (c) Spin-density surface of 58 and 59 in the triplet state. Calculated at the B3LYP/6-31G(d) level using Gaussian 09W. Reproduced with permission from ref. 90.

It should be pointed out that the localization of the T₁ state is dependent on the energy levels of the Bodipy and the C₆₀ moieties.

For 59, the S₁ state energy level of the antenna decreased by *ca.* 0.3 eV as compared with that of the antenna in 58, but the T₁ state energy level of the antenna in 59 does not decrease significantly, because the triplet state of 59 is still localized on the C₆₀ moiety ($E_{T_1} = 1.65 \text{ eV}$), not on the Bodipy moiety. It was reported that Bodipy is at the T₁ state energy level of *ca.* 1.69 eV. Thus, the relationship between the molecular structure (such as the size of the π -conjugation framework) and the T₁ state energy level is far from clear for organic chromophores.

We prepared styrylBodipy–C₆₀ triad 60 (Fig. 40), which shows red-shifted absorption than 58 and 59.¹⁵⁷ The styrylBodipy antenna shows absorption at 645 nm ($\epsilon = 56\,800 \text{ M}^{-1} \text{ cm}^{-1}$). Notably the triplet state is localized on the styrylBodipy moiety, not on the C₆₀ unit (Fig. 41 and Table 6). This conclusion is based on the ns TA spectroscopy, and the spin density surface analysis (Fig. 41).

The triplet state lifetime of 60 was determined to be 105.6 μs . Notably the 2,6-diiodostyrylBodipy gives the triplet state lifetime

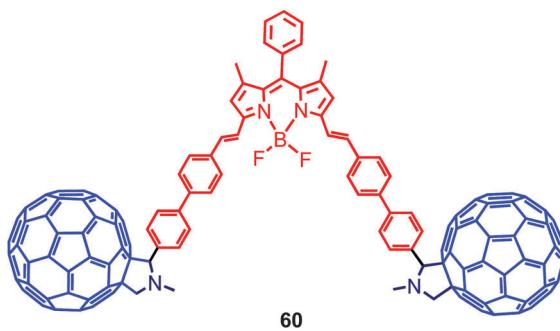


Fig. 40 StyrylBodipy–C₆₀ triad **60** with red light absorption.¹⁵⁷

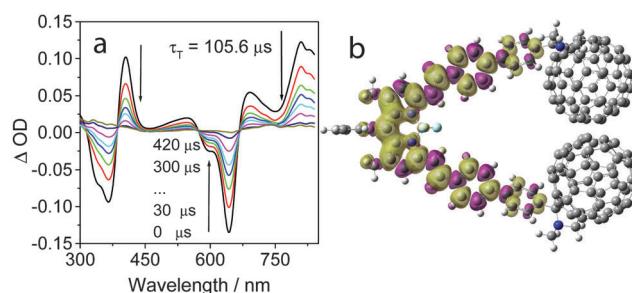


Fig. 41 (a) Nanosecond transient absorption spectra of **60** ($\lambda_{\text{ex}} = 532 \text{ nm}$). In deaerated toluene. (b) Spin-density surface of **60** in the triplet state. Calculated at the B3LYP/6-31G(d) level using Gaussian 09W. Reproduce with permission from ref. 157.

of 1.8 μs (Table 6).⁸⁷ The reason for this drastically different triplet state lifetime is unclear. The Φ_{Δ} value of **60** was determined to be 85%, indicating that the Φ_T value of **60** is high. No femtosecond transient absorption spectra of the triad were studied, and thus it is still open for question whether the triplet state is produced by CR or by backward triplet-triplet energy transfer from the C₆₀ moiety to the styrylBodipy moiety.

We studied the formation of the triplet state of styrylBodipy via intermolecular energy transfer by C₆₀-containing and Bodipy hydrogen bonding modules **61–64** (Fig. 42).¹⁵⁸ **61** is the hydrogen bonding module with C₆₀ as the spin converter, and **62–63** are the hydrogen bonding modules with Bodipy or styrylBodipy as the antenna, which are energy donors. Titration of the Bodipy antenna with the C₆₀ module induces fluorescence quenching, which indicated either singlet energy transfer or electron transfer. Electrochemical studies indicated that intra-assembly photoinduced electron transfer is prohibited, and thus the intra-assembly singlet energy transfer is the most probable mechanism for the fluorescence quenching of the antenna.

Based on the nanosecond transient absorption spectra, triplet state localized on the C₆₀ moiety was observed for the hydrogen bonding assembly of **61–62**. For **61–63** and **61–64**, however, the triplet state localized on the styrylBodipy moiety was also observed. This result is due to the much lower T₁ state energy level of the styrylBodipy (ca. 1.0 eV, based on TD-DFT computation),¹⁵⁹ than the C₆₀ moiety (1.62 eV).¹⁵⁵ The formation

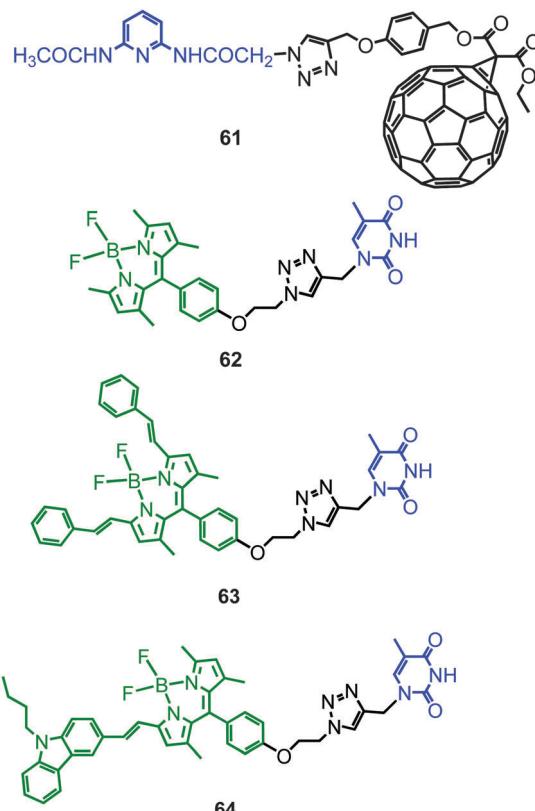


Fig. 42 Hydrogen bonding modules for the formation of the triplet excited state of Bodipy. **62–64** are light-harvesting modules, and **61** is the triplet formation module (singlet energy acceptor and triplet energy donor).¹⁵⁸

of the triplet state localized on the styrylBodipy is most probably due to the intra-assembly TTET. By using the non-hydrogen bonded mixture of the reference modules we demonstrated that the production of the styrylBodipy-localized triplet state for the hydrogen assemblies is not due to intermolecular TTET, which gives slow energy transfer kinetics.¹⁵⁸

Formation of the Bodipy triplet state by CR is not limited to the C₆₀–Bodipy dyads. A Bodipy–N-methylpyridinium dyad **65** was reported to produce a triplet state upon CR (Fig. 43).¹⁶⁰ The fluorescence of the Bodipy moiety was quenched significantly in **65**. The fluorescence quantum yield is only 0.5%, and the majority of the emission of **65** are attributed to the emission from CTS, which is centered at 610 nm, a much longer wavelength than the Bodipy.



Fig. 43 Bodipy–N-methylpyridinium dyad.¹⁶⁰

With nanosecond transient absorption spectra, the triplet state of the Bodipy chromophore was observed, with a triplet state lifetime of $2.0 \pm 0.5 \mu\text{s}$. Interestingly, this lifetime is much shorter than that of the diiodoBodipys (generally longer than $50 \mu\text{s}$).⁸⁵ The quantum yield for formation of the triplet state (Φ_T) is *ca.* 75%. Such a high triplet state quantum yield will be interesting for applications.¹⁶⁰

2.6. Using the FRET effect in designing triplet photosensitizers: broadband visible light-absorption

FRET was extensively used for designing fluorescent molecular probes,¹⁰⁷ light-harvesting molecular arrays,^{66,67,161} and photosensitizers for solar cells.¹⁶² However, FRET was rarely used for designing of triplet photosensitizers.^{47,131,134} One of the advantages of the FRET-based triplet photosensitizers is the broadband absorption of the visible light absorption, and thus photosensitizing ability can be improved if a broadband light source, such as solar light, was used.

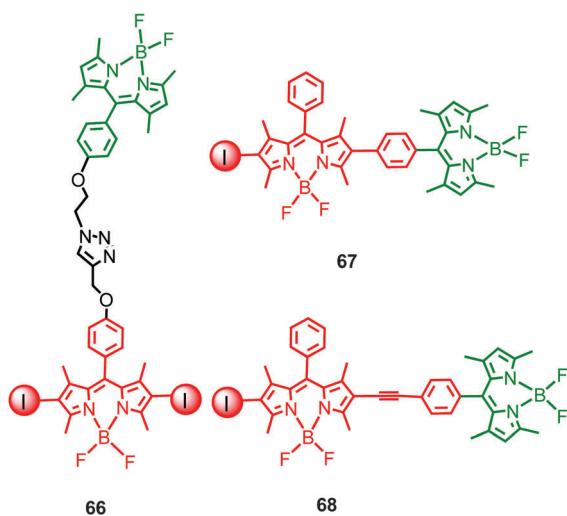


Fig. 44 Bodipy-diiodoBodipy dyads as triplet photosensitizers (**66–68**) (the Bodipy moiety is the singlet energy donor, the diiodoBodipy moiety is the energy acceptor and the spin converter).¹¹⁵

Previously a Bodipy-PtTPTBP (TPTBP = tetraphenyl-tetra-benzoporphyrin) conjugate (compound **34**, Fig. 24) was prepared, and singlet energy transfer from the peripheral Bodipy moieties to the central PtTPTBP coordination center was observed by femtosecond transient absorption spectroscopy.¹³⁴ Interestingly, backward triplet energy transfer from the PtTPTBP coordination center to the Bodipy moieties was also observed. Triplet state equilibrium was proposed and the phosphorescence lifetime of the conjugate is $67 \mu\text{s}$ (was attributed to the Pt(II) coordination center; the Bodipy moieties are non-emissive), which is much longer than the reference complex which contains no Bodipy moieties ($30 \mu\text{s}$). Other Bodipy-containing Pt(II) complexes were also studied and similar forward singlet energy transfer and backward triplet energy transfer were observed.¹³¹

Our group developed the organic mimics of the above dye-precious metal complex conjugates. We designed the dyads **66–68** with Bodipy and iodoBodipy moieties (Fig. 44).¹¹⁵ In **66**, **67** and **68**, the Bodipy moiety gives a shorter absorption wavelength than the iodoBodipy moieties, and its emission band overlaps with the absorption of the diiodoBodipy moiety. Efficient FRET was observed for **66–68** based on comparison of the fluorescence excitation spectra with the UV-vis absorption spectra. Moreover, the diiodoBodipy moiety in **66** is the spin converter.⁸⁵ The absorption wavelength range of **66**, **67** and **68** is broader than diiodoBodipy.¹¹⁵ Based on ns TA spectra, we found that the triplet state of the dyads is delocalized on the two Bodipy moieties in the dyads, *i.e.* a triplet state equilibrium was established. The triplet state lifetimes of the dyads **66**, **67** and **68** were determined to be 286.1 , 241.6 and $262.2 \mu\text{s}$, respectively (Table 7).

In order to obtain dyads with broadband absorption in the more red-shifted wavelength range, we used Bodipy, or carbazole-conjugated Bodipy as the energy donor (variable absorption wavelength was achieved), and diiodo-azaBodipy as the energy acceptor to prepare triplet photosensitizers (triad **69** and **70**, Fig. 45).¹⁶³ The singlet energy transfer efficiency was determined to be 40–50% by comparison of the fluorescence excitation spectra and the UV-vis absorption spectra. It was proposed that this method is more reliable than the very often used energy donor quenching evaluation approach,¹⁶⁴ although this method

Table 7 Photophysical properties of compounds **66–78^a**

	λ_{abs} , nm	ε	λ_{em} , nm	Φ_F	Φ_Δ	τ_T , μs	Ref.
66	505/537	89 800/69 700	554	0.043	0.65	286.1	115
67	504/533	110 400/85 800	577	0.128	0.50	241.6	115
68	506/556	87 800/66 200	584	0.143	0.67	262.2	115
69	593/683	220 000/81 000	610/714	0.16/0.22	0.58	4.1	163
70	504/683	165 000/71 000	520/714	0.53/0.15	0.69	5.5 (3.7)	163
71	551	52 700	659	0.058	0.738/0.524	1.64	159
72	552	29 400	698	0.086	0.396/0.087	3.29	159
73	<i>ca.</i> 650	—	—	—	—	—	103
74	<i>ca.</i> 650	—	<i>ca.</i> 680	—	—	—	103
75	<i>ca.</i> 650	—	<i>ca.</i> 680	—	—	—	103
76	<i>ca.</i> 690	—	<i>ca.</i> 625	—	—	—	103
77	630–660	—	—	—	—	—	179
78	652	121 000	715	0.42	—	—	69
78 + H⁺	650	105 000	700	0.02	—	—	69

^a For detailed information, please refer to the main text and the references.

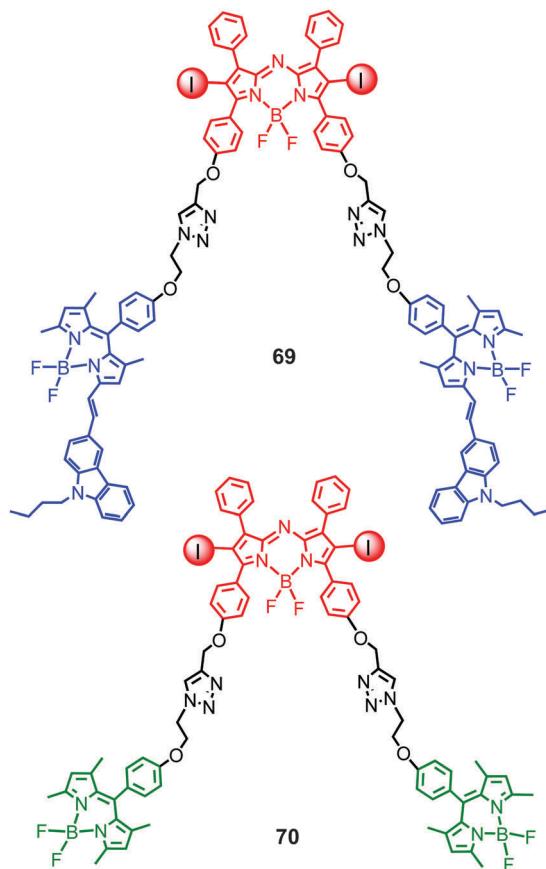


Fig. 45 Diiodo-azaBodipy derived broadband visible light-absorbing triplet photosensitizers **69** and **70**.¹⁶³

of comparison of the excitation/absorption spectra gives apparently a lower energy transfer efficiency value.

The singlet energy transfer in triads **69** and **70** was confirmed by the femtosecond transient absorption spectra, and the FRET rate constants were determined to be $(5.1 \pm 0.4) \times 10^{11} \text{ s}^{-1}$ and $(4.3 \pm 0.3) \times 10^{10} \text{ s}^{-1}$, respectively. The different energy transfer rate constants were attributed to the different spectral overlap in triads **69** and **70**. The energy donor and the acceptor in triad **69** show better spectral overlap than that in **70**. It should be pointed out that the singlet energy transfer mechanism for **70** is probably through-bond-energy-transfer (TBET), not FRET, because the spectral overlap is poor, which is detrimental to the FRET.² Based on ns TA spectra, we concluded that the triplet state is localized on the diiodoazaBodipy moieties. The triplet state lifetimes of **69** and **70** were determined to be 4.1 μs and 5.5 μs , respectively.

Rhodamine is a well known visible light-absorbing chromophore, and has been widely used in the preparation of FRET molecular dyads.^{165–167} However, no application of rhodamine in the construction of an organic triplet photosensitizer was reported. Rhodamine normally shows weak ISC.¹⁶⁸ On the other hand, rhodamine derivatives usually contain a carboxylic moiety, which may complicate the application due to the acid/base- or solvent-driven reversible spirolactam \leftrightarrow opened amide transformation.^{166,169} The spirolactam structure of rhodamine

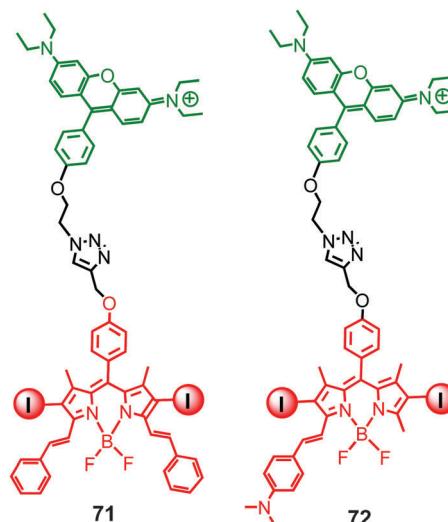


Fig. 46 Rhodamine-diido-styrylBodipy dyad triplet photosensitizers (**71** and **72**) which give broadband visible light-absorption.¹⁵⁹

gives no visible light-absorption, while the opened-amide form gives strong absorption at *ca.* 570 nm.¹⁶⁶ In order to eliminate this complicity in the photophysical study, we used a rhodamine framework which is without the carboxylic moiety for the preparation of broadband visible light absorbing triplet photosensitizers **71** and **72** (Fig. 46).¹⁵⁹

In dyads **71** and **72**, rhodamine was used as a singlet energy donor and diiodostyrylBodipy was used as a singlet energy acceptor, as well as a spin converter for triplet formation, so that these conjugates can be used as broadband visible light-absorbing triplet photosensitizers.⁴⁷ The UV-vis absorption of **71** indicated that there is no strong interaction between the components in the ground state. Fluorescence quenching of the rhodamine part in **71**, and the comparison of the fluorescence excitation spectrum and the UV-vis absorption spectrum of **71** supports singlet energy transfer (the efficiency is calculated to be *ca.* 50%). Femtosecond TA spectra indicate the FRET rate constant of dyad **71** is $k_{\text{FRET}} = 6.7 \times 10^{11} \text{ s}^{-1}$. The triplet state localized on the styrylBodipy moiety was observed. The triplet state lifetimes of **71** and **72** were determined to be 1.64 μs and 3.29 μs , respectively (Table 7). For **71**, the Φ_{Δ} value was determined to be 52% upon excitation of the rhodamine part.¹⁵⁹ At a longer excitation wavelength, *i.e.* upon excitation into the styrylBodipy moiety, the Φ_{Δ} value increased to 73%. The $^1\text{O}_2$ photosensitizing ability of **71** is higher than the diiodostyrylBodipy reference compound which contains only a single light-harvesting chromophore.

3. To switch the triplet excited state of Bodipy

Switching or modulation of the singlet excited state of Bodipy gives a vast amount of functional materials, such as fluorescent molecular probes,⁵⁷ molecular logic gates,^{170–175} and visible light-harvesting molecular arrays.⁶⁷ Similarly, it will be important

to modulate the triplet excited state of Bodipy. However, the related research is still in the infancy and we believe that this area will flourish. Due to the difference of the energy levels and the spin multiplicity of the triplet state and the singlet excited state, the principles governing the modulation of the triplet excited state may be different from the modulation of the singlet excited states, and this postulation was supported by preliminary studies.¹⁷⁶ Herein we summarize the recent development on the switching/modulation of the triplet excited states of Bodipy.

3.1. Switching the triplet state with the controlling PET effect

PET is one of the most popular mechanisms to switch the singlet excited state of organic chromophores,⁵⁷ including Bodipy (such as fluorescence).^{177,178} Concerning the controlling of the triplet excited states, previously O'shea studied the acid-activated PDT effect of the azaBodipy derivatives under neutral and acidic conditions (Fig. 47).¹⁰³ 74–76 contain amino groups, and thus protonation of the amino moiety may inhibit the PET,⁵⁷ as a result the $^1\text{O}_2$ photosensitizing ability may be enhanced. This molecular designing rational is based on the study of the PET modulated fluorescence.⁵⁷ 76 shows *in vitro* PDT activity toward MRC5 cell lines. With DPBF as the $^1\text{O}_2$ scavenger, the $^1\text{O}_2$ photosensitizing ability was enhanced for 73 and 74 in the presence of acid. The triplet state was not studied in detail by nanosecond transient absorption spectroscopy.

A molecular logic gate based on Bodipy was reported (77), with the $^1\text{O}_2$ photosensitizing as the output (Fig. 48).¹⁷⁹ The crown ether moiety in 77 is the Na^+ binding site, whereas the pyridine moiety is the acceptor for H^+ . It was shown that in the presence of only Na^+ or only H^+ (TFA in acetonitrile), the $^1\text{O}_2$ production is weak. It is only in the presence of both Na^+ and H^+ , the $^1\text{O}_2$ production was greatly enhanced. It was proposed that the enhanced $^1\text{O}_2$ production in the presence of acid is due to the red-shifting of the absorption band upon protonation of the pyridine moiety (from 630 nm to 660 nm) (Table 7), as a result, the absorption band at 660 nm matches the light



Fig. 48 Bodipy derived molecular logic gate with $^1\text{O}_2$ production as an output.¹⁷⁹

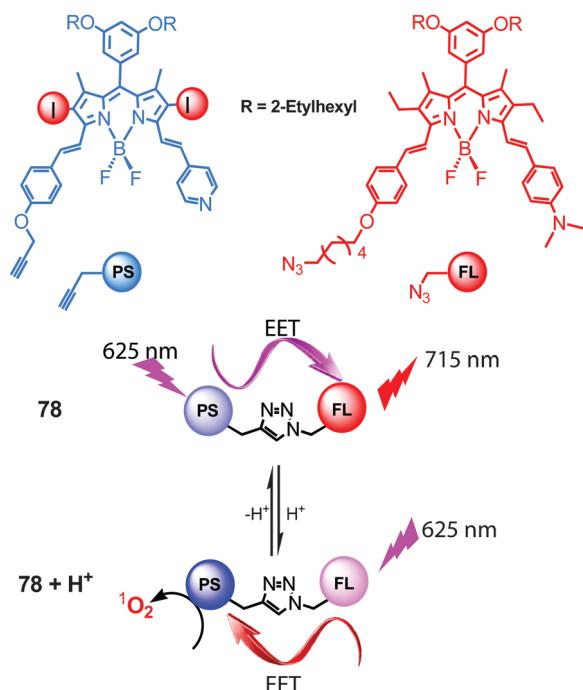


Fig. 49 Modular assembly of the molecular logic device with two different outputs depending on the acidity of the medium. EET stands for electronic energy transfer. Reproduced with permission from ref. 69.

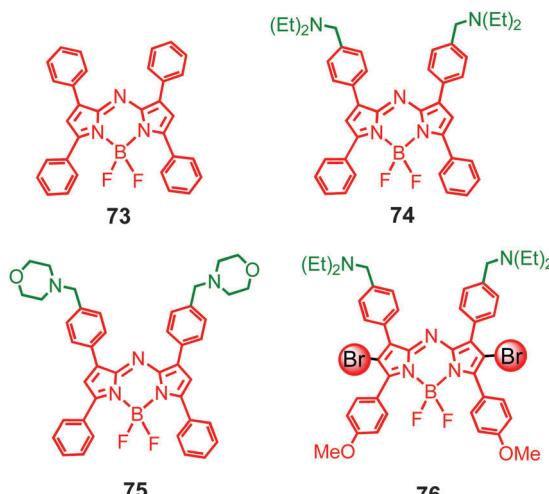


Fig. 47 AzaBodipy derivatives 74–76 with the PET effect.¹⁰³

source better (660 nm LED array), and thus the production of $^1\text{O}_2$ was enhanced.

Akkaya prepared Bodipy dyad logic gates with $^1\text{O}_2$ photosensitizing ability as one of the outputs (Fig. 49).^{69,180} A Bodipy derived dyad 78 was prepared. The diiodostyrylBodipy part is the FRET energy donor, and the uniodinated styrylBodipy part is the energy acceptor. The ISC of the singlet energy donor is assumed to be quenched by FRET, and thus, no $^1\text{O}_2$ photosensitizing ability should be observed for the dyad. However, another possibility exists, *i.e.* there is intramolecular TTET and the triplet energy acceptor shows a short-lived triplet excited state, which is inefficient to photosensitize singlet oxygen ($^1\text{O}_2$).

With addition of acid, *i.e.* upon protonation of the uniodinated styrylBodipy unit, the absorption of the singlet energy acceptor is blue-shifted, and thus the initial FRET is inhibited (which was assumed to be competitive to the ISC); as a result, the $^1\text{O}_2$

photosensitizing ability of the iodinated styrylBodipy unit was observed.⁶⁹ Upon addition of acid, the $^1\text{O}_2$ photosensitizing ability of compound **78** was enhanced by 7-fold.

3.2. Chemical-activated triplet photosensitizers

The triplet excited state can be switched by chemical inputs.^{181,182} For example, thiol-activated $^1\text{O}_2$ photosensitizer **79** was studied (Fig. 50).¹⁸³ Thiol compounds are biologically significant, for example, it was known that the concentration of glutathione (GSH) in cancer cells is much higher than that in normal cells. Thus a thiol-activatable PDT reagent can be used as a targeted PDT reagent. To achieve this goal, a 2,4-dinitrobenzenesulfonate (DNBS) moiety was attached onto the dibromostyrylBodipy triplet photosensitizer (Fig. 50). Previously it was known that DNBS is an electron trap to quench the fluorescence, *i.e.* for caging of fluorescence, and thiol-selective fluorescent molecular probes have been developed using this strategy.^{184–188} In photosensitizer **79** (Fig. 50), DNBS was presumably used for quenching the triplet excited state, probably *via* the PET process.¹⁸³

The photosensitizer gives strong absorption at 650 nm. Without thiols such as GSH, the caged photosensitizer hardly gives any $^1\text{O}_2$ production upon photoexcitation. In the presence of GSH, the cleavage of the DNBS moiety can be traced by the fluorescence recovery at 683 nm. The effect of the caging effect of the DNBS moiety on the triplet state formation (thus the $^1\text{O}_2$ photosensitizing ability) was demonstrated by the comparison of the $^1\text{O}_2$ photosensitizing ability of **79** and the reference photosensitizer **80**. It was shown that the $^1\text{O}_2$ photosensitizing ability of sensitizer **80** is much more efficient than the caged photosensitizer **79**. The *In vivo* photodynamic effect of **79** was demonstrated with HCT116 cells. Interestingly, no phototoxicity was found for **79** toward normal cells, such as MRC-5 cells.

With compounds **81** and **82** (Fig. 51), we systematically studied the different quenching effect of the DNBS moiety on the fluorescence (singlet excited state) and the triplet state of Bodipy in detail.¹⁷⁶

The quenching effect of DNBS on the fluorescence (singlet excited state) of Bodipy was studied with compound **81**. It was shown that the fluorescence of compound **81** ($\Phi_F = 0.6\%$) is greatly reduced as compared to Bodipy ($\Phi_F = 90\%$). The fluorescence

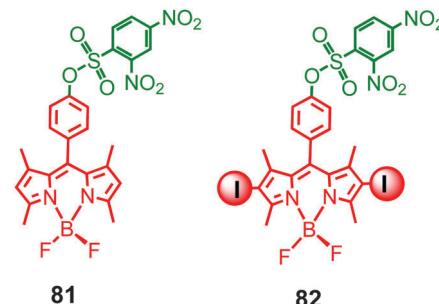


Fig. 51 Compounds used for comparison of the different quenching effect of DNBS on the singlet excited state (fluorescence, **81**) and the triplet state of the Bodipy chromophore (**82**).¹⁷⁶

lifetime was reduced to 1.67 ns for compound **81**, as compared with the lifetime of 3.86 ns for Bodipy.

The Gibbs free energy changes (ΔG_{CS}°) of the PET process of **81** was calculated based on the electrochemical and spectral data. The results show that the PET process for **81** is thermodynamically allowed in solvents of toluene, CH_2Cl_2 and acetonitrile. The ΔG_{CS}° values were calculated to be -0.27 eV , -0.61 eV and -0.71 eV , respectively. The energy levels of the charge transfer states (CTS) of **81** in different solvents were also calculated to be 2.15 eV , 1.81 eV and 1.71 eV in toluene, dichloromethane and acetonitrile, respectively. Note that the S_1 state (emissive state) of Bodipy is *ca.* 2.48 eV . Thus the quenched fluorescence of compound **81** can be fully rationalized by the low-lying CTS, which is below the S_1 state. These data are in full agreement with the fluorescence quenching experimental results.¹⁷⁶

On the other hand, we found that the PET in **82** is prohibited. For example, the ΔG_{CS}° values for **82** in toluene, dichloromethane and acetonitrile were calculated to be $+0.90\text{ eV}$, $+0.46\text{ eV}$ and $+0.33\text{ eV}$ (with the triplet state of Bodipy as the electron donor). The CTS energy level was also calculated for **82**. The energy levels of the CTS are 2.42 eV , 1.98 eV and 1.85 eV . All these CTS energy levels are higher than the T_1 state energy levels of the Bodipy moiety (*ca.* 1.52 eV). Thus, the triplet state of **82** is unlikely to be quenched efficiently by the putative PET. Experimentally, we found that the $^1\text{O}_2$ quantum yield of **82** does not increase significantly upon cleavage of the DNBS (electron acceptor). For example, the Φ_Δ value of **82** in acetonitrile is 74% , and it increases only slightly to 88% upon cleavage of the DNBS by thiols. Note that diiodoBodipy gives a Φ_Δ value of 79% .⁸⁷ This result is in stark contrast to the distinct switch-ON effect of fluorescence in **81** upon cleavage of the DNBS moiety. In less polar solvents, such as toluene and dichloromethane, the Φ_Δ value of **82** increases only slightly upon cleavage of the DNBS moiety by thiols.¹⁷⁶ The triplet state lifetime of **82** is only increased from $24.7\text{ }\mu\text{s}$ to $86.0\text{ }\mu\text{s}$ (in CH_3CN), upon cleavage of the DNBS with thiols. In less polar solvents, no significant triplet state lifetime changes were observed with cleavage of the DNBS moiety. For example, in CH_2Cl_2 , the triplet state lifetime of **82** was determined to be $166.6\text{ }\mu\text{s}$ and $168.1\text{ }\mu\text{s}$, in the absence and presence of thiols, respectively. Thus, we conclude that the triplet state of the Bodipy moiety in **82** was not significantly quenched by DNBS (PET) (Table 8).

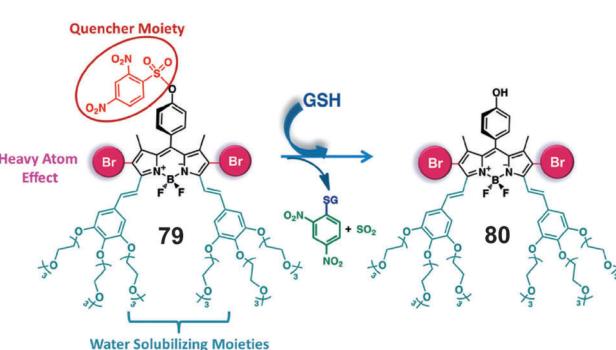


Fig. 50 Caged triplet photosensitizer based on dibromostyrylBodipy **79**, and the reference compound **80**.¹⁸³ Reproduced with permission from ref. 183.

Table 8 Photophysical properties of compounds 81–87^a

	λ_{abs} , nm	ε	λ_{em} , nm	Φ_F	Φ_Δ	τ_T , μs	Ref.
81	506	92 600	519	0.006	—	—	176
82	533	91 000	556	0.017	0.74	24.7	176
83	589/660	109 000/56 000	693	0.0046	—	—	189
84	573	120 000	591	0.003	0.0019	168.6	192
85	627	109 000	644	0.004	0.0011	—	192
86	535	132 000	553	0.03/0.016	0.876/0.369	105.1/40.9	206
87	504	—	518	0.817	—	—	209

^a For detailed information, please refer to the main text and the references.

Based on the above analysis, it is clear that the effect of the same electron acceptor on the singlet and the triplet excited state of the same chromophore may vary drastically. This preliminary conclusion is reasonable, since the driving force for the PET with the molecule in the singlet excited state and the triplet excited state should be drastically different because of the large energy level difference of the singlet and triplet excited states of Bodipy (or other normal chromophores); thus according to the Weller equation, the $\Delta G_{\text{CS}}^\circ$ value will be different for the singlet excited state and the triplet excited state.¹⁵²

We prepared an acid-responsive Bodipy-based dyad triplet photosensitizer **83** (Fig. 52), to study the modulation of the triplet by controlling FRET, as well as ICT.¹⁸⁹ In **83**, the diiodostyryl-Bodipy unit is the triplet-formation unit, and the dimethylaminostyrylBodipy part is the acid-responsive part, for which the absorption wavelength and the S_1 state energy level can be changed by protonation.¹⁹⁰ Protonation of the dimethylamino group will change the absorption wavelength (singlet excited state energy level),¹⁹⁰ and most probably also the T_1 state energy level of the moiety.

The fluorescence intensity of **83** decreased in polar solvents, but the emission wavelength did not change.¹⁸⁹ With reference compounds, we confirmed that the emission of **83** is due to the diiodostyrylBodipy unit. The changing of the fluorescence emission intensity is due to the modulated FRET effect by protonation of the dimethylamino group. The dimethylaminostyrylBodipy part is the singlet energy acceptor, yet it shows shorter absorption wavelength than the singlet energy donor. This is due to the larger Stokes shift of the dimethylaminostyrylBodipy part, and this is a rare example in FRET that the singlet energy acceptor shows a shorter absorption wavelength than the energy donor. Normally, the singlet energy acceptor in FRET gives a longer absorption wavelength than the singlet

energy donor.^{2,67,191} As proof of these postulations, the reference compound of the dimethylaminostyrylBodipy showing a solvent-polarity-dependent fluorescence emission wavelength was studied.^{189,190} The two units in **83** (diiodoBodipy and the uniodinated Bodipy parts) give absorption at 586 nm and 663 nm, respectively. Upon addition of acid HCl (in mixed MeCN/H₂O, 9 : 1, v/v), the absorption band at 586 nm decreased, while a new absorption band at 552 nm developed. The absorption band at 663 nm did not change.

The triplet excited state of **83** was studied by ns TA spectroscopy.¹⁸⁹ In toluene, triplet state localized on the diiodostyryl-Bodipy part was observed, with a triplet state lifetime of 1.6 μs . In polar solvents of DCM and MeCN, however, no triplet state was observed. This result can be attributed to either an efficient FRET, or the formation of the triplet state localized on dimethylaminostyrylBodipy by intramolecular TTET, which is very short-lived. Based on the fluorescence study, it is more likely that the TTET occurred, and the triplet state localized on the dimethylaminostyrylBodipy part was produced, but it is short lived, probably quenched by the ICT effect.¹⁸⁹ Upon addition of acid (protonation of the dimethylamino group), triplet state localized on the diiodostyrylBodipy moiety was observed, as well as slight population of the protonated dimethylaminostyrylBodipy moiety (in mixed MeCN/H₂O, 9 : 1, v/v). Thus switching of the triplet state by acid was observed in polar solvents. The switching effect was demonstrated by $^1\text{O}_2$ photosensitizing. For **83**, the Φ_Δ value is 6.0% (in mixed MeCN/H₂O, 9 : 1, v/v). Upon addition of acid, the Φ_Δ value increased to 59.2%.

We also prepared styrylBodipy-C₆₀ dyads for triplet excited state switching (**84** and **85**, Fig. 53).¹⁹² The switching is based on either the acid-inhibited PET (**84** with styrylBodipy as the energy donor and the C₆₀ unit as the energy acceptor), or the acid-activated FRET-ISC-TTET cascade photophysical processes (**85**).

In **84**, the S_1 state energy level of the antenna is higher than the S_1 state of the fullerene, thus singlet EnT from the styrylBodipy moiety to the C₆₀ unit is probable. In toluene, the triplet state localized on the styrylBodipy part was observed ($\tau_T = 168.6 \mu\text{s}$). In polar solvents such as dichloromethane, however, no triplet excited state signal was observed. This result is attributed to the electron transfer in dichloromethane ($\Delta G_{\text{CS}} = -0.10 \text{ eV}$), but not in toluene ($\Delta G_{\text{CS}} = +0.40 \text{ eV}$). ICT of the styrylBodipy may also contribute to the different triplet state property in different solvents. Upon addition of acid, the absorption band at 623 nm decreased, and the absorption band

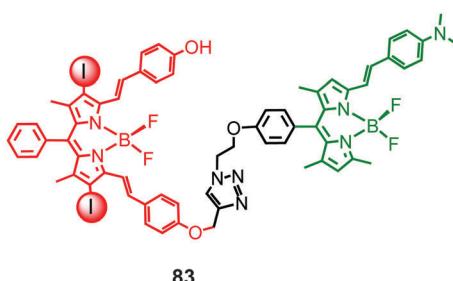


Fig. 52 Acid-responsive Bodipy based dyad triplet photosensitizer.¹⁸⁹

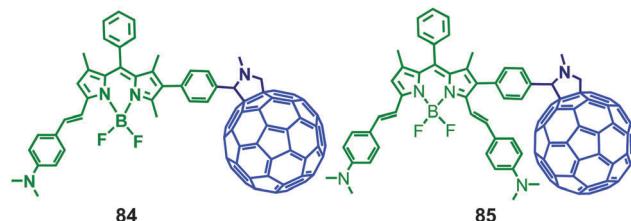


Fig. 53 Acid-responsive Bodipy–C₆₀ dyad triplet photosensitizer.¹⁹²

at 573 nm developed. Upon addition of acid, thus protonation of the dimethylamino group, the triplet state was observed for **84** in polar solvents, with a triplet state lifetime of 4.4 μ s. Thus in polar solvents, the formation of the long-lived triplet state is switched on by inhibition of the PET process between the antenna and the C₆₀ moieties, as well as the ICT effect of the dimethylaminostyrylBodipy moiety.

For **85** (Fig. 53), the photophysical processes are different from that of **84**. Firstly, the S₁ state energy level of the antenna is lower than that of C₆₀. Thus even in non-polar solvents such as toluene, no triplet state was observed for **85**, notably PET is prohibited for **85** in toluene ($\Delta G_{CS}^{\circ} = +0.31$ eV), and thus the lack of formation of triplet state of the styrylBodipy unit can only be attributed to the frustrated singlet energy transfer, not any PET or ICT processes. Upon addition of acid, the absorption band of the antenna at 721 nm decreased, and an absorption band at 627 nm appeared. The triplet state was observed for **85** upon protonation, even in a polar solvent such as dichloromethane. The triplet state lifetime is $\tau_T = 74.8$ μ s.

3.3. Photoswitching of the triplet excited state of Bodipy

Besides the chemical-stimulated triplet state switching, light-switching is of particular interest, because it is a minimal invasive method.^{193,194} Light-switching of the triplet state of Ru(II) and Ir(II) complexes by using photochromic compounds has been studied.^{195–197} On the other hand, the fluorescence (singlet excited state) of Bodipy was also switched by photochromic units.^{198–201} However, to the best of our knowledge, the triplet state of Bodipy has never been photoswitched.

Inspired by the study of switching the ¹O₂ photosensitizing ability of ZnTPP (TPP = tetraphenylporphyrin) by photochromic dithienylethene (DTE),²⁰² recently our group used DTE compounds to control the triplet state property of diiodoBodipy (Fig. 54).²⁰³ DTE is a well known photochromic chromophore, due to the distinctly different absorption and the excellent stability of the two isomers.¹⁹³

It is well known that the singlet excited state energy level of DTE-1(o) and DTE-1(c) is different (therefore it is photochromic!). For example, the S₁ state energy level of DTE-1(o) is 4.79 eV, and the S₁ state energy of the DTE-1(c) is 2.18 eV. Actually the T₁ state energy level of the DTE change substantially upon photocyclization/photoreversion.^{195,204,205} The T₁ state energy of the DTE-1(o) is 1.97 eV, and it is 1.23 eV for the DTE-1(c).¹⁹⁵ Note that the T₁ state energy level of diiodoBodipy is ca. 1.50 eV (Fig. 54).⁸⁵ Thus, the T₁ state of the diiodoBodipy can probably be quenched by DTE-(c), via intermolecular TTET (the long-lived

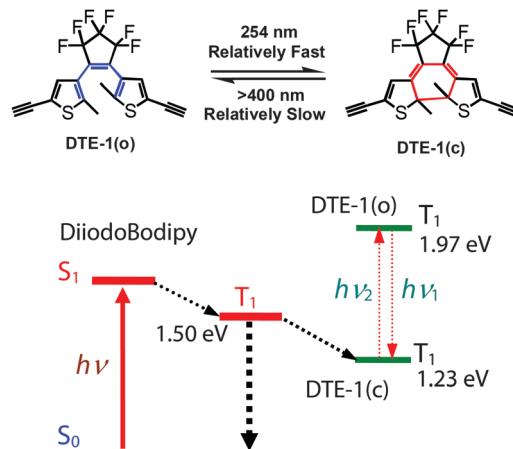


Fig. 54 Photoswitching of the triplet state of diiodoBodipy by using DTE, via intermolecular TTET.²⁰³

triplet excited state of diiodoBodipy makes this process efficient), but not by DTE-(o) (Fig. 54). Since the DTE-(o) and DTE-(c) is reversibly transformed by UV-visible light irradiation, the T₁ state lifetime of diiodoBodipy can be reversibly reduced by light. Note that the singlet excited state of diiodoBodipy (or other chromophores) is unlikely to be significantly quenched via intermolecular energy transfer because the singlet excited state lifetime is much shorter than the triplet excited state.²

The quenching constant of DTE-(c) on the triplet state of diiodoBodipy was determined to be $k = (3.05 \pm 0.11) \times 10^5 \text{ M}^{-1}$ by using ns TA measurements. The triplet excited state lifetime of diiodoBodipy can be quenched from 84.7 μ s to 15.9 μ s, in the presence of the closed form of DTE.²⁰³ We also used this switch to control the TTA upconversion, and a distinct upconversion switching effect was observed.²⁰³

Note that the success of using DTE-(c) as a quencher for the T₁ state of diiodoBodipy is due to the ‘dark quencher’ feature of DTE-(c). That is, photoreversion (closed form \rightarrow open form of DTE) occurs with a much lower quantum yield ($\Phi_{C \rightarrow O} = 0.045$) than the UV-driven photocyclization quantum yield ($\Phi_{O \rightarrow C} = 0.299$), and also importantly, the fact that the T₁ state of DTE-(c) is short lived (much shorter than 1 ns).¹⁹⁵ Thus DTE-(c) is a ‘dark’ triplet state quencher, because no further intermolecular process can be initiated efficiently with the shorted-lived triplet state localized on the DTE-(c) moiety.

We also studied the photoswitching of the triplet state of 2,6-diiodoBodipy with the DTE moiety in a molecular triad (**86**, Fig. 55).²⁰⁶ Upon photocyclization of the DTE unit, the triplet state lifetime of the diiodoBodipy unit in **86** is decreased from 105.1 μ s to 40.9 μ s. Calculation of the ΔG_{CS}° value indicated that PET is thermodynamically prohibited for **86** with the DTE either in the open form or the closed form. Thus the decrease of the triplet state lifetime of the diiodoBodipy moiety is due to TTET. The formation of the triplet state of the diiodoBodipy is also inhibited by the singlet energy transfer to the closed-DTE moiety, demonstrated by the quenching of the fluorescence of the diiodoBodipy part upon photocyclization of the DTE unit.²⁰⁶

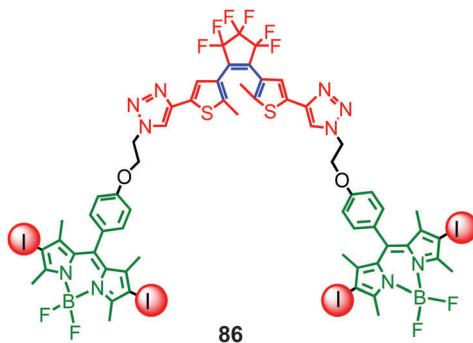


Fig. 55 Photoswitching of the triplet state of diiodoBodipy by using DTE, via intramolecular TTET.²⁰⁶

It should be pointed out that a photostationary state (PSS) is always established for the photochromic compounds,^{193,207} and thus the photocyclization of the DTE unit in **86** is incomplete (the closed form is 85.2% of the mixture at the PSS, by HPLC analysis).²⁰⁶ Therefore, the triplet excited state lifetime of diiodoBodipy with DTE in **86** in the closed form may be due to the intermolecular quenching, not the incomplete intramolecular TTET. We anticipate that quenching of the triplet state of diiodoBodipy by intramolecular TTET may be very efficient. Isolation of the pure **86** with the DTE moiety in the closed-ring formation may help to clarify this situation.²⁰⁸ The $^1\text{O}_2$ production of **86** with the DTE unit in the opened form is 87.6%, and it was reduced to 36.9% upon UV irradiation (the photocyclization of the DTE unit). Photoswitching TTA upconversion was also performed with **86**.²⁰⁶

For **86** (Fig. 55), excitation into the diiodoBodipy unit will not sensitize the photocyclization of the DTE unit, which is different from the previously reported DTE-containing Ru(II) complexes, for which photocyclization was sensitized by the triplet state of the Ru(II) coordination centre.¹⁹⁵ Although it is an advantage that the photocyclization of DTE can be performed with visible light excitation *via* sensitizing, the DTE and the Ru(II) coordination center cannot be independently addressed. For **86**, however, the two chromophores (diiodoBodipy and the DTE unit) can be independently photo-addressed.

Our group also developed a Bodipy-derived photoswitchable triplet energy acceptor (a DTE-Bodipy triad) for application in TTA upconversion (**87**, Fig. 56).²⁰⁹ The designing rational for **87** is to use the DTE unit to photoswitch the fluorescence of the Bodipy part, and thus the TTA upconversion (with PdTPBP as the triplet photosensitizer, because of its proper triplet state energy level. TPTBP = tetraphenyltetrazenoporphyrin). As a triplet energy acceptor, the triplet state of the Bodipy units in **87** can also be quenched by the closed-form of DTE.

Based on the nanosecond transient absorption spectra, it was found that **87** with the DTE unit in the closed-form is a more efficient triplet acceptor than **87** with the DTE unit in the opened form. This result also indicates that DTE-(c) is a more efficient energy acceptor than the Bodipy moiety because for **87** the effective triplet acceptor is the Bodipy moiety, and for **87** with DTE in the closed form, the effective triplet acceptor may be the

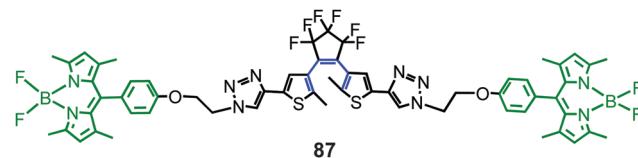


Fig. 56 Triad **87** based on dithienylethene (DTE) and Bodipy was used as a triplet acceptor/emitter in the photoswitching of TTA upconversion. The photochromism of **87** is illustrated with DTE-o and DTE-c in Fig. 54.²⁰⁹

DTE-c unit, which is at lower triplet state energy level than that of Bodipy, and thus the driving force for the intermolecular TTET is larger. The bimolecular quenching rate constants are $k_q = 2.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_q = 6.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for **87** with the DTE unit in the open and the closed form, respectively.

Photoswitchable TTA upconversion was observed with **87** as the triplet acceptor/annihilator.²⁰⁹ With the DTE moiety in the open form, TTA upconversion may be observed. Based on our previous study, however, we proposed that the intramolecular TTET may quench the triplet state of the Bodipy moiety, and thus the TTA upconversion will be switched off upon UV irradiation, with photocyclization of the DTE moiety in **87**. Moreover, the singlet excited state of the Bodipy can also be quenched by the closed form of DTE. Thus, three mechanisms, the intermolecular TTET, intramolecular TTET and the FRET may play the switching role at the same time for photomodulation of the TTA upconversion with **87** as the triplet acceptor.²⁰⁹ A similar strategy for photoswitching of the TTA upconversion was also applied in a DTE-DPA triad (DPA = 9,10-diphenylanthracene).²¹⁰

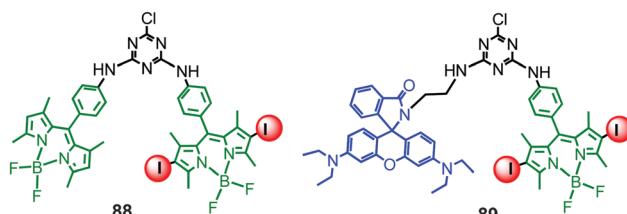
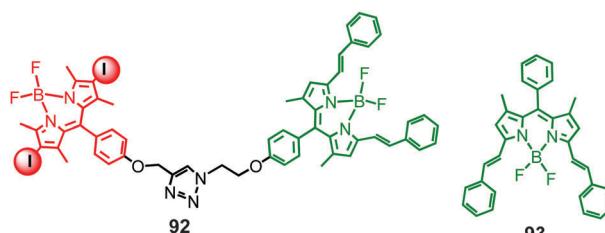
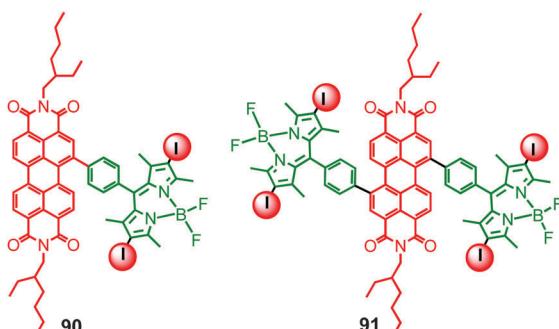
3.4. Modulation of the triplet excited state of Bodipy by competing FRET process

The formation of the triplet excited state of Bodipy can be controlled by a competing FRET process. Chromophore conjugates with such a photophysical process were rarely studied.⁶⁹ We constructed a diiodoBodipy-rhodamine conjugate to study the competing ISC and FRET effect on the photophysical properties. We used cyanuric chloride as a rigid linker between the diiodoBodipy and the rhodamine moiety (**89**, Fig. 57).²¹¹ Firstly we prepared a Bodipy-diiodoBodipy dyad **88**. Similar to our previous study,¹¹⁵ triplet state delocalization was observed for **88**, indicating that the cyanuric chloride linker is efficient for triplet state energy transfer (probably *via* electron exchange (Dexter mechanism)).

Without acid, the triplet state localized on diiodoBodipy moiety in **89** was observed, with $\tau_T = 51.7 \mu\text{s}$. In the presence of acid, the featured absorption of rhodamine developed. However, nanosecond transient absorption spectra show that the triplet state is still localized on the Bodipy part, and the triplet state lifetime is $34.4 \mu\text{s}$.

Femtosecond transient absorption spectra show that FRET to the rhodamine moiety ($\tau = 81 \text{ ps}$) is a much faster process than the ISC of the iodoBodipy part ($\tau_{\text{ISC}} = 178 \text{ ps}$), yet the formation of the triplet state of Bodipy was not inhibited.

The PBI-diiodoBodipy (PBI = perylenebisimide) dyad and triad were prepared (Fig. 58).²¹² Based on the spectral overlap of

Fig. 57 Bodipy dyads **88** and **89** with a cyanuric chloride linker.²¹¹Fig. 59 DiiodoBodipy-styrylBodipy dyad **92** and a reference compound **93**.²¹³Fig. 58 DiiodoBodipy-PBI dyad **90** and triad **91**.²¹²

the two chromophores, FRET from the diiodoBodipy moiety to the PBI unit is assumed. In the dyad and the triad, the fluorescence emission of the singlet energy acceptor was significantly quenched. The calculation of the ΔG_{CS} values based on the electrochemical and spectra data indicated that PET is thermodynamically allowed for the dyad and the triad even in a non-polar solvent such as toluene. The energy level of the CST is generally lower than the S_1 state of the PBI moiety.

The triplet excited state localized on the PBI moiety was observed for both the dyad and the triad upon selective photoexcitation into the diiodoBodipy moiety. The triplet state lifetimes were determined to be 150 μ s and 148 μ s, respectively. The Φ_Δ values of the dyad and the triad (Fig. 58) were determined to be 80% and 78%, respectively. These results indicated that although the fluorescence of PBI in the dyad and the triad was significantly quenched, yet the triplet state of PBI was not quenched by PET. The energy level of the CTS is much higher than that of the T_1 state of the PBI moiety. With uniodinated dyads and triads, we proved that the triplet state is unable to be produced by CR.

Femtosecond TA spectra indicated that the FRET rate constant of **90** is $k_{\text{ENT}} = 5 \times 10^{10} \text{ s}^{-1}$, larger than the ISC of diiodoBodipy ($k_{\text{ISC}} = 7.7 \times 10^9 \text{ s}^{-1}$), yet the triplet state yield of **90** is as high as 80% (approximated using the Φ_Δ value). These results infer that the singlet excited state of diiodoBodipy was trapped somehow from decaying by the FRET.²¹²

Intermolecular triplet energy transfer between the diiodoBodipy and PBI reference compounds were studied by using ns TA spectroscopy. Upon selective photoexcitation of diiodoBodipy in the mixture, the transient absorption spectrum of diiodoBodipy diminished. The triplet state of PBI was observed, which is produced by the intermolecular TTET.²¹²

In order to achieve a more significant spectra discrimination, we studied the competing FRET and ISC of diiodoBodipy-styrylBodipy dyad **92** (Fig. 59).²¹³

Singlet energy transfer in **92** was confirmed by the fluorescence excitation spectrum. ΔG_{CS}° values indicate that PET is thermodynamically allowed for **92** in polar solvents, which is in agreement with the fluorescence studies. Upon selective photoexcitation into the diiodoBodipy moiety, the triplet state localized on styrylBodipy was observed, with a lifetime of 385.0 μ s. This result indicated that intramolecular TTET. A Φ_T value of 35% was observed for **92**, as compared to **93** (for which the triplet state quantum yield is negligible) (Table 9). For 2,6-diiodoBodipy, $\Phi_\Delta = 0.85$. Thus, we proposed the ISC was efficiently competed by FRET. Femtosecond transient absorption spectra indicate that the FRET rate constant of $k = 6.9 \times 10^{10} \text{ s}^{-1}$ ($\tau = 14.5 \text{ ps}$), which is much faster than the ISC of the diiodoBodipy moiety.

The slow intermolecular TTET between the reference diiodoBodipy compound and the reference styrylBodipy compound was studied by nanosecond transient absorption spectroscopy (Fig. 60).²¹³

Upon selective photoexcitation into diiodoBodipy using a 530 nm nanosecond pulsed laser, the featured triplet excited state absorption (ESA) of diiodoBodipy appeared at 350 nm, as well as the significant bleaching band at 530 nm. With the elapse of the delayed time after pulsed excitation, these feature diminished, and the transient absorption of the styrylBodipy moiety developed, indicated by the bleaching band at 630 nm and the ESA band at 370 nm (Fig. 60a). The intermolecular TTET was monitored by following the transient absorbance at 530 nm and 630 nm (Fig. 60b). In the presence of the triplet energy acceptor **93** (Fig. 59), the decay of diiodoBodipy ($\tau = 17.5 \mu$ s) is much faster than the intrinsic decay of the diiodoBodipy alone ($\tau = 133 \mu$ s). The intermolecular triplet state energy transfer rates are in the range from $k = 2.5 \times 10^4 \text{ s}^{-1}$ to $k = 6.0 \times 10^4 \text{ s}^{-1}$, depending on the triplet acceptor concentration. The energy transfer efficiency is up to 90%. Such an efficient intermolecular long range energy transfer will be beneficial for the application of the triplet excited states, such as in photocatalysis or artificial photosynthesis studies.²¹⁴

4. The application of the triplet excited state of Bodipy

The application of the triplet excited state of Bodipy is an emerging area, such as in photodynamic therapy and

Table 9 Photophysical properties of compounds 88–93^a

	λ_{abs} , nm	ε	λ_{em} , nm	Φ_F	Φ_Δ	τ_T , μs	Ref.
88	503/537	102 000/73 400	523/552	0.071	—	130.6	211
89	534	71 500	552/580	0.036/0.145	—	51.7/34.4	211
90	537	103 000	566	0.0018	0.80	150	212
91	541	132 000	597	0.0005	0.78	148	212
92	630/537	141 000/98 000	643	0.690	0.35/0.19	385	213
93	628	118 000	641	0.590	—	—	213

^a For detailed information, please refer to the main text and the references.

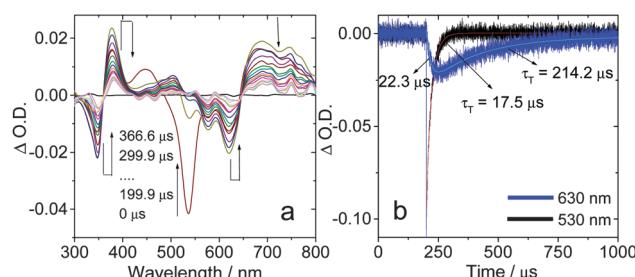


Fig. 60 (a) Intermolecular triplet–triplet energy transfer (TTET) from **8** to **93**, monitored by nanosecond transient absorption spectra of the mixture of **8** and **93**. The concentration of compound **8** was at $c = 1.0 \times 10^{-5}$ M, and the molar ratio of **8**:**93** was 1:1. (b) The decay traces were monitored at 530 and 630 nm, respectively. The energy donor (compound **8**) was selectively excited with OPO pulsed laser at 536 nm (note: excitation of compound **93** alone will not give the triplet excited state). In deaerated toluene. 20 °C. Reproduced with permission from ref. 213.

photocatalysis.^{4,21,22,46,47,215} The two principal photophysical processes initiated by the triplet excited state of Bodipy in these applications are the triplet energy transfer and electron transfer.^{1,47} Concerning these aspects, the strong absorption of visible light, and the long-lived triplet excited state of Bodipy are crucial for the applications of the triplet state of Bodipy in photodynamic therapy,^{21,110} photocatalysis,^{216–220} and triplet–triplet annihilation (TTA) upconversions.^{40,47}

4.1. Photodynamic therapy (PDT)

Photodynamic therapy (PDT) is a noninvasive method for the treatment of a variety of cancers by the combined use of visible or near-IR light with a photosensitizing drug. The principle is that upon photoexcitation of the triplet photosensitizer, the triplet excited state will be populated, *via* ISC. Intermolecular TTET will produce $^1\text{O}_2$, which is a potent oxidant. Notably, the lifetime of $^1\text{O}_2$ is *ca.* 0.6 μs ,²²¹ during which $^1\text{O}_2$ can diffuse less than 0.1 μm . Thus PDT is a highly confined and selective treatment for cancer tissue.

The conventional PDT reagents are the porphyrin derivatives.^{23,89} These compounds are difficult to prepare and purify; as a result, some compounds are used as a mixture of the isomers. Concerning these aspects, the application of the Bodipy-derived triplet photosensitizers in the PDT study is promising, because the Bodipy dyes show strong absorption of visible, or near-IR light (such as azaBodipy derivatives).^{76,89} Moreover, the molecular structures of the Bodipy chromophore is capable of being modified feasibly, and thus it is convenient for tagging or labeling purpose.

As previously discussed, 2,6-diiodoBodipy has been studied for the PDT effect.⁸⁸ **8** (Fig. 5) shows phototoxicity toward HeLa cells (PDT effect). Upon incubation of HeLa cells with **8** (1 μM), and photoirradiation (535 nm), the phototoxicity was confirmed by staining with ethidium homodimer-1 (dead cell marker). The drawback of this compound is the visible light-absorption of the Bodipy chromophore. Near IR absorption is desired for *in vivo* PDT, due to the deeper penetration of the near IR light in tissues.⁷⁷

Concerning this aspect, azaBodipy is the ideal chromophore due to the near IR absorption.^{76,109} DibromoazaBodipy (Fig. 47) was studied as a triplet photosensitizer for PDT application.⁸⁹ The absorption maxima varied from 600 nm to 700 nm. Light-induced cytotoxicity was studied with MRC5-SV40 cells. The EC₅₀ value for **76d** is 1.4×10^{-8} M. With attachment of an amino group to dibromoazaBodipy, an acid-activatable PDT reagent was developed.¹⁰³

In recent years, the development of activatable PDT reagents is of particular interest due to their targeting feature. Some cancer cell-related chemicals, such as thiols (GSH), enzymes, or acceptors can be used to activate the PDT effect. For example, **79** (Fig. 50) was used as a GSH-activatable PDT reagent, because the GSH concentration in cancer tissue is much higher than that in the normal tissue.¹⁸³ **79** gives absorption in the 600–700 nm range. It was shown that upon incubation of HCT116 cells with **79**, and then upon photoirradiation, apoptosis was induced.¹⁸³ **79** showed no apparent photocytotoxicity (or dark toxicity) on the MRC-5 (human fetal lung fibroblast cells) cell line, which is a normal cell line.¹⁸³

Targeted PDT reagents are of particular interest, because the treatment of the tumor tissue becomes more efficient and is confined to the tumor tissues in which the PDT reagent is selectively accumulated, to enhance their selectivity. On the other hand, the advantage of the feasible derivatization of Bodipy was demonstrated by tagging Bodipy with targeting modules to prepare targeted PDT reagents.⁷⁷ For example, the 2,6-diiodoBodipy module was connected with Tyr/Ile chains in **94** (Fig. 61), which is similar to the natural TrkC neurotrophin ligand NT3. These side chains as targeting modules toward the TrkC receptor, which is associated with some forms of cancer (*e.g.*, neuroblastoma, medulloblastoma, and breast cancer) and with melanoma.²²²

Compound **94** absorbs at 520 nm (Table 10). It has sub-micromolar photocytotoxicities to cells that were engineered to express TrkC (NIH3T3-TrkC) or that naturally express high levels of TrkC (such as SY5Y neuroblastoma lines). Control experiments showed that **94** is not cytotoxic in the dark and has

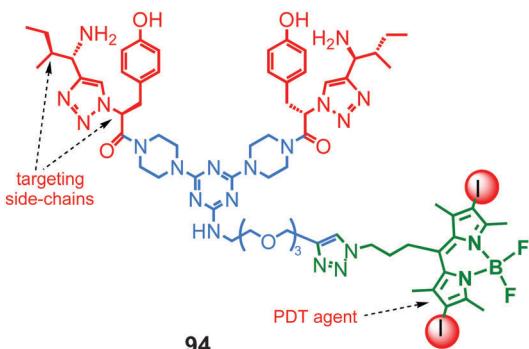


Fig. 61 Double-targeting PDT reagent **94** with diiododistyryl BODIPY as the PDT module and Tyr/Ile side chains as the targeting module (the target is the TrkC receptor).²²²

Table 10 Photophysical properties of **94–111**^a

	$\lambda_{\text{abs}}/\text{nm}$	ε	$\lambda_{\text{em}}/\text{nm}$	Φ_F	Φ_Δ	$\tau_T/\mu\text{s}$	Ref.
94	ca. 540	—	ca. 520	—	—	—	222
95a	662	48 978	687	0.20	—	—	77
95b	662	61 660	689	0.20	—	—	77
96	506	136 000	527	0.022	0.64	115.6	149
97	509/541	87 000/58 000	578	0.176	0.42	140.9	149
98	508/542	82 000/43 000	644	0.023	—	—	149
99	505/518	—	548	0.78	—	—	224
102	504	62 800	517	0.58	—	—	228
103	509	80 300	—	—	—	—	234
104	541	73 700	—	—	—	—	234
105	549	69 100	—	—	—	—	234
106	540	68 900	—	—	—	—	234
107	548	66 000	—	—	—	—	234
108	630	77 000	654	0.051	0.69	1.8	87
109	629	65 300	644	0.01	0.82	71.5	157
110	657	64 600	667	0.0009	0.85	123.2	157
111	517	76 000	535	0.004	0.81	27.4	239

^a For detailed information, please refer to the main text and the references.

significantly less photocytotoxicity toward cells that do not express TrkC (NIH3T3-WT).

A folic acid receptor was usually over-expressed in tumor cells. Thus a PDT module can be connected with folic acid to prepare a targeting PDT reagent (Fig. 62).⁷⁷

Two folate-conjugated diiododistyryl boron dipyrromethenes (**95a** and **95b**) were prepared and characterized by various

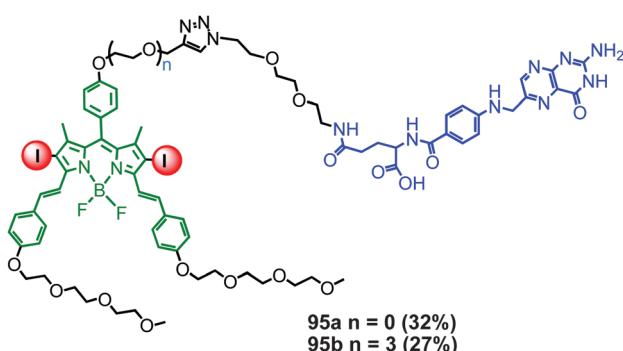


Fig. 62 Targeting PDT reagent with diiododistyryl BODIPY as the PDT module and folate as the targeting module.⁷⁷

spectroscopic methods (Fig. 62).⁷⁷ The two compounds show strong absorption in the red spectral region (662 nm, $\varepsilon = 61\ 660\ \text{M}^{-1}\ \text{cm}^{-1}$), and low fluorescence quantum yields ($\Phi_F = 0.20$). The Φ_Δ values of these compounds were not reported.⁷⁷ However, previously we have shown 2,6-diiododistyryl BODIPY shows a high Φ_Δ value of 69% (Table 10).⁸⁷

95a and **95b** exhibit high photocytotoxicity toward the KB human nasopharyngeal carcinoma cells, which have high expression of folate receptors when compared with the MCF-7 human breast adenocarcinoma cells. Higher phototoxicity was observed for **95a**, *i.e.* the conjugate with a shorter oligoethylene glycol linker, due to its higher cellular uptake and slightly lower aggregation tendency. Its IC₅₀ value toward KB cells (0.06 μM) is 43-fold lower than that for MCF-7 cells upon photoirradiation, while the difference is only 6-fold for the analogue with a longer linker (**95b**). The length of the spacer also affects their sub-cellular localization. While compound **95a** shows high affinity toward the endoplasmic reticulum of KB cells, conjugate **11b** is mainly localized in the lysosomes.

Due to the feasibly derivatizable molecular structures, and the tunable absorption wavelength, we envision that BODIPY derivatives will play a significant role in the development of new activatable PDT reagents.

4.2. TTA upconversion

TTA upconversion shows the advantage of efficient harvesting of the excitation light, high upconversion quantum yields, and supramolecular features of the system, so that tuning is more feasible than the conventional upconversion methods.^{40–45} Moreover, non-coherent light is sufficient for TTA upconversion, such as solar light.²²³

The desired photophysical properties of the triplet photosensitizers for TTA upconversion include strong absorption of visible light and a long triplet state lifetime. These properties will make the intermolecular TTET more efficient, which is crucial to TTA upconversion. Porphyrin or benzoporphyrin complexes have been used for TTA upconversion.⁴⁰ Although these photosensitizers show red or near IR absorption, it is difficult to modify the molecular structures. On the other hand, the above challenges can be addressed by using BODIPY-based triplet photosensitizers.

Previously we used iodoBODIPY derivatives (Fig. 5) for TTA upconversion, and satisfactory upconversion quantum yields were obtained (up to 6.1%).^{85,105} The advantage of using BODIPY derivatives is the tunable absorption wavelengths (from 510 nm to 629 nm for the derivatives we prepared).

We also used the C₆₀-BODIPY dyads as the triplet photosensitizers for TTA upconversion.^{90–92} An upconversion quantum yield of 7.0% was observed for the C₆₀-BODIPY dyads as triplet photosensitizers.⁹⁰

Inspired by the previous finding that the triplet state can be produced by a BODIPY dimer,⁹⁵ we used heteroBODIPY dimers for TTA upconversion (Fig. 63).¹⁴⁹

Note that from **96** to **98**, the structures of the two components of the BODIPY dimer show more significant differences, such as the π-conjugation framework (Fig. 63). As a result, we observed a

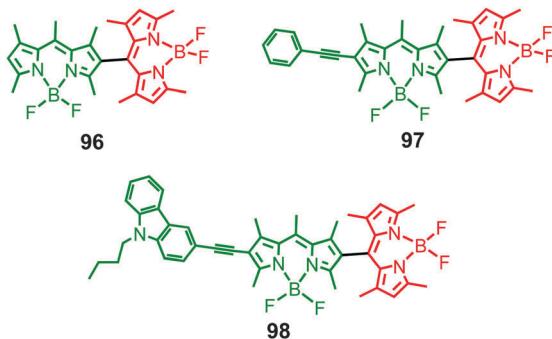


Fig. 63 HeteroBodipy dimers as heavy-atom-free triplet photosensitizers for TTA upconversion.¹⁴⁹

clear trend that the triplet state formation quantum yield of the compounds decreased from **96** to **98**. For example, the Φ_{Δ} for **96** is 64%, and it decreases to 42% for **97**, whereas for **98**, no $^1\text{O}_2$ photosensitizing ability was observed. For **96** and **97** the triplet state lifetimes were determined to be 115.6 μs and 140.9 μs , respectively (Table 10). No triplet state was observed for **98**.

96, **97** and **98** were used as triplet photosensitizers for TTA upconversion, with perylene as a triplet acceptor/emitter. Upconversion quantum yields of 3.7% and 2.7% were observed. For **98**, however, the upconversion is negligible.¹⁴⁹

Bodipy derivatives can also be used as triplet energy acceptor/emitters in TTA upconversion (Fig. 64).^{224,225} The T_1 state energy level of Bodipy is *ca.* 1.5 eV, which is lower than the triplet photosensitizers, such as Pt/PdTPTBP (TPTBP = tetraphenyltetra-benzoporphyrin).

Bodipy-derivatives **14** and **99** have been used as triplet acceptors for TTA upconversion (Fig. 64).^{224,225} Note that the iodine atoms are attached onto the phenyl moiety at the *meso* position of the Bodipy core; thus the heavy atom effect is weak and the fluorescence quantum yields of the compounds are 69% and 78%, respectively (Table 10).²²⁴ PtTPTBP was used as a triplet photosensitizer, with a T_1 state energy level of 1.62 eV. Upon 635 nm excitation of PtTPTBP, the triplet state of the Bodipy derivatives was populated by intermolecular TTET. *Via* triplet-triplet annihilation, green emission from the Bodipy derivatives was observed.²²⁴ The upconversion quantum yield is 7%. It should be pointed out that attachment of iodine atoms in **14** and **99** is unnecessary, although the fluorescence quantum yields of **14** and **99** were not reduced by the presence of the iodine atoms in the molecules. As proof of this postulation,



Fig. 64 Bodipy derivative as the triplet acceptor/emitter in TTA upconversion.²²⁴

we used non-iodinated Bodipy as a triplet acceptor/emitter for TTA upconversion.^{176,209}

In order to attain a high TTA upconversion quantum yield, concerted excited state energy levels of the triplet photosensitizers and the triplet acceptor must be met. For example, a relationship of $2E_{T_1} > E_{S_1}$ is required for the triplet acceptor/emitter, to ensure the efficient TTA process. Failure to meet this requirement will reduce the TTA yield, as well as the upconversion yield. This prerequisite was not well satisfied for some typical triplet acceptors.

For example, one of the popular triplet acceptors, perylene, has a T_1 state energy level of 1.53 eV, and the S_1 state energy level of at least 2.78 eV; thus the requirement of $2E_{T_1} > E_{S_1}$ is only marginally met (the driving force for TTA is *ca.* 0.2 eV). In order to optimize the excited state energy levels, Bodipy was connected with a perylene moiety (Fig. 65) to tune the excited state energy level to improve TTA. It was known that Bodipy has a S_1 state energy level of 2.35–2.45 eV, and thus $2E_{T_1} > E_{S_1}$ can be better met (the driving force for TTA is *ca.* 0.6 eV). It was observed that the upconversion quantum yield can be improved from 6.6% to 11.3%.²²⁶ Zhang found that using a mixture of different triplet acceptors (such as DPBF and DPA) leads to an efficient hetero-TTA process.²²⁷

We studied the detail photophysics of a similar Bodipy–perylene dyad, with an aim to optimize the energy levels further (**102**, Fig. 66).²²⁸ We found that the TTA efficiency for **102** is *ca.* 2-fold of that of perylene. Moreover, we found that the PET is thermodynamically allowed in **102**, especially in polar solvents, such as dichloromethane and acetonitrile.

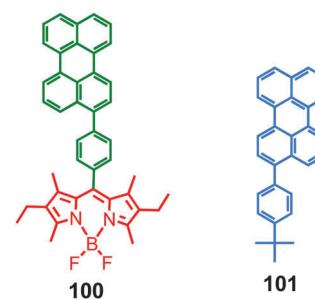


Fig. 65 Bodipy–perylene dimer **100** for tuning of the excited state energy levels to optimize TTA upconversion.²²⁶ The reference compound **101** is also presented.

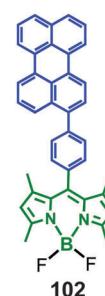


Fig. 66 Bodipy–perylene dimer to tune the excited state energy levels to optimize TTA upconversion.²²⁸

The fluorescence of **102** in polar solvents was studied, it was found that the fluorescence of **102** was significantly quenched in polar solvents than that in non-polar solvents, yet the emission wavelength (assigned to the Bodipy moiety) did not change. Moreover, the separate components of the dyad did not show such solvent polarity-dependent fluorescence emission intensity. These results clearly indicated the PET process in **102** in polar solvents (with perylene as the electron donor and the Bodipy moiety as the electron acceptor).²²⁸ This information will be useful for future designing of dyad triplet photosensitizers. Hetero-TTA was also studied for a intermolecular approach with DPA and 1,3-diphenylisobenzofuran (DPBF).²²⁷

4.3. H₂ production

Renewable energy has attracted much attention in recent years, such as the photocatalytic hydrogen (H₂) production.^{229–233} Usually a transition metal complex was used as the photosensitizer/electron donor, with a water reduction center (such as cobaloxime complexes); H₂ evolution was observed in the presence of a sacrificial electron donor, such as triethanolamine.^{231,232} However, the conventional Ir(III) or Ru(II) complexes give weak absorption of visible light and short triplet excited states, and thus the electron transfer process may be nonefficient. In order to improve the H₂ production, photosensitizers with strong absorption of visible light and a long-lived triplet excited state are desired.

A diiodoBodipy or dibromoBodipy-binded Co(II) complex was prepared as a novel photocatalyst for H₂ evolution (Fig. 67).^{234,235} The Bodipy moiety is the electron donor, and the cobaloxime moiety is the water reduction catalysts. The bromo- or the iodo-Bodipy unit show a long-lived triplet excited state, and thus the electron transfer to the water reduction centre (WRC) is supposed to be more efficient.

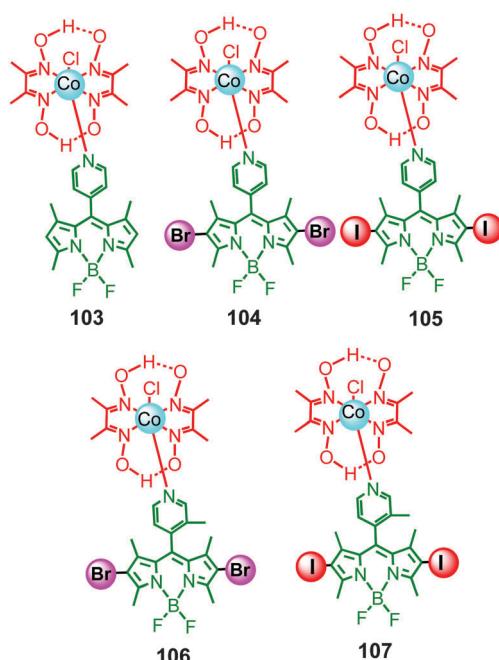


Fig. 67 Bodipy-cobaloxime complexes as photocatalysts for H₂ evolution.²³⁴

Four cobaloxime catalyst complexes with Bodipy chromophores are synthesized (Fig. 67).²³⁴ In contrast to the photocatalytically inactive, nonhalogenated reference complex **103**, **104–107** are active for photocatalytic hydrogen evolution, with a maximum turnover number (TON) of 30.9 mol equiv. of H₂ per catalyst for the mesomethylpyridyl 2,6-diido Bodipy-sensitized cobaloxime complex **107**. It was proposed that accessing of the photoexcited triplet state of the Bodipy chromophore by introducing heavy atoms (*i.e.*, bromine or iodine) is necessary for efficient electron transfer in this system, enabling catalytic H₂ generation. Without accessing of the triplet state of the Bodipy chromophore, the singlet excited state of Bodipy (complex **103**, Fig. 67) only gives stoichiometric H₂.²³⁶

4.4. Photoredox catalytic organic reactions

Photoredox catalytic organic reaction is an emerging research area.^{20,216–219} This synthetic methodology gives functionalized organic compounds with a concise and clean synthesis route, by formation of C–C or C–N bonds. For this kind of catalytic synthetic reaction, the photocatalyst (triplet photosensitizers) plays the role of an electron acceptor/donor, or a triplet energy donor.²⁰ Thus, the photocatalytic activity will be improved by using triplet photosensitizers with strong absorption of visible light and a long-lived triplet excited state.⁴⁷ It should be pointed out that in the following discussions, the effect of the triplet state lifetime on the photocatalytic activity is limited to the homogeneous catalysis. For heterogeneous catalysis, the catalytic activity is also affected by other factors such as charge carrier mobility.

Popular triplet photosensitizers include the complexes such as Ru(bpy)₃Cl₂ and Ir(ppy)₃.²⁰ These transition metal complexes show only moderate or weak absorption in the visible spectra range ($\epsilon < 20\,000\text{ M}^{-1}\text{ cm}^{-1}$ in the spectral range beyond 400 nm). The absorption maximum is $< 500\text{ nm}$, and the triplet state lifetimes of these complexes are short (less than 5 μs).^{20,237} Therefore, the photocatalytic reaction efficiency is low and the reaction times are usually long. We propose that the weak absorption of these complexes in the visible spectral region is due to the weakly allowed $S_0 \rightarrow ^1\text{MLCT}$ transition because of its charge transfer character. The short triplet excited state is probably due to the strong heavy atom effect, which facilitates the $S_1 \rightarrow T_1$ ISC, but also the $T_1 \rightarrow S_0$ transition, and thus the lifetime of the T_1 state is short.

In order to tackle these challenges, we used diiodoBodipy derivatives that show strong absorption of visible light and long-lived triplet excited states as organic catalysts for photoredox catalytic organic reactions (Fig. 68).⁸⁷ The photocatalyzed reactions were mediated by singlet oxygen ($^1\text{O}_2$), that is, the aerobic oxidative coupling of amines and the photooxidation of dihydroxynaphthalenes, which is coupled to the subsequent addition of amines to the naphthoquinones, *via* C–H functionalization of 1,4-naphthoquinone, to produce aryl-2-amino-1,4-naphthoquinones (one-pot reaction), which are potential anticancer and antibiotic reagents. The photoreactions were substantially accelerated with the diiodoBodipy organic photocatalysts as compared to that catalyzed with the conventional

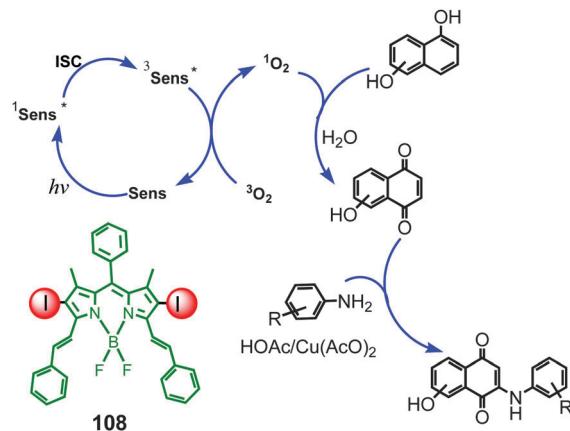


Fig. 68 Proposed one-pot reaction mechanism for the photooxidation with **8** and **108** as the organic photocatalysts to produce aminonaphthoquinone.⁸⁷

Ru(II)/Ir(III) complexes.⁸⁷ Moreover, the organic photocatalysts show excellent photostability.

The above results show that the triplet excited state of Bodipy dyes, or more general, the triplet state of organic chromophores, are ideal for photoredox catalytic organic reactions. Along this line, we prepared C₆₀-styrylBodipy conjugates **109** and **110** (Fig. 69), which show strong absorption of visible light ($\varepsilon = 65\,000\,\text{M}^{-1}\,\text{cm}^{-1}$ at 650 nm), and a long-lived triplet excited state ($\tau_T = 120\,\mu\text{s}$), to explore the potential of C₆₀ for photocatalysis.¹⁵⁷ We used these organic triplet photosensitizers as photocatalysts for the photo-oxidation of 1,5-dihydroxynaphthalene to produce juglone, *via* photosensitization of $^1\text{O}_2$. The photocatalytic efficiency was compared with that of the conventional photocatalysts, such as Ir(ppy)₃bpy, methylene blue, and C₆₀. It was found the photo-reaction rates are 10-fold that of the conventional Ru(II)/Ir(III) photocatalyst, and the reaction yields with the new organic photosensitizers are much higher. It should be pointed out that both property of strong absorption of visible light and the long-lived triplet excited state are crucial for the photocatalytic reaction.

Pyrrolo[2,1-*a*]isoquinoline are bioactive compounds.²³⁸ Recently a photoredox catalytic reaction scheme was developed for the preparation of these highly functionalized compounds (Fig. 70).

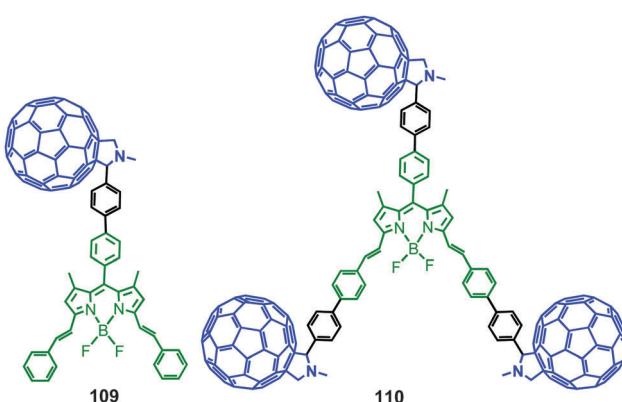


Fig. 69 StyrylBodipy-C₆₀ dyad **109** and tetrad **110** as photocatalysts for photooxidation of 1,5-dihydroxynaphthalene.¹⁵⁷

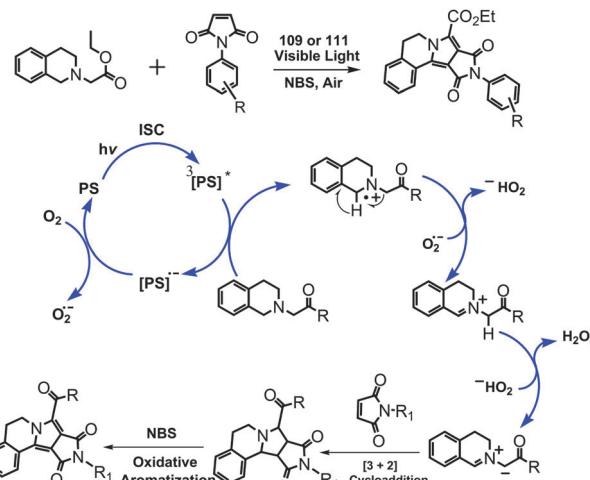


Fig. 70 Photocatalytic tandem oxidation/[3+2] cycloaddition reactions to prepare pyrrolo[2,1-*a*]isoquinoline.²³⁹

Previously Ru(bpy)₃Cl₂ was used as a photocatalyst,²³⁸ but the reaction time is long (9–72 h).

The key steps of the reaction mechanism are the electron transfer between the photocatalyst and the O₂, and the electron transfer between the photocatalyst radical cations and the substrate (Fig. 70).²³⁸ Concerning this aspect, C₆₀ is a well-known electron acceptor, and thus we used Bodipy-C₆₀ conjugates **109** and **111** as new organic photocatalysts for the reactions (Fig. 71), and a much higher catalytic efficiency was observed. For example, the reaction time required for the photocatalyst Ru(bpy)₃Cl₂ is 4 h, and the yield is 37%. With the Bodipy-C₆₀ dyads as the new photocatalysts, the reaction time is only 1 hour and the yield is up to 91%.²³⁹

We also used similar C₆₀-Bodipy conjugates for visible-light-induced aerobic oxidative hydroxylation of aryl boronic acids.²⁴⁰ We found that C₆₀-Bodipy dyads can act as efficient electron-mediator between the sacrificial electron donor and the substrates.

Other photoredox catalytic organic reactions, such as the aza-Henry reaction of tetrahydroisoquinoline (Fig. 72),²⁴¹ and C–H arylation of heteroarenes with diazonium salts were also reported (Fig. 72).²⁴² Iodo-Bodipys were used as organic catalysts for these different photoredox catalytic organic reactions, (Fig. 72).⁸⁶ The organic photocatalysts act as either electron acceptors (reductive quenching) or electron donors (oxidative quenching) in the single electron transfer (SET) of the catalytic cycles. Different from the widely used Ru(bpy)₃[PF₆]₂, Ir(ppy)₃,



Fig. 71 Bodipy-C₆₀ dyad as **111** photocatalysts for photocatalytic tandem oxidation/[3+2] cycloaddition reactions.²³⁹

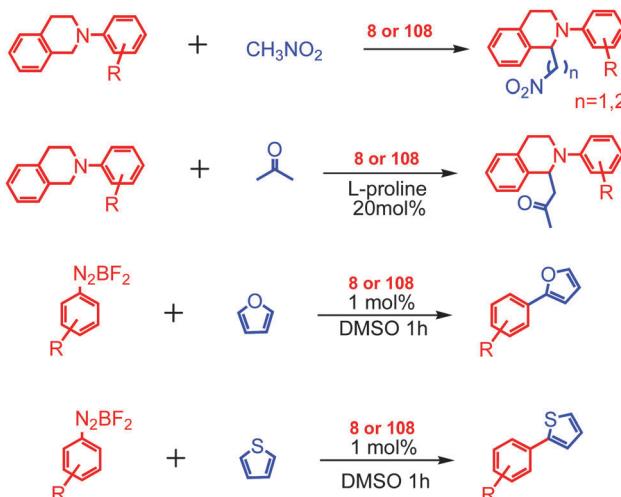


Fig. 72 The photoredox catalytic organic reactions catalyzed by compounds **8** and **108**. Photocatalytic tandem oxidation/[3+2] cycloaddition reactions to prepare pyrrolo[2,1-*a*]isoquinoline is not shown.⁸⁶

or halo-xanthane photocatalysts (Eosin Y or Rose Bengal), the new organic photocatalysts show strong absorption of visible light and long-lived triplet excited states, which are beneficial for SET, a crucial step for photoredox catalytic organic reactions. The absorption wavelength of the photocatalysts was readily tuned from 529 nm to 630 nm. The three different types of organic reactions are accelerated with the new organic photocatalysts (typical reaction times are 1–2 h) compared to Ru(bpy)₃[PF₆]₂ or Ir(ppy)₃ (reaction time: 12–72 h).⁸⁶

In order to achieve easy recycling of the photocatalysts, we immobilized the diiodoBodipy photocatalyst on porous silica,²⁴³ and an efficient recyclable photocatalyst was obtained for photoredox catalytic tandem oxidation-[3+2] cycloaddition reactions of tetrahydroisoquinoline with *N*-phenylmaleimides to prepare pyrrolo[2,1-*a*]isoquinoline. We found that the immobilized organic catalyst is still efficient for the photocatalytic reactions. The photocatalyst was easily recycled by filtration after the photocatalytic reaction.²⁴³

Moreover, the broadband visible light-absorbing Bodipy-diiodoazaBodipy **69** (Fig. 45) was used for tandem oxidation/[3+2] cycloaddition reactions to prepare pyrrolo[2,1-*a*]isoquinoline, the coupled photocatalytic oxidation and the Cu(i) catalyzed alkynylation reactions, and the photooxidation–alkynylation reaction with tetrahydroisoquinolinol as the substrate.²⁴⁴ The photocatalytic reaction with the broadband visible light-absorbing organic triplet photosensitizers as photocatalysts is generally more efficient than the normal triplet photosensitizers.^{159,240,245}

Recently it was found that the singlet excited state of Bodipy is able to catalyze the cross-dehydrogenative-coupling reactions with tetrahydroisoquinoline and nitromethane as substrates.²⁴⁶ The photocatalytic efficiency is close to the diiodoBodipy photocatalysts. This results is interesting since the lifetime of the singlet excited state of Bodipy is at least 10⁶ times shorter than the triplet state of Bodipy.⁸⁶ The quenching constant of the isoquinoline substrate on the singlet excited state of Bodipy is determined to be $K_{SV} = 52.8 \text{ M}^{-1}$ (*via* photoinduced intermolecular electron transfer).

We measured the same constant with diiodoBodipy and the same tetrahydroisoquinoline substrate, based on the quenching of the triplet state lifetime of diiodoBodipy to be $K_{SV} = 120 \text{ M}^{-1}$. These results infer that the electron transfer between the excited photocatalyst and the substrate (tetrahydroisoquinoline) may not be the rate-limiting step of this specific photocatalytic reaction.

The application of efficient organic triplet photosensitizers as photocatalysts is still in the early stage. The results are promising and we envision that the extending of the application to other areas such as photovoltaics will be interesting, considering the strong absorption of visible light and the long-lived triplet excited state of the organic materials.

5. Summary, challenge and outlook

In summary, the production, modulation and application of the triplet excited state of Bodipy were discussed. Bodipy is one of the most popular chromophores. Different from the extensive investigations on the singlet excited state of Bodipy, such as its fluorescence and visible light-harvesting ability, the study on the triplet excited state of Bodipy is still in its infancy. The formation of the triplet state of Bodipy upon photoexcitation is usually based on the heavy atom effect (such as I, Br, Ru, Ir, Pt and Re). Moreover, new methods, such as using a spin converter (*e.g.* C₆₀), or by charge recombination, exciton coupling and the double substituted excited state, were developed in recent years. The preparation of the broadband visible light-harvesting Bodipy triplet photosensitizers was also discussed. All these organic Bodipy-based triplet photosensitizers show strong absorption of visible light (*ca.* 80 000 M⁻¹ cm⁻¹ in the range 500–700 nm) and long-lived triplet excited states (50–200 μs).

The switching or modulation of the triplet state of Bodipy was not investigated intensively. This is in stark contrast to the study on switching of the singlet excited state of the Bodipy, based on which vast amounts of molecular materials were developed, such as fluorescent molecular probes, and light-harvesting molecular arrays. The methods for switching of the triplet excited state of Bodipy were discussed, such as those based on the photo-induced electron transfer (PET), by controlling the competing FRET, or the intermolecular charge transfer (ICT). Preliminary studies show that switching of the triplet excited states may follow different rules as compared with that of switching of the singlet excited state. For example, the switching of the singlet excited state and the triplet state of Bodipy by a same electron acceptor (or donor) may follow a different rule, due to the difference in driving force for the PET process. We envision that investigation of the switching/modulation of the triplet state of Bodipy will give novel functional materials such as activatable photodynamic therapeutic (PDT) reagents.

Applications of the triplet excited states of Bodipy in PDT, TTA upconversion, hydrogen (H₂) production and photoredox catalytic organic reactions were briefly discussed. The two principle photophysical processes involved in these applications are intermolecular electron transfer and energy transfer, which can be enhanced using triplet photosensitizers which show

strong absorption of visible light and long-lived triplet excited states. The triplet state of Bodipy derivatives fulfill these requirements, and the Bodipy-derived triplet photosensitizers have been proved more efficient than the conventional triplet photosensitizers such as $\text{Ru}(\text{bpy})_3\text{Cl}_2$ or $\text{Ir}(\text{ppy})_3$ for photocatalytic hydrogen (H_2) production and TTA upconversion.

Despite above developments, challenges as well as opportunities still exist. For example, singlet fission is being studied for efficient formation of the triplet excited state (with a quantum yield of up to 200%) upon photoexcitation. But this strategy was not yet extended to the Bodipy chromophore. Related research will foster a new area and novel materials. On the other hand, designing of heavy atom-free triplet photosensitizers is still a major challenge for organic chemists, because the molecular structure-ISC property is far from clear. It is not a trivial task for organic chemists to design new molecules with matching of S_1/T_n states to facilitate efficient ISC. The relationship between the molecular structure and the T_1 state energy level of the Bodipy derivatives is almost an uninvestigated area, and it is not solely dependent on the size of the π -conjugation framework. The organic chemists must be joined by the physical chemists and photochemists to tackle the challenges. It is almost certain that the photochemistry of the triplet excited state of Bodipy, or other feasibly derivatizable organic chromophores, will flourish in the near future, because it is crucial for the fundamental photochemistry studies, and for the developments of the areas such as PDT, photocatalysis and upconversion.

Abbreviations

Bodipy	Boron dipyrromethane
BDP	Boron dipyrromethane
bpy	2,2'-Bipyridine
DPA	9,10-Diphenylanthracene
CTS	Charge-transfer state
EnT	Energy transfer
IC	Internal conversion
IL	Intra-ligand
ISC	Intersystem crossing
LED	Light emitting diode
MB	Methylene blue
MLCT	Metal-to-ligand-charge-transfer
PDT	Photodynamic therapy
ppy	2-Phenylpyridine
PS	Photosensitizer
RB	Rose Bengal
RT	Room temperature
$^1\text{O}_2$	Singlet oxygen
SOC	Spin-orbit coupling
TA	Transient absorption
TON	Turn-over number
TPP	Tetraphenylporphyrin
TTA	Triplet-triplet annihilation
TTET	Triplet-triplet-energy-transfer
UC	Upconversion

WRC	Water-reduction catalyst
ε	Molar absorption coefficient
Φ_Δ	Singlet oxygen quantum yield
Φ_F	Fluorescence quantum yield
Φ_P	Phosphorescence quantum yield
τ_T	Triplet excited state lifetime
τ_P	Phosphorescence lifetime
fs	Femtosecond
ns	Nanosecond
μs	Microsecond
ms	Millisecond

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