Triplet excited state of Bodipy: formation, modulation and application

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REVIEW

Triplet excited state of Bodipy: formation, modulation and application

Jianzhang Zhao,* Kejing Xu, Wenbo Yang, Zhijia Wang and Fangfang Zhong

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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 (include I, Br, Ru, Ir, etc), and the new methods, such as with spin converter (e.g. C_{60}), charge recombination, exciton coupling and the doublely substituted excited state, are summarized. All the Bodipy-based triplet photosensitizers show strong absorption of visible or near IR light and 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 of the triplet excited state will give functional molecules such as activatable PDT reagents or molecular devices. It is worth to note 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 (H_2) production, photoredox catalytic organic reactions and TTA upconversion were discussed. The challenges and the opportunities in these areas were briefly discussed.

1. Introduction

1.1 General background.

Triplet excited state is fundamentally important in photochemistry.[1–10] For example, the production of triplet excited state upon photoexcitation is dependent on aborption of light (thus $S_0 \rightarrow S_n$ transition), intersystem crossing (ISC), exiton coupling,[11] and charge recombination,[12] etc. On the other hand, application of triplet excited state covers a vast areas such as electroluminescence,[13–18] photocatalysis,[19,20] photodynamic therapy (PDT),[4,21–24] photovoltaics,[25–29] luminescent bioimaging and sensing,[30–39] and recently the triplet-triplet annihilation (TTA) upconversion.[40–45]

Triplet photosensitizers are compounds that produce triplet excited state efficiently upon photoexcitation.[4,21,22,46] The development of new triplet photosensitizers is retarded to 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 ketone,[49] and porphyrin derivatives.[33] Transition metal

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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 proper chromophores for the preparation of organic triplet photosensitizer is also crucial, e. g. for the sake of easy derivatization, photostability. Concerning this aspect, boron-dipyrromethene (Bodipy) is in particular interest, due to its robust photophysical properties, such as strong absorption of visible light, high fluorescence quantum yield (suppressed non-radiative decay), good photostablity and 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 easier to introduce substituents to 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 a ideal candidate for preparation of new triplet photosensitizer, but it is perhaps the most investigated chromophore for triplet state production than any other chromophore, except the conventional porphyrin derivatives.[47] Bodipy has being 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 generation of 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 athracene.[93,94] Besides, the well known heavy atom-effect, the exciton coupling,[11] and the population of the double substitued excited state,[95,96] were also reported to be responsible for formation of triplet excited state upon photoexcitation. Moreover, some illusive mechanisms, such as the match of the S_1/T_n state energy level, may contribute significantly to the formation of triplet excited.[1,97] Charge recombination (CR) was also reported to be able to produce 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 moleular structure-T_1 state energy level relation of organic chromophores are not as clear as those for the relation between the S_1 state energy level and the molecular structure.

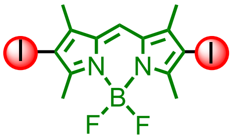
It should be pointed out that the spectroscopies used for the study of *triplet* excited state are also different from that of the singlet excited state (usually fluorescence) of Bodipy. Most of the triplet photosensitizers do not phosphoresce in fluid solution at room temperature, thus the triplet excited state was very often studied with the nanosecond transient *absorption* spectroscopy,[99] A complimentary method is the time-resolved photoacoustic spectroscopy, or laser induced optoacoustic spectroscopy, which is based on the photothermal effect. These methods have been used for 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-diiodo Bodipy **1** as PDT reagent (Fig. 1).[88] The compound gives strong visible light absorption (molar absorption coefficients $\varepsilon = 110000\ M^{-1}\ cm^{-1}$ at 535 nm), and a low fluorescence quantum yield ($\Phi_F = 0.02$ in MeOH. **Table 1**). Low fluorescence quantum yield is a prerequisite for efficient ISC.



1

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

However, the triplet state property of 2,6-diiodoBodipy was not studied with the nanosecond transient absorption spectroscopy.[88] Instead, the singlet oxygen ($^1O_2$) photosensitizing ability of **1** was studied with 1,3-diphenylisobenzofuran (DPBF) as the singlet oxygen ($^1O_2$) scavenger.[106] The $^1O_2$ photosensitizing ability of 2,6-diiodoBodipy is 1.6-fold of that of Rose Bengal (RB) (in methanol). Electrochemical studies show that the 2,6-diiodoBodipy is more difficult to be oxidized (E_{ox} = 1.13 V vs SCE) than RB (0.89 V vs SCE), thus 2,6-diiodoBodipy is more stable toward $^1O_2$ (strong oxidant) than RB. The PDT effect on living HeLa cells was studied, and it was found the cells were killed by photoirradiation after incubation with 2,6-diiodoBodipy.[88]

The normal Bodipys give 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

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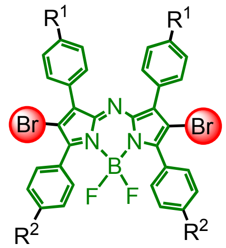
penetration can be achieved with near IR light. O'Shea et al prepared brominated azaBodipy.[89] AzaBodipy absorbs at 680 nm,[76,103,107] which is red-shifted by ca. 180 nm as compared with that of normal Bodipy.[53,54] The ε of the AzaBodipy derivatives are up to 80000 M^{-1} cm^{-1}. Upon bromination, the fluorescence quantum yields (Φ_F) of the compounds decreased from 20–30% to less than 1% (Fig. 2). Reduced fluorescene quantum yield upon bromination is an indication of ISC, facilitated by the heavy atom effect.



2

	R^1	R^2
2a:	H	H
2b:	H	OCH_3
2c:	OCH_3	H

Fig. 2 Bromo AzaBodipy as organic triplet photosensitizers showing near IR absorption.[89]

The triplet state property of the bromo-AzaBodipy **2** was not studied with nanosecond (ns) transient absorption (TA) spectroscopy (Fig. 2).[89] The $^1O_2$ photosensitizing ability was studied by comparison with that of hematoporphyrin, a known PDT reagent. Bromo AzaBodipy is 4-times more efficient than hematoporphyrin to produce $^1O_2$. However, the $^1O_2$ quantum yields (Φ_Δ) of the compounds were not determined, thus the apparent fast $^1O_2$ production may be also due to the stronger absorption of the bromoAzaBodipy than hematoporphyrin in visible spectral region. It was found the $^1O_2$ photosensitizing ability was greatly reduced when the bromo atoms were attached on the peripheral phenyl moieties, not 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 T_1 state energy level of 0.79–0.87 eV for the brominated AzaBodipy, slightly higher than that of $^1O_2$, thus photozensitizing $^1O_2$ is rationalized.[108]

Ramaiah reported iodinated AzaBodipy **3** as triplet photosensitizer (Fig. 3).[76,109] The compound shows absorption at 666 nm, with molar absorption coefficients of 699 00 M^{-1} cm^{-1}. The triplet state lifetime of the compound was determined as 1.6 μs with the ns TA spectroscopy, which is much shorter than the 2,6-diiodoBodipy (> 50 μs).[85] The Φ_T was determined as 0.78 ± 0.02. The Φ_Δ of the compound was determined as 0.70 ± 0.03. In comparison MB gives Φ_Δ of 0.52 (Table 1).

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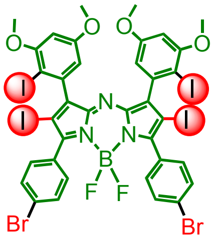
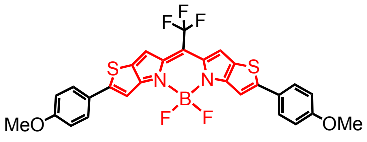


3

Fig. 3 Iodinated Aza Bodipy as triplet photosensitizer.[109]

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 microenvironment of the tumer tissues makes the PDT difficult, due to the low O_2 concentration in the tumor tissue. Thus, only the triplet photosensitizers with long triplet excited state lifetime (ca. 100 μs, for example) are highly sensitive to sensitize $^1O_2$ even at low O_2 concentration, and they are more efficient $^1O_2$ photosensitizers as compared with that of the photosensitizers with shorter triplet state lifetime (few μs). This postulations have been confirmed with 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]



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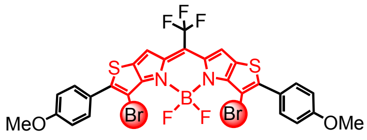


5

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

Thienyl-fused Bodipy **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. ε is up to 89000 – 200 000 M^{-1} cm^{-1} (Table 1).

With DPBF as the $^1O_2$ scavenger, the $^1O_2$ photosensitizing of compounds were studied. Compound **5** shows $^1O_2$ photosensitizing ability. But no $^1O_2$ quantum yields were reported.[112] The triplet state of the compound was not studied with 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.[113,114]

Inspired by the feasible derivatization of 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**–**14**. Fig. 5), and the triplet excited state lifetimes were studied with ns TA spectra (Table 1).[85]

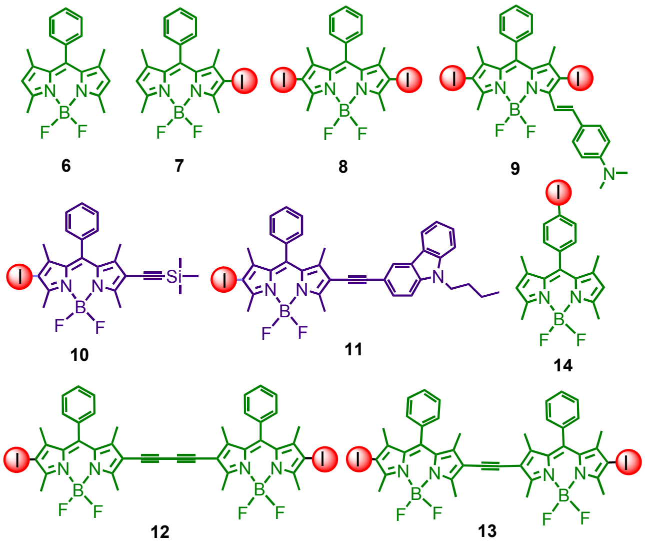


Fig. 5 Bodipy-derived organic triplet photosensitizers library with variable absorption wavelength.[85] Compound **14** was used as reference.

With introducing of different conjugation moieties onto the π–core of the 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 on the π-conjugation framework, 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 significant intramolecular charge transfer (ICT) feature was also prepared (such as **9**. Fig. 5). It should be pointed out that for **14**, the production of triplet state is negligible, because the iodine atom is not attached on the π–core of the Bodipy.

With introducing iodine atoms on the π-conjugation framework of the compounds, the fluorescence quantum yields of the compounds (Φ_F < 10%) were decreased as compared with that of the unsubstituted Bodipy (Φ_F = 71 %). This is the indication of the probable ISC in the iodinated compounds.[85]

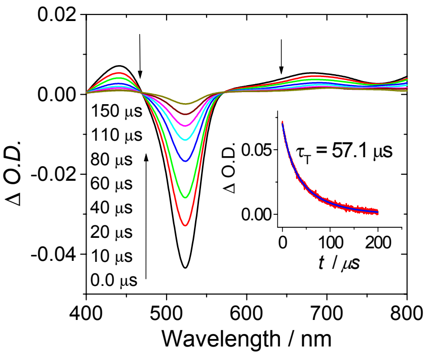


Fig. 6 Nanosecond TA spectra of compound **8** in deaerated CH_3CN after pulsed laser excitation (λ_{ex} = 532 nm). Inset: decay trace of compound **8** at 525 nm; 1.5×10^{-5} M; 20 °C. Reproduced with permission from Wu et al.[85]

The triplet excited state property of the compounds was studied with the ns TA spectroscopy.[85] For compound **8**, 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 (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 as 57.1 μs. The triplet state lifetime (τ_T), especially for the compounds with 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 sever self-quenching, and the triplet state lifetime will become shorter. This is in stark constrast 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).

Reliable triplet state lifetime can be determined by concentration exploitation into indefinitely diluted solution. Later we determined the triplet state lifetime of diiodoBodipy as 228.9 μs.[115] These triplet excited state lifetimes are generally much longer than the normal ^{3}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** (τ_T = 4.0 μs) 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]

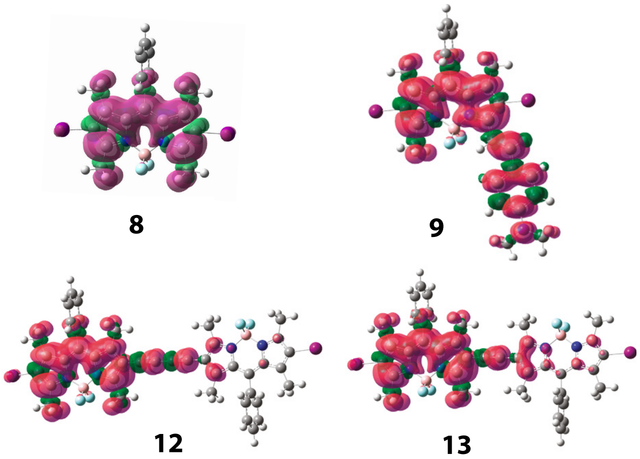
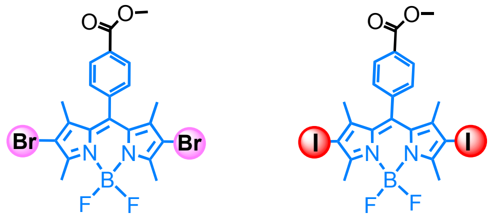


Fig. 7 Isosurfaces of spin density of Bodipy triplet photosensitizers and the model compound **8** at the optimized triplet state geometries. Calculation was performed at B3LYP/6-31G(d)/LanL2DZ level with Gaussian 09W. Reproduced with permission from Wu et al.[85]

Triplet state energy level is one of the crucial parameters for triplet photosensitizers.[116,117] For the non-phosphorescent compounds, it is not a trival task to derive the T_1 triplet state energy level. TDDFT computations do not always give reliable estimation, especially for the Bodipy chromophores.[118] 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**, althought the S_1 state energy level decreased by ca. 0.28 eV.[85] Concerning this aspect, the spin density surface of the compounds give a clue in that the spin density surface of **12** and **13** are distributed on one of the two Bodipy moieties in the dimers (Fig. 7), thus the triplet state energy level of these Bodipy dimers does not decrease as the singlet excited state does.



15 **16**

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

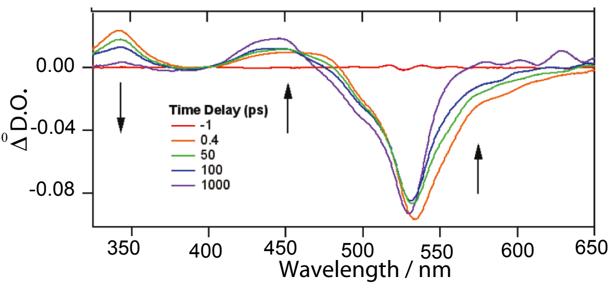
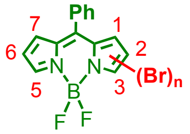


Fig. 9 Femtosecond transient absorption spectra of the Bodipy **16** in acetonitrile. Arrows indicate spectral changes as time progresses. Reproduced with permission from Ref. 119.

The ISC rate constants of the halogenated Bodipy (Fig. 8) were studied with femtosecond (fs) TA spectroscopy (Fig. 9).[119] Upon femtosecond photoexcitation, the ESA band at 340 nm decreases (Fig. 9), 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 growing was determined as 131 ps, which was assigned as the intersystem crossing (ISC) process.[119] This process is much faster than the fluorescence of Bodipy chromophores (a few ns), thus iodination is an efficient approach for Bodipy chromophore to form triplet excited state.



17

	n	position of Br atoms
17a:	0	
17b:	1	2
17c:	2	2, 6
17d:	4	2, 3, 5, 6
17e:	6	1, 2, 3, 5, 6, 7

Fig. 10 Polybrominated Bodipy derivatives at triplet photosensitizers.[104]

The $^1O_2$ generation and the triplet excited state quantum yield (Φ_T) of poly brominated Bodipy were studied (Fig. 10).[104,120] The Φ_T increased to 0.66 for the hexa bromoBodipy. The corresponding Φ_Δ is up to 0.64.

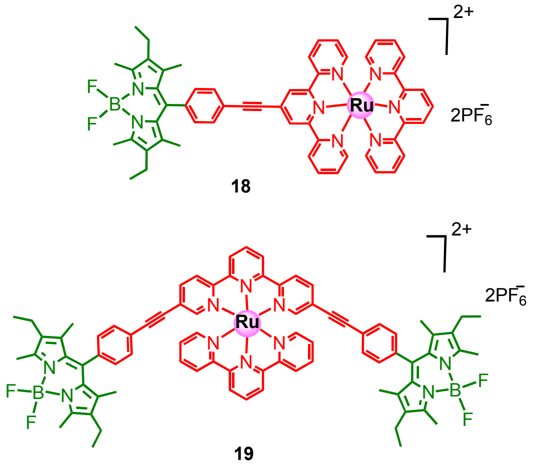
Table 1. Photophysical properties of compounds **1** – **17**. [a]

	λ_{abs}/nm [b]	ε [c]	λ_{em}/nm [d]	Φ_F [e]	Φ_Δ [f]	τ_T/μs [g]	Ref.
1	535	110000		0.02	–	–	88
2a	650	79000	673	0.01	–	–	89
2b	679	75000	714	0.1	–	–	89
2c	653	80000	679	<0.01	–	–	89
3	666	69900	694		0.70 ±0.03	1.5	109
4	731	201000	754	0.37	–	–	112
5	720	89000	754	0.45	–	–	112
6	503	82000	515	71.2±0.4	–	0.02	85
7	510	88000	532	3.6±0.3	–	66.3	85
8	529	89000	552	2.7±0.3	–	57.1	85
9	629	72800	706	9.5±0.1	–	4.0	85
10	539	75400	563	7.8±0.4	–	57.2	85
11	557	59400	631	4.6±0.2	–	54.6	85
12	576	180000	623	10.5±0.2	–	26.9	85
13	575 /618	90900 /89500	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 detail information, please refer to the maintext and the references. [b] Absorption wavelengths at the maxima. [c] Molar absorption coefficient. [d] Emission wavelength. [e] Fluorescence quantum yield. [f] Singlet oxygen quantum yield. [g] Triplet state lifetime.

2.2. Bodipy-containing transition metal complexes

Heavy atom effect is not limited to bromine or iodine atoms. Precious metal atoms, such as Ru, Pt, Ir, Re, were also widely used for 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 ligands were also studied.



18

19

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

Bodipy-containing Ru(II) complexes were prepared (Fig. 11).[82] In order to avoid π-conjugation between the Bodipy units and the Ru(II) coordination center, the acetylide linkers were attached on 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 not observed.

At 77 K (in 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, not the Ru(II) coordination center. The triplet state lifetimes of complexes **18** and **19** were determined as 8 μs and 30 μs, respectively. In comparison, the Ru(II) terpyridine coordination center, without Bodipy moiety, gives much shorter triplet state lifetime (a few hunderds ps).[6,123,124]

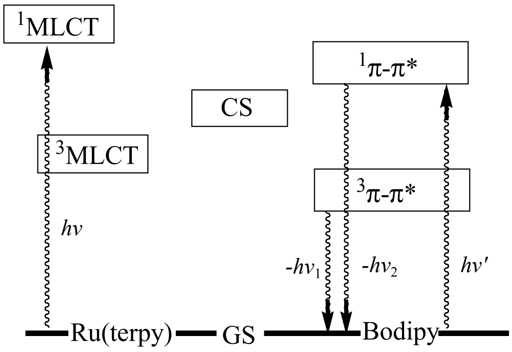
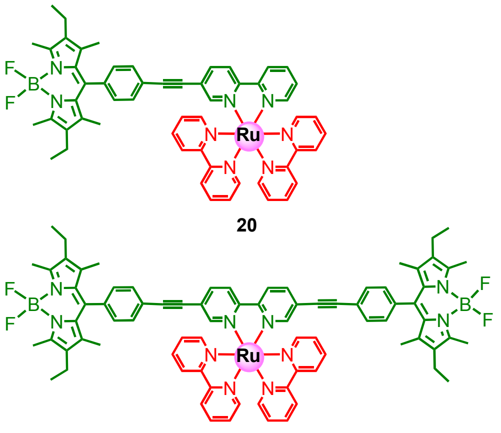


Fig. 12 Excited state levels of the Ru(terpy)–Bodipy dyads **18** and **19**. GS stands for ground state, CS stands for charge-separated state. Re-produced with permission from Ref. 82.

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 $^1\pi$-π* 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}Bodipy*→^{1}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}MLCT state will also produce the Bodipy-localized $^3\pi$-π* 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 fluorescene of the Bodipy ligand at low temperature, 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).

Similar photopysical properties were observed with the Ru(bpy)$_3$-Bodipy complexes (Fig. 13).[83] Ultrafast TA spectroscopy shows that the intramolecular singlet energy transfer from the ^{1}MLCT state to the $^1\pi$-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.



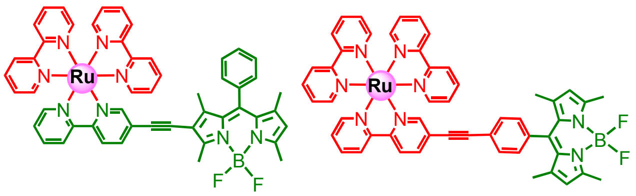
20

21

Fig. 13 Bodipy-containing Ru(II)(bpy)$_3$ complexes **20** and **21**.[83]

Different from the complexes in Fig. 11 and Fig. 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 a reference without the conjugation between the Bodipy and the Ru(II) coordination center. Fig. 14).[125] In **22**, an ethynyl linker was attached on 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 fascilitate the ISC, thus the harvested photoexcitation energy of the complex can be efficiently funnled to the triplet excited state manifold. Non π-conjuated chromophore and coordination center may render a situation that strong absorption of visible light is observed, but the absorbed photoexcitation energy is unable to be efficiently funneled to the triplet excite state manifold, i.e. it is trapped on the light-harvesting ligand.



22 **23**

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]

The absorption of **22** (528 nm) is slightly red-shifted as compared with that of **23** (499 nm). Both complexes show strong absorption (ε = 65200 M^{-1} cm^{-1} and 76700 M^{-1} 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 (Φ_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 ^{3}IL state, not an ^{3}MLCT state. Charge transfer emissive state, such as ^{3}MLCT state, usually give much larger thermally induced Stokes shift.

Table 2. Photophysical properties of **18** – **23**. [a]

	λ_{abs} nm	ε	λ_{em}/ nm	Φ_Δ	τ_T, μs	τ_p	Ref.
18	523	66100	536/774 (77 K)	–	8	50 ms	82
19	523	89600	540/ 774 (77 K)	–	30	50 ms	82
20	523	61340	536 (77 K)	–	–	5 ns	83
21	523	86700	535 (77K)	–	–	6 ns	83
22	528	65200	748/ 741 (77K)	0.93	279.7	33.9 ms	125
23	499	76700	513/ 510 (77K)	0.64	246.6	4.4 μs	125

[a] For detail information, please refer to the maintext and the references.

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 T_1 state of the complexes was localized on the Bodipy ligand, not 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 as 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.

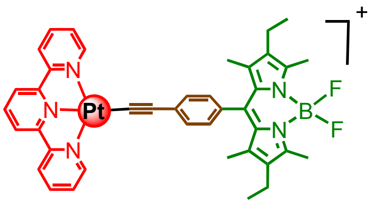
The Φ_Δ of **22** and **23** were determined. The Φ_Δ of **22** (0.93) is higher than **23** (0.64). The higher Φ_Δ value of **22** than that of **23** indicates efficient ISC in **22** than **23**, although the contribution from other factors, such as CT and CR, are unable to be excluded. The complexes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

Based on the results in literatures and those from our own group, we propose it is a general rule to use bulky ligands to achive long-lived triplet excited state, due to the reduced heavy atom effect (SOC) for these $^3\pi$-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 $\Delta E_{T1/S0}$, the $T_1 \rightarrow S_0$ ISC required much stronger SOC (eq. 1).[126]

$$k_{\mathrm{isc}} \propto \frac{\langle T_1|H_{SO}|S_1\rangle^2}{(\Delta E_{S1-T1})^2} \qquad \text{(eq. 1)}$$

This postulation is supported by the photophysics of the well known complex $Ru(bpy)_3Cl_2$. Note 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}MLCT→^{3}MLCT ISC of $Ru(bpy)_3Cl_2$ takes less than 1 ps, yet the ^{3}MLCT→S_0 decay takes hundreds of ns.[7] These results infer that the effect of the same heavy atom on the ^{1}MLCT→^{3}MLCT and ^{3}MLCT→S_0 processes is different.

To us it is always in doubt that 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 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 lack of quantitative data. Study on the following Bodipy-containing Pt(II) complexes clarified the above question to large extent.



24

Fig. 15 Bodipy-containging N^N^N Pt(II) acetylide complex **24**.[127]

In N^N^N Pt(II) acetylide complex **24** (Fig. 15), the Bodipy moiety and the Pt(II)-coordination center is not in π-conjugation due to the *meso* phenyl moiety of the Bodipy chromophore. The Φ_F of the Bodipy ligand in **24** is 27%, as compared to that of the uncoordinated ligands (Φ_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) cooridnation center (to be centered at 635 nm) was not observed in **24**.

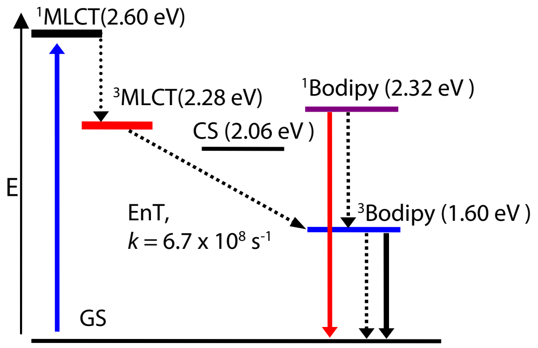
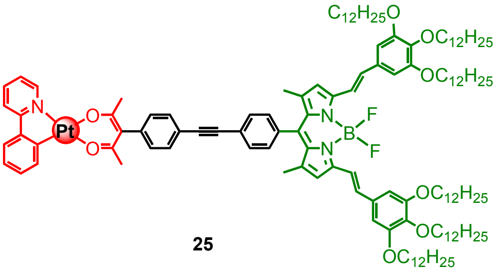


Fig. 16 The photophysical processes in **24** upon photoexcitation.[127] Reproduced with permission from Ref. 127.

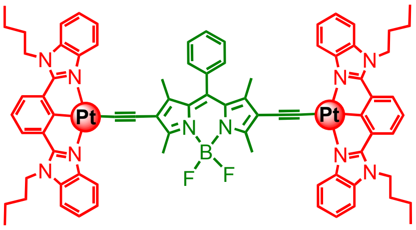
UV–vis absorption spectra and the electrochemical studies indicate that the components in **24** are in supramolecular feature, i.e. there is no electronic interaction between the components at ground state. Fluorescence lifetime of **24** and the reference Bodipy ligands indicate that there is no significant fluorescence quenching at low temperature (77 K). Electrochemical studies indicate the presence of CS state, lying between the ^{3}MLCT state and the ^{3}Bodipy state (Fig. 16). Due to the ultrafast ISC in the Ru(II) coordination center (<1 ps), excitation into the ^{1}MLCT state does not contribute to the fluorescence of the Bodipy moiety, which requires ^{1}MLCT$\rightarrow$^{1}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}Bodipy state is populated mainly from the ISC (^{1}Bodipy $\rightarrow$ ^{3}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 C^N Pt(II) acac complex (acac = acetyl-acetonate. Fig. 17),[128] i.e. non-efficient ISC of the Bodipy chromophore.



25

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

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 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]



26

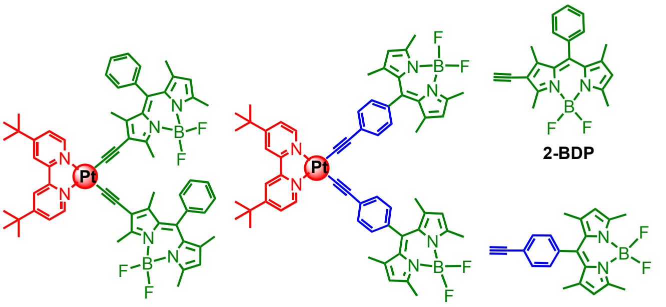
Fig. 18 Bodipy-containing Pt(II) complex **26** with the π-conjugation framework of Bodipy linked to Pt(II) atoms.[129]

Complex **26** shows 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 Fig. 17). The absorption maximum of **26** is at 574 nm (ε = 53800 M^{-1} cm^{-1}). The absorption band is broader than the free ligand (centered at 543 nm, ε = 85800 M^{-1} cm^{-1}).

An intense emission band at 770 nm was observed for **26** at room temperature in fluid solution (Φ_P = 3.5%) (Table 3). The luminescence lifetime of this near IR emission band was determined as 128.4 μs. 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 phosphoresence 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 as an ^{3}MLCT emission. Note the triplet state lifetime of **26** is much longer than that of the normal N^N Pt(II) acetylide complexes (usually the emissive state is in ^{3}MLCT/^{3}IL feature and the lifetime is shorter than 10 μs).[8] This is due to the ^{3}π-π* 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 as 125.8 μs (Table 3). The complex was used as triplet photosensitizer for TTA upconversion, upconversion quantum yield of 5.2% was observed.

The molecular structural designing rationale 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) bisacetylide 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.



27 **28** **2-BDP** **8-BDP**

Fig. 19 N^N Pt(II) bisacetylide complexes **27** and **28** with Bodipy ligands.[130]

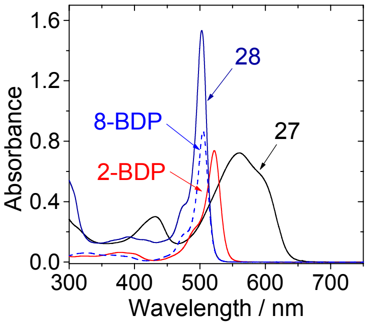


Fig. 20 UV-vis absorption of free ligands 2-BDP, 8-BDP and the complexes **27** and **28**.[130]

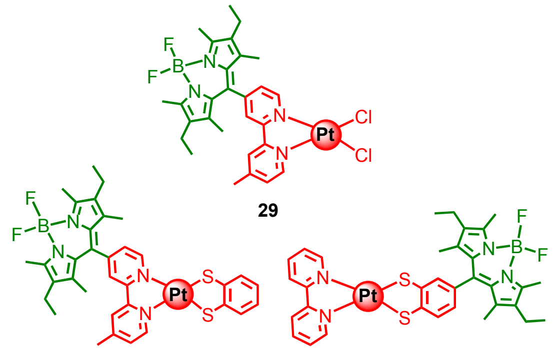
For **28**, the residual fluorescence of the Bodipy ligand was observed. The phosphorescence of the Pt(II) coordination center (at 567 nm for the N^N Pt(II) bisphenylacetylide complex, Φ_P = 16%) was not observed, which is attributed to the triplet-triplet energy transfer (TTET) from the ^{3}MLCT state to the ^{3}Bodipy state. For **27**, however, two emission bands at 631 nm and 792 nm were observed, luminescence lifetimes of 0.9 ns and phosphorescence lifetime of 35.9 µs were observed, respectively. Thus the two emission bands can be attributed to the fluorescence and phosphorescence, respectively. The triplet state lifetime of **27** was determined as 37.9 µs by ns TA spectroscopy. On the other hand, the triplet state lifetime of **28** was determined as 162.1 µs. Our later study shows that the Φ_T of **27** is ca. 2-fold of that of **28**. These results indicate that direct metalation of 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]

Table 3. Photophysical properties of **24** – **35**.[a]

	λ_{abs}/nm	ε	λ_{em} / nm	Φ_F	τ_T, µs	τ_p	Ref.
24	523	54610	536/ 535(77K)	0.27	–	6 ns	127
25	650	126000	670/ 665(77K)	0.45	–	3.90 ns	128
26	406/574	33900 /53800	660/770	0.035(Φ_P)	125.8	1.5 ms	129
27	561	72000	631/792	0.003 /0.0006(Φ_P)	35.9	–	130
28	503	153000	521	0.0188	162.1	–	130
29	537	53000	590	0.33	–	–	131
30	536/597	60200 /8300	–	–	–	–	131
31	524/568	107700 /11800	–	–	–	–	131
32	522/612	–	–	–	–	–	132
33	522/600	–	–	–	–	–	132
34	514/619	–	628/772/ 764(77K)	<0.001/ 0.26(Φ_P)	95	67 µs/ 92 µs (77K)	134
35	425/620	–	–	–	–	30 µs	134

[a] For detail information, please refer to the maintext and the references.

Eisenberg used Bodipy ligand to preparation of Pt(II) diimide(dithiolate) complexes, with the intension 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 on either the bipyridine ligand (**29** and **30**), or the dithiolate ligand (**31**).[131] Note 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, thus there is no significant electronic interaction between the components in the dyads at 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.


29

30 **31**

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

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

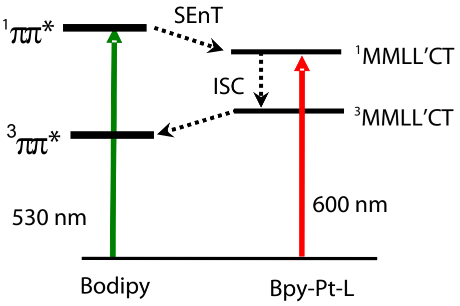
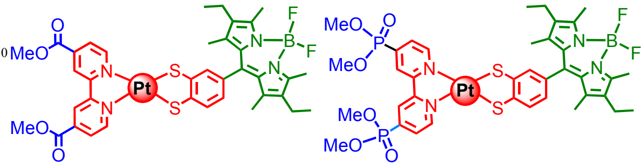


Fig. 22 Energy level diagram relevant to the photochemistry of complex **30** and **31**. Reproduced with permission from Ref. 131.[131]

The photophysical processes of **30** were summarized in Fig. 22.[131] Upon selective photoexcitation, the ^{1}Bodipy singlet excited state was produced, 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 producesd the triplet excited state (^{3}MMLL'CT). Then intramolecular TTET produced) the triplet excited state of Bodipy. Thus, both the *fluorescence* of the Bodipy moiety and the *phosphosrescence* of Pt(II) coordination center should be quenched.

The poor spectral overlap and the unfavorable dipole moments orientation in dyad **30** predict slow singlet energy transfer (calculated as 1/k_{EnT} = 710 ps), given the energy transfer is via the Förster mechanism (FRET). However, the experimental singlet energy transfer time is 1/k_{EnT} = 0.6 ps. Thus it was proposed the electron exchange is responsible for the ultrafast singlet energy transfer in **30**, not the Förster mechanism.[2] The triplet excited state lifetime 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, electron withdrawing groups were attached on the bpy ligand (complexes **32** and **33**, Fig. 23), thus the energy level of the ^{3}MMLL’CT state become lower than that of the Bodipy triplet state, thus the T_1 state of the dyads **32** and **33** is localized on the Pt(II) coordination center, not on Bodipy antenna (Fig. 23).[132]



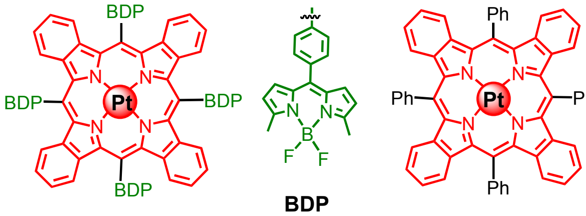
32 **33**

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

It should be pointed out that direct attachment of an organic chromophore to the Pt(II) center does not guarantee long-lived triplet excited state, rather, the lifetime of the triplet state is dependent on the molecular structure of the chromophore to large extent. For example, with perylenebisimide (PBI) attached to Pt(II) center in a N^N Pt(II) bisacetylide complex, 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-tetraphenyltetrabenzoporphyrin (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 Bodipy antenna and the benzoporphyrin-Pt(II) coordination center. However, fast non-raditive decay channel exists for the specific Bodipy chromophore used in the conjugates (Fig. 24). Note these is no methyl groups at the 1,7-position of the Bodipy, thus the rotation of the *meso* phenyl moiety dissipates the enery of the S_1 state. This property was later empolyed to develop fluorescent viscosity molecular probes.[135,136] However, this fast decay channel does not necessarily mean an inhibition of FRET, given the FRET process is faster.

The Bodipy moiety shows strong absorption at 514 nm. Thus with four Bodipy antenna, **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 (τ_P = 30 µs). Thus the Bodipy chromophore exerted substantial influence on the excited state of the complex **35** (Table 3).



34 **BDP** **35**

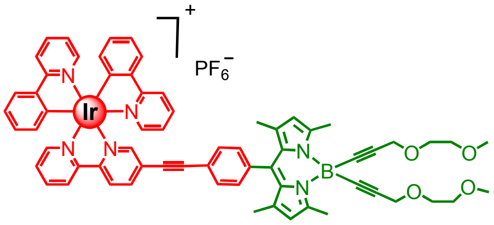
Fig. 24 The broadband visible light-harvesting Bodipy-tetraphenyl-tetrabenzporphyrin complex (**34**). The Bodipy chromophore (BDP) and the unsubstituted Pt(TPBP) complex (**35**) were also presented.[134]

The ultrafast TA spectra of the complex was recorded upon selective photoexcitation into the Bodipy part. Singlet energy transfer in the complex **34** was confirmed, on a time sacle of 1/k_{EnT} = 1.29 ± 0.11 ps. The transient spectrum indicated the backward TTET from the Pt(TPBP) coordination center to the Bodipy moiety. The rate constant is k_{TTET} = 1.0 × 10^{10} 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]

ns TA spectroscopy of **34** was studied. Three bleaching bands at 430 nm, 515 nm, 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, indicates 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 feature and the components of the dyad show their respective absorption and electrochemical properties.

The phosphorescene of the Ir(III) coordination center was quantitatively quenched in the complex **36**, due to the triplet-triplet energy transfer (TTET) to the Bodipy moiety, which is with lower triplet state energy level (E_{T1} = 1.69 eV) than the Ir(III) coordination center (E_{T1} = 1.97 – 2.10 eV). The formation of the ^{3}Bodipy* 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 fluorescenec of the Bodipy ligand.



36

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

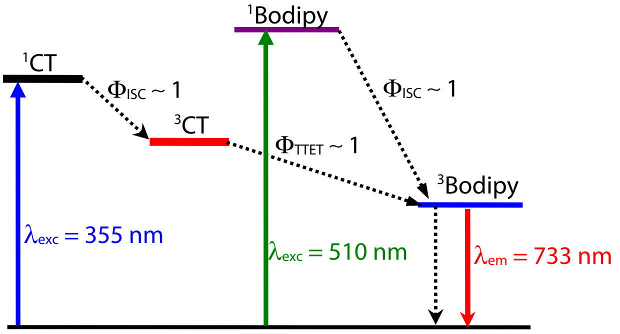
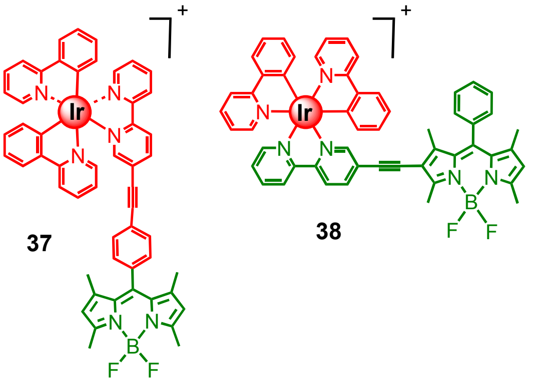


Fig. 26 The photophysical processes of Bodipy-containing Ir(III) complex **36**.[84]

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

In order to clarify the effect of different linker between the Bodipy chromophore and the Ir(III) coordination center, i.e. either 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, wheareas in **38** the Bodipy chromophore is in π-conjugation with the Ir(III) coordination center.



37 **38**

Fig. 27 Bodipy-containing Ir(III) complex **37** and **38**.[137]

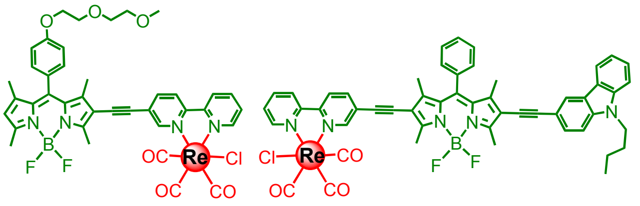
The absorption of **38** is slightly red-shifted as compared with **37**. The residual fluorescence of the Bodipy moiety was observed in both **37** and **38**. The residual Bodipy fluorescence in **38** is only 16% of that of **37**, thus the ISC is more efficient in **38**. As a support of this postulation, 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 as 23.7 μs and 87.2 μs, respectively. As a further prove for the efficient ISC in **38** but not in **37**, the Φ$_\Delta$ were determined as 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 long-lived triplet excited state. We prepared series complexes to verify this postulation.[47]

Re(I) complexes have attracted much attention due to the applications in luminescent bioimaging,[31,34,138–142] photovoltaics.[143] and triplet photosensitizers for photocatalysis.[144–146] However, most of these complexes show weak absorption in the visible spectra region, 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]

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	83600	730(77K)	–	–	25	–	84
37	499	71400	514	1.8	0.52	23.7	–	137
38	527	83000	553/742	0.3/0.03	0.97	87.2	4.5 ms(77K)	137
39	536	91700	556/742	0.0013	0.88	104.0	–	147
40	574	64600	647	0.171	0.06	127.2	–	147

[a] For detail information, please refer to the maintext and the references.



39 **40**

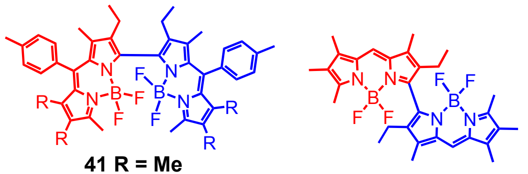
Fig. 28 Bodipy-containing Re(I) tricarbonyl chloride complexes **39** and **40**.[147]

Different Bodipy ligands were used in **39** and **40** to tune the absorption wavelength. **39** shows intensive absorption at 536 nm (ε = 91 700 M^{-1} cm^{-1}), whereas **40** shows absorption at 574 nm (ε = 64 600 M^{-1} cm^{-1}). For both complexes, the residual Bodipy ligand fluorescence were observed, and the fluorescence quantum yield of **39** and **40** were determined as 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).

With ns TA spectroscopy, the triplet state lifetime of **39** and **40** were determined as 104.0 μs and 127.2. μs, respectively. The singlet oxygen quantum yield (Φ_{Δ}) of **39** and **40** were determined as 88% and 6%, respectively. Therefore, we propose that with 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 heavy atom effect. With two identical chromophores connected in close vicinity, but without π-conjugation, then 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 states 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 splitted into two different absorption bands in the dimer (Fig. 30). **42** shows a Φ_F of 0.69. Similar Bodipy dimers showing the exciton coupling effect was reported (**43**, Fig. 42).[148] The dimers show Φ_F of 0.67–0.76. Φ_{Δ} of **43** was determined as 0.4 (with TPP as standard, Φ_{Δ} = 0.70 in aerated toluene) (Table 5). Thus the ISC in these Bodipy dimers is far from efficient. However, no new progess in this area was made in recent years.



41 R = Me
42 R = Et

43

Fig. 29 Bodipy dimers **41**–**43** show the exciton coupling effect.[11,148]

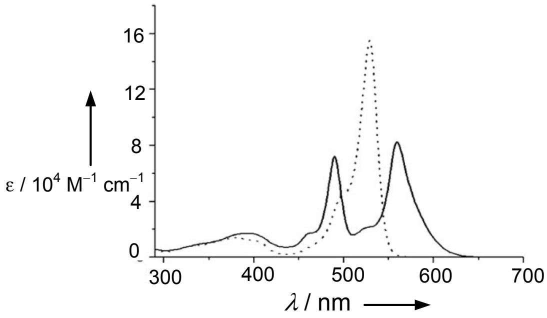
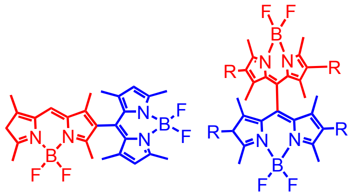


Fig. 30 The spectroscopic properties of **42** (solid line) and **43** (dot line) in toluene. Reproduced with permission from ref. 148.

2.4. Orthogonal Bodipy dimers showing double substituted excited state



44

45 R = H
46 R = Et

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

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	67100/77100	638	0.67	–	–	–	11
42	490/559	72000/82600	638	0.69	–	–	–	11
43	3492/565	64400/73600	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	211000	695	0.39	0.47	–	–	113
48	698	146000	705	0.38	0.20	–	–	113
49	709	287000	712	0.67	–	–	–	113
50	688	120000	700	0.22	0.42	–	–	113
51	731	185000	755	0.38	–	–	–	113
52	738	160000	763	0.10	–	–	–	113
53	571	83500	582	0.040	0.581	170.5	–	114
54	529	56500	608	0.112	0.0493	389.9	–	114

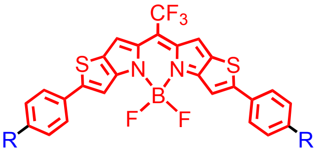
[a] For detail information, please refer to the maintext and the references.

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

2.5. Heavy atom-free Bodipy-drived triplet photosensitizers.

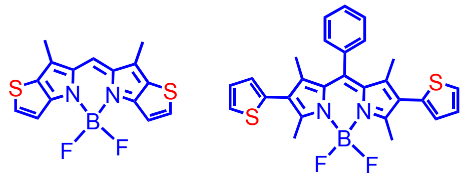
Recently heavy atom free thienyl-fused Bodipy derivatives were reported to show efficient ISC (Fig. 32).[113] The compound **47** shows strong absorption of visible light at 688 nm (ε = 211000 M^{-1} cm^{-1}), the fluorescence quantum yield (Φ_F) is 22%, and the singlet oxygen quantum yield (Φ_{Δ}) is 42%.[113] Femtosecond TA spectroscopy was used for study of the singlet excited state, but no detail 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 triplet state quantum yield (Φ_T) of 63.7%, whereas for **54**, the triplet state quanyum yield (Φ_T) is only 6.1%.[114] The fluorescence quantum yield 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). With nanosecond TA spectra, the triplet state lifetimes of **53** and **54** were determined as 170.5 μs and 389.9 μs, respectively.



47 R = CF$_3$
48 R = F
49 R = CH$_3$
50 R = H
51 R = OMe
52 R = OH

Fig. 32 Thieno-pyrrole fused Bodipy dyes showing ISC upon photoexcitation.[113]

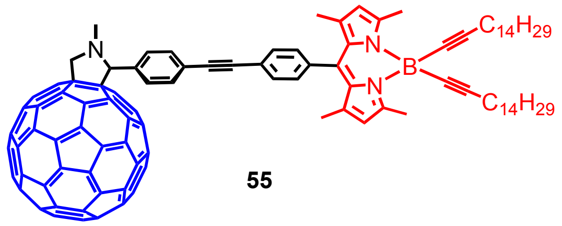


53 **54**

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

TDDFT computation indicate that the S_1/T_2 energy gap for **53** is small (0.24 eV), 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 these results to molecular structure designing, since the S_1/T_2 energy gap is not readily available. TDDFT computations may be helpful.

Concerning formation of triplet excited state of Bodipy without heavy atom effect, C_{60}-Bodipy dyad is an important molecular structure motif for formation of Bodipy triplet excited state upon photoexcitation.[12]



55

Fig. 34 Bodipy-C_{60} dyad **55**.[150]

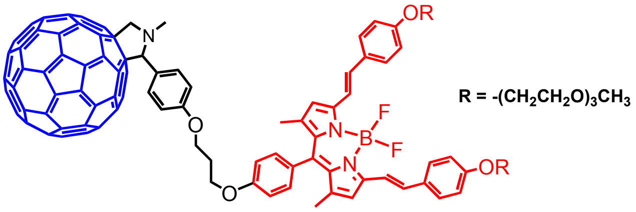
Ziessel studied the photophysics of a C_{60}-Bodipy dyad **55** in detail (Fig. 34).[150] It was found that the solvent polarity dictates the photophysical processes of the C_{60}-Bodipy dyad. In non-polar solvent, such as toluene, no photoinduced charge separation occured, this is a general rule that the Gibb free energy change ($\Delta G°$) of PET in non-polar solvent is less negetive than that in polar solvents.[151–154] Instead, singlet energy transfer from the Bodipy to the C_{60} moiety was predicated. The ISC of the C_{60} moiety produce the triplet excited state,[155] which is localized firstly on the C_{60} 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 C_{60} moiety ($\Delta G° = -0.18$ eV), no C_{60} π-radical anion was detected with the fs TA spectra (the featured ESA band is at 1000 nm), upon selective photoexcitation into the Bodipy moiety by 490 nm excitation (Table 6). FRET may be not the main mechanism for the energy transfer, due to the poor spectral overlap of the energy donor and the energy acceptor, as well as the weak absorption of C_{60} (prohibited $S_0 \rightarrow S_1$ transition for C_{60}, the singlet energy acceptor).

With ns TA spectroscopy, equilibrium between the C_{60} triplet state and the Bodipy triplet state was observed, although most of the triplet state is localized on the C_{60} moiety. These results are interesting, since it is shown that heavy atom-free organic triplet photosensitizers can be developed with visible light-harvesting antenna and C_{60}, with C_{60} as the spin converter.[47]

In polar solvents such as benzonitrile, upon photoexcitation into the C_{60} part, S_1 state is populated and it decays within 125 ps, and the CTS formed, indicated by the C_{60} 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 C_{60} and the Bodipy moieties, thus no triplet state was produced by charge recombination (CR), instead the ground state (S_0) was produced by CR. Photoexcitation into the Bodipy moiety gives similar photophysical processes.

In less polar solvents such as CH_2Cl_2 and methyltetrahydrofuran, photoexcitation into the Bodipy or the C_{60} units also lead to the formation of CTS. The CTS is higher in energy than the triplet state, thus CR produce the triplet state of C_{60}. These conclusions are based on the TA spectral data.

Using different Bodipy antenna for the dyad may change the photophysics. For example, with styrylBodipy as the antenna, no singlet energy transfer from the styrylBodipy antenna to the C_{60} 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-C_{60} dyad (dyad **55** in Fig. 34), for which the CR selectively gives the C_{60}-localized triplet excited state.



56

Fig. 35 StyrylBodipy-C_{60} dyad **56** with triplet state formation.[152]

The fluorescence of the styrylBodipy antenna in dyad **56** was dramatically quenched, but no enhancement of the C_{60} emission was observed, thus it is proposed the photoinduced charge separation is responsible for the fluoresence quenching. Electrochemical studies show that formation of charge transfar state (CTS) is favorable in either PhCN or toluene, with $\Delta G_{CS} = -0.68$ eV and -0.40 eV, respectively.[152]

Femtosecond TA spectra indicated the formation of C_{60} radical anion, which shows absorption at 1000 nm, as well as the absorption of the radical cation of styrylBodipy moiety at 767 nm. The rate constant of the charge separation is 3.1×10^{10} s^{-1}, and the CR rate constant is 2.1×10^{9} s^{-1}. Nanosecond TA spectra show that the styrylBodipy triplet excited state was produced upon photoexcitation, the triplet state lifetime was determined as 476 µs. The photophysical processes are summaried in Fig. 36.

AzaBodipy is interesting due to its absorption in the red/near IR region (600 – 700 nm).[89,107] Note the normal Bodipy gives absorption at about 500 nm.[53] AzaBodipy was used for preparation of dyad **57** (Fig. 37).[156]

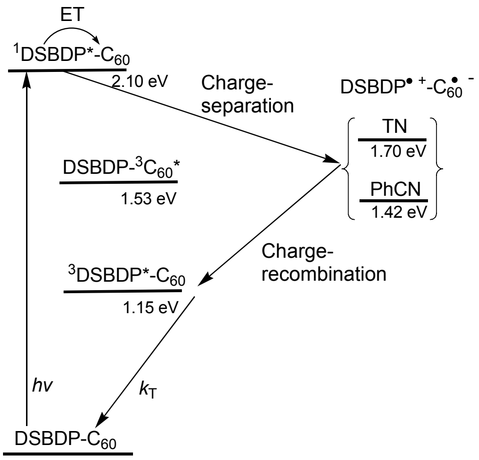
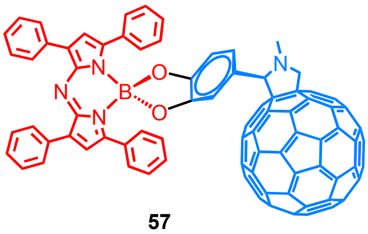


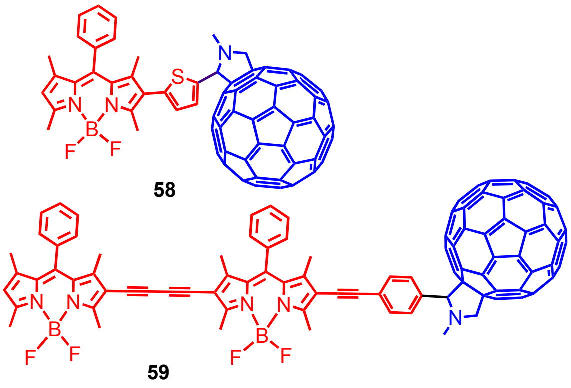
Fig. 36 The photophysical processes involved in StyrylBodipy-C_{60} dyad **56**. Reproduced with permission from Ref. 152.

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 C_{60} 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 as 1.0×10^{12} s^{-1}, and the CR process is with rate constant of 5.0×10^9 s^{-1}. The T_1 state energy level of the azaBodipy (0.79–0.87 eV),[108] which is much lower than that of C_{60} (1.62 eV).[155] Thus the CR may produce the triplet state of azaBodipy moiety. The formation of the azaBodipy triplet state was confirmed by ns TA spectra. The triplet state lifetime was determined as 83.3 μs.



57

Fig. 37 AzaBodipy-C_{60} dyad.[156]



58

59

Fig. 38 Bodipy-C_{60} dyads **58** and **59** with variable visible light absorption.[90]

Our group prepared Bodipy-C_{60} dyads **58** and **59** (Fig. 38).[90] For **58**, the absorption band is centered at 515 nm (ε = 704 00 M^{-1} cm^{-1}). For **59**, the absorption wavelength is red-shifted to 590 nm (ε = 82 500 M^{-1} cm^{-1}). The fluorescence of the antenna was significantly quenched in the dyads, indicating singlet energy transfer, although CS cann't be excluded, especially in polar solvents. ns TA spectra show that for both dyads, the triplet states localized on the C_{60} moieties were produced upon photoexcitation, indicated by the ESA band of T_1 state of C_{60} at 720 nm (Fig. 39). The triplet state lifetimes of **58** and **59** were determined as 33.3 μs and 35.2 μs, respectively, which is close to the intrinsic triplet state lifetime of C_{60} (40 ± 4 μs).[155] It should be pointed out that the localization of the T_1 state is dependent on the energy levels of the Bodipy and the C_{60} moieties.

For **59**, the S_1 state energy level of the antenna decreased by ca. 0.3 eV as compared with that of the antenna in **58**, but the T_1 state energy level of the antenna in **59** does not decrease significantly, because the triplet state of **59** is still localized on the C_{60} moiety (E_{T1} = 1.65 eV), not the Bodipy moiety. It was reported that Bodipy is with T_1 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 T_1 state energy level, is far from clear.

We prepared styrylBodipy-C_{60} triad **60** (Fig. 40), which show red-shifted absorption than **58** and **59**.[157] The styrylBodipy antenna shows absorption at 645 nm (ε = 56800 M^{-1} cm^{-1}). Notably the triplet state is localized on the styrylBodipy moiety, not the C_{60} unit (Fig. 41. Table 6). This conclusion is based on the ns TA spectroscopy, and the spin density surface analysis (Fig. 41).

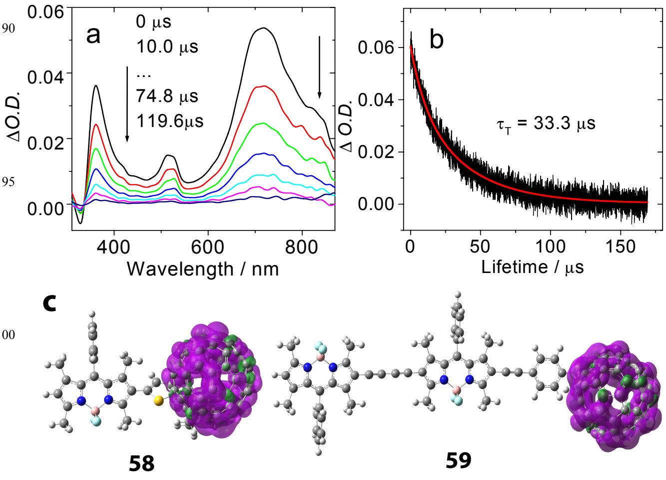
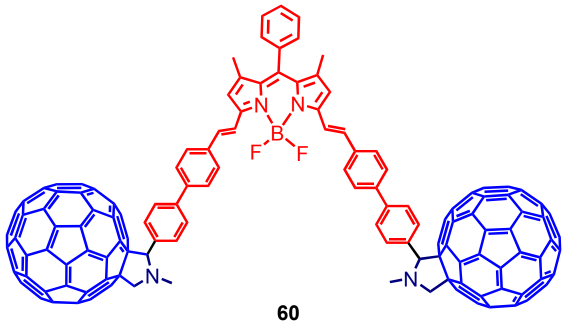


Fig. 39 (a) Nanosecond transient absorption spectra of **58** (λ_{ex} = 532 nm) and (b) the decay trace at 720 nm. In deaerated toluene, 25 °C. (c) Spin-density surface of **58** and **59** at the triplet state. Calculated at B3LYP/6-31G(d) level with Gaussian 09W. Reproduced with permission from Ref.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

The triplet state lifetime of **60** was determined as 105.6 μs. Notably the 2,6-diiodostyrylBodipy gives triplet state lifetime of 1.8 μs (Table 6).[87] The reason for this drastically different triplet state lifetime is unclear. The Φ_Δ of **60** was determined as 85%, indicating that the Φ_T of **60** is high. No femtosecond transient absorption spectra of the triad were studied, thus it is still open for question whether the triplet state is produced by CR or by backward triplet-triplet energy transfer from the C_{60} moiety to the styrylBodipy moiety.



60

Fig. 40 StyrylBodipy-C_{60} triad **60** with variable visible light absorption wavelength.[157]

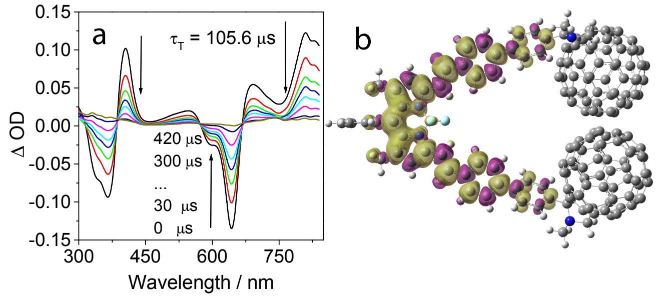


Fig. 41 (a) Nanosecond transient absorption spectra of **60** (λ_{ex} = 532 nm). In deaerated toluene. (b) Spin-density surface of **60** at the triplet state. Calculated at B3LYP/6-31G(d) level with Gaussian 09W. Reproduce with permission from Ref. 157.[157]

Table 6. Photophysical properties of compounds **55** – **60** [a]

	λ_{abs}, nm	ε	λ_{em}, nm	Φ_F	τ_T, μs	Ref.
55	335/501/693	–	516/720	–	–	150
56	375/648	–	592/662	–	–	152
57	312/479/640	–	682	–	–	156
58	515	70400	710	–	33.3	90
59	590	82500	627	0.017	35.2	90
60	645	56800	662	0.01	105.6	157
61	331	51000	–	–	–	158
62	505	102000	517	–	–	158
63	630	115000	642	–	–	158
64	593	106000	611	–	–	158
65	535	–	610	0.005	2.0±0.5	160

[a] For detail information, please refer to the maintext and the references.

We studied the formation of the triplet state of styrylBodipy via intermolecular energy transfer by C_{60}-containing and Bodipy hydrogen bonding modules **61** – **64** (Fig. 42).[158] **61** is the hydrogen bonding module with C_{60} as the spin converter, **62** – **63** are the hydrogen bonding modules with Bodipy or styrylBodipy as the antenna, which are energy donor. Titration of the Bodipy antenna with C_{60} module induces fluorescence quenching, which indicated either singlet energy transfer or electron transfer. Electrochemical studies indicated that intra-assembly photoinduced electron transfer is prohibited, thus the intra-assembly singlet energy transfer is the most probable mechanism for the fluorescence quenching of the antenna.

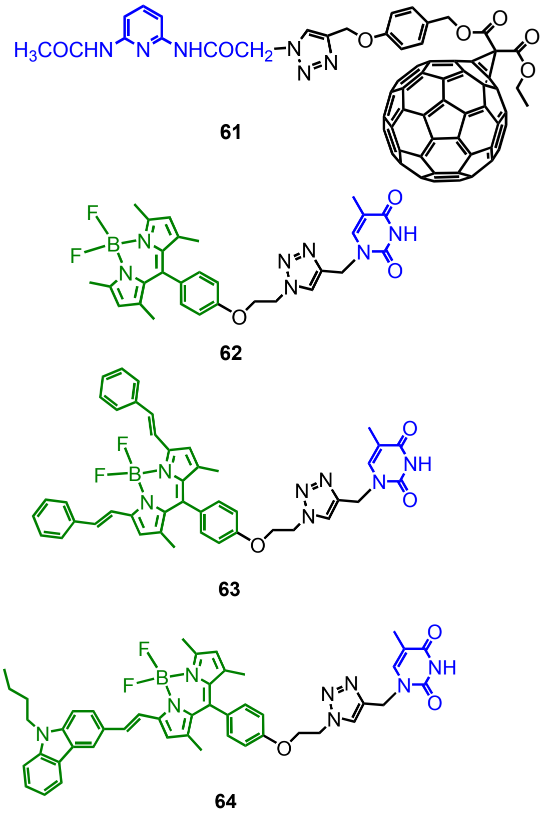
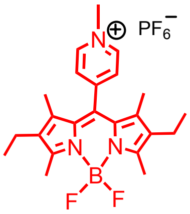


Fig. 42 Hydrogen bonding modules for formation of triplet excited state of Bodipy. **62** – **64** are light-harvesting modules, and **61** is the triplet formation module (singlet energy acceptor and triplet energy donor).[158]

Based on the nanosecond transient absorption spectra, triplet state localized on the C_{60} 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 moeity was also observed. This result is due to the much lower T_1 state energy level of the styrylBodipy (ca. 1.0 eV, based on TD-DFT computation).[159] than the C_{60} moiety (1.62 eV).[155] The formation 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 C_{60}-Bodipy dyads. A Bodipy-*N*-methylpyridinium dyad **65** was reported to produce triplet state upon CR (Fig. 42).[160] The fluorescence of the normal Bodipy fluorescence was quenched significantly in **65**. The fluorescence quantum yield is only 0.5%, and the majority of the emission of **65** is attributed to the emission from CTS, which is centered at 610 nm, much longer wavelength than the Bodipy.



65

Fig. 42 Bodipy-*N*-methylpyridinium dyad.[160]

With nanosecond transient absorption spectra, the triplet state of Bodipy chromophore was observed, with triplet state lifetime of 2.0 ± 0.5 μs. Interestingly, this lifetime is much shorter than that of the diiodoBodipys (generally longer than 50 μs).[85] The quantum yield for formation of triplet state (Φ_T) is ca. 75%. Such a high triplet state quantum yield will be interesting for applications.[160]

2.6. Using 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, thus photosensitizing ability can be improved if a broadband light source, such as solar light, was used.

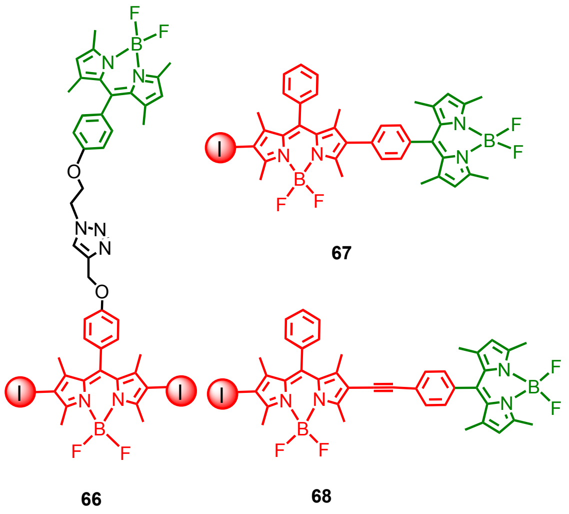


Fig. 43 Bodipy-diiodoBodipy dyads as triplet photosensitizers (**66** – **68**) (Bodipy moiety is the energy donor, diiodoBodipy moiety is the energy acceptor and the spin converter).[115]

Previously Bodipy-PtTPTBP (TPTBP = tetraphenyltetrabenzoporphyrin) conjugate (compound **34**, Fig. 24) was prepared, singlet energy transfer from the peripheral Bodipy moieites 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 μs (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 μs). 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 organic mimics of the above dye-precious metal complex conjugates. We designed the dyads **66** – **68** with Bodipy and iodoBodipy moieties (Fig. 43).[115] In **66**, **67** and **68**, Bodipy moiety gives 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 fluroescence 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. triplet state equilibrium was established. The triplet state lifetimes of the dyads **66**, **67** and **68** were determined as 286.1, 241.6 and 262.2 μs, respectively (Table 7).

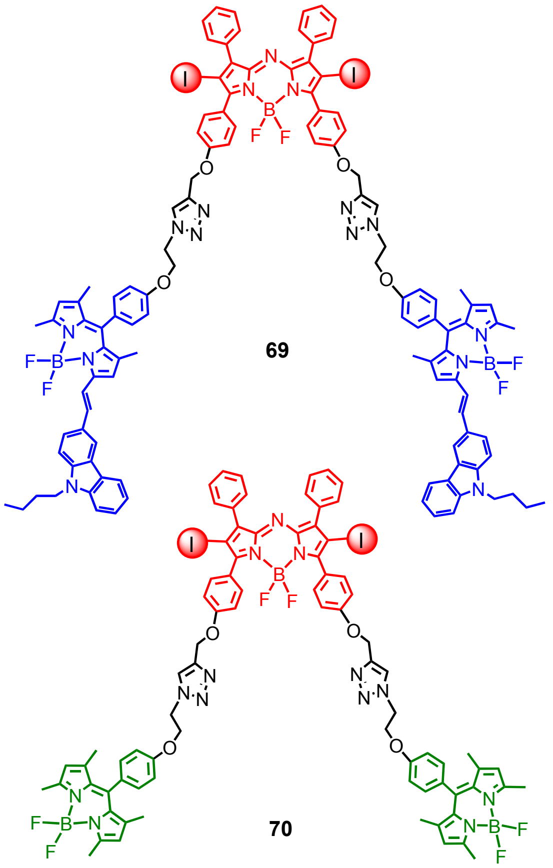


Fig. 44 Diiodo-azaBodipy derived broadband visible light-absorbing triplet photosensitizers **69** and **70**.[163]

In order to obtain dyads with broadband absorption in more red-shifted wavelength range, we used Bodipy, or carbazole-conjugated Bodipy as energy donor (variable absorption wavelength was achived), and diiodo-azaBodipy as the energy acceptor to prepare triplet photosensitizers (triad **69** and **70**. Fig.

44).[163] The singlet energy transfer efficiency was determined as 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 of comparison of the excitation/absorption spectra gives apparently 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 as $(5.1 \pm 0.4) \times 10^{11}$ s^{-1} and $(4.3 \pm 0.3) \times 10^{10}$ 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 diiodo azaBodipy moieites. The triplet state lifetimes of **69** and **70** were determined as 4.1 μs and 5.5 μs, respectively.

Rhodamine is a well known visible light-absorbing chromophore, and has been widely used in preparation of FRET molecular dyads.[165–167] However, no application of rhodamine in construction of organic triplet photosensitizer was reported. Rhodamine normally show weak ISC.[168] On the other hand, rhodamine derivatives usually contain carboxylic moiety, which may complicate the application due to the acid/base- or solvent-driven reversible spirolactam↔opened amide transformation.[166,169] The spirolactam structure of rhodamine 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 photophysical study, we used a rhodamine framework which is without the carboxylic moiety for prepration of broadband visible light absorbing triplet photosensitizers **71** and **72** (Fig. 45).[159]

In dyads **71** and **72**, rhodamine was used as singlet energy donor and diiodostyrylBodipy was used as singlet energy acceptor, as well as 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 at ground state. Fluorescence quenching of the rhodamine part in **71**, and the comparison of the fluorescene excitation spectrum and the UV−vis absorption spectrum of **71** supports singlet energy transfer (the efficiency is calculated as ca. 50%). Femtosecond TA spectra indicates the FRET rate constant of dyad **71** is $k_{FRET} = 6.7 \times 10^{11}$ s^{-1}. Triplet state localized on the styrylBodipy moiety was observed. The triplet state lifetimes of **71** and **72** were determined as 1.64 μs and 3.29 μs, respectively (Table 7). For **71**, the Φ_Δ was determined as 52% upon excitation of the rhodamine part.[159] At longer excitation wavelength, i.e. upon excitation into the styrylBodipy moiety, the Φ_Δ increased to 73%. The $^1O_2$ photosensitizing ability of **71** is higher than the diiodostyrylBodipy reference compound which contains only a single light-harvesting chromophore.

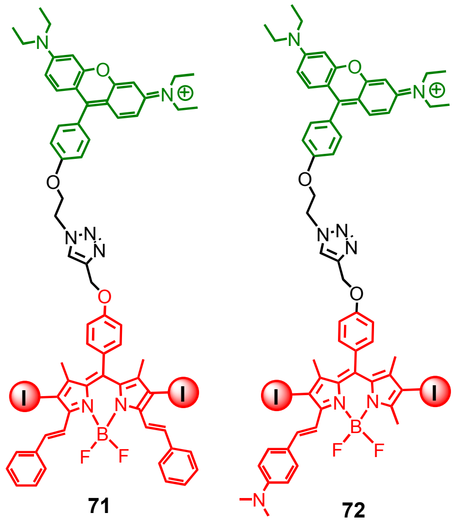


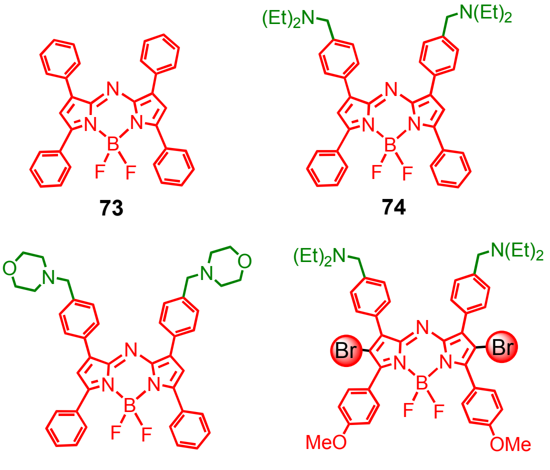
Fig. 45 Rhodamine-diiodo-styrylBodipy dyad triplet photosensitizers (**71** and **72**) which give broadband visible light-absorption.[159]

3. To switch the triplet excited state of Bodipy

Switching or modulation of the singlet excited state of Bodipy gives vast of functional materials, such as fluorescent molecular probes,[57] molecular logic gates,[170–175] visible light-harvesting molecular arrays,[67] etc. 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 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 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 controlling PET effect

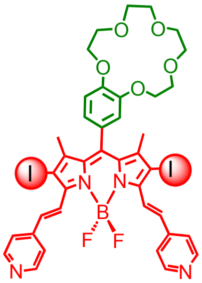
PET is one of the most popular mechanisms to switch the *singlet* excited state of organic chromophores,[57] include Bodipy (such as fluorescence).[177,178] Concerning the controlling of the triplet excited states, previously O'shea studied the acid-activated PDT effect of the azaBodipy derivatives under neutral and acidic conditions (Fig. 46).[103] **74** – **76** contain amino group, thus protonation of the amino moiety may inhibit the PET,[57] as a result the $^1O_2$ photosensitizing ability may be enhanced. This molecular designing rationale is based on the study of the PET modulated fluorescence.[57] **76** shows in vitro PDT activity toward MRC5 cell lines. With DPBP as the $^1O_2$ scavenger, $^1O_2$ photosensitizing ability was enhanced for **73** and **74** in the presence of acid. The triplet state was not studied in detail with nanosecond transient absorption spectroscopy.



73 **74** **75** **76**

Fig. 46 AzaBodipy derivatives **74** – **76** with PET effect.[103]

A molecular logic gate based on Bodipy was reported (**77**), with the $^1O_2$ photosensitizing as the output (Fig. 47).[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 $^1O_2$ production is weak. It is only in the presence of *both* Na^+ and H^+, the $^1O_2$ production was greatly enhanced. It was proposed that the enhanced $^1O_2$ 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 source better (660 nm LED array), thus the production of $^1O_2$ was enhanced.



77

Fig. 47 Bodipy derived molecular logic gate with $^1O_2$ production as output.[179]

Akkaya prepared Bodipy dyad logic gates with $^1O_2$ photosensitizing ability as one of the outputs (Fig. 48).[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, thus, no $^1O_2$ photosensitizing ability should be observed for the dyad. However, another possibility exists, i.e. there is intramolecular TTET and the triplet energy acceptor shows short-lived triplet excited state, which is inefficient to photosensitize singlet oxygen ($^1O_2$).

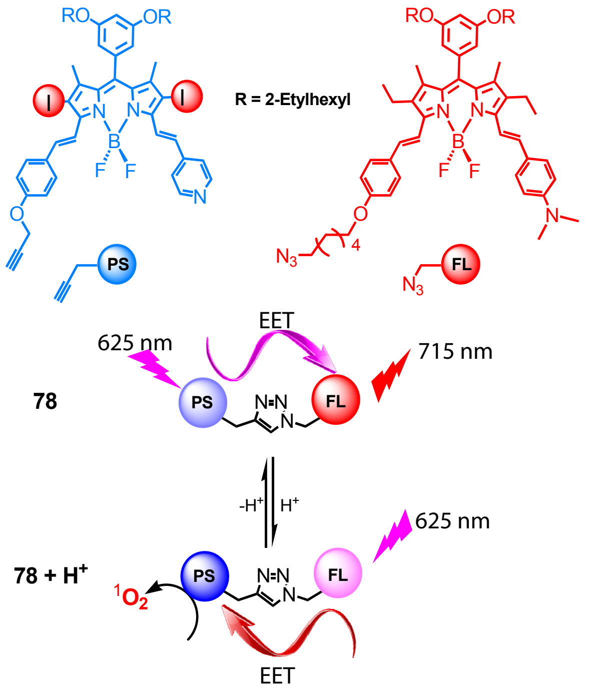


Fig. 48 Modular assembly of the molecular logic device with two different outputs depending on the acidity of the medium. Reproduced with permission from Ref. 69.

With addition of acid, i.e. upon protonation of the uniodinated styrylBodipy unit, the absorption of the singlet energy acceptor is blue-shifted, thus the initial FRET is inhibited (which was assumed to be competitive to the ISC), as a result, the $^1O_2$ photosensitizing ability of the iodinated styrylBodipy unit was observed.[69] Upon addition of acid, the $^1O_2$ photosensitizing ability of compound **78** was enhanced by 7-fold.

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	89800/69700	554	0.043	0.65	286.1	115
67	504/533	110400/85800	577	0.128	0.50	241.6	115
68	506/556	87800/66200	584	0.143	0.67	262.2	115
69	593/683	220000/81000	610/714	0.16/0.22	0.58	4.1	163
70	504/683	165000/71000	520/714	0.53/0.15	0.69	5.5(3.7)	163
71	551	52700	659	0.058	0.738/0.524	1.64	159
72	552	29400	698	0.086	0.396/0.087	3.29	159
73	ca.650	–	–	–	–	–	103
74	ca.650	–	ca.680	–	–	–	103
75	ca.650	–	ca.680	–	–	–	103
76	ca.690	–	ca.625	–	–	–	103
77	630–660	–	–	–	–	–	179
78	652	121000	715	0.42	–	–	69
78+H$^+$	650	105000	700	0.02	–	–	69

[a] For detail information, please refer to the maintext and the references.

3.2. Chemical-activated triplet photosensitizer

The triplet excited state can be switched by chemical inputs.[181,182] For example, thiol-activated $^1O_2$ photosensitizer **79** was studied (Fig. 49).[183] Thiols 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 reagents can be used as a targetted PDT reagent. To achieve this goal, 2,4-dinitrobenzenesulfonate (DNBS) moiety was attached on the dibromostyrylBodipy triplet photosensitizer (Fig. 49). 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 with this strategy.[184–188] In photosensitizer **79** (Fig. 49), DNBS was presumably used to quenching the triplet excited state, probably via PET process.[183]

The photosensitizer gives strong absorption at 650 nm. Without thiols such as GSH, the caged photosensitizer hardly gives any $^1O_2$ 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 moeity on the triplet state formation (thus the $^1O_2$ photosensitizing ability) was desmonstrated by the comparison of the $^1O_2$ photosensitizing ability of **79** and the reference photosensitizer **80**. It was shown the $^1O_2$ photosensitizing ability of sensitizer **80** is much more efficient than the caged photosensitizer **79**. 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.

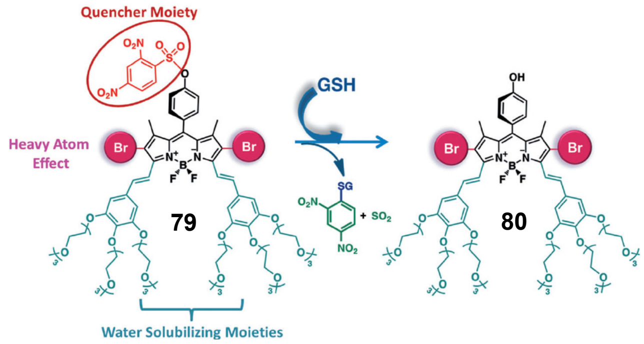
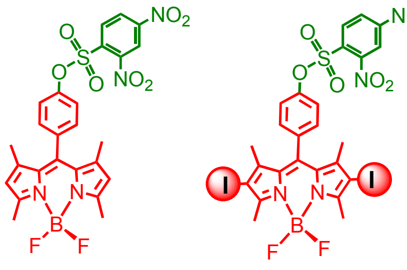


Fig. 49 Caged triplet photosensitizer based on dibromostyrylBodipy **79**, and the reference compound **80**.[183] Reproduced with permission from Ref. 183.

With compounds **81** and **82** (Fig. 50), we systematically studied the different quenching effect of the DNBS moeity 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 the fluorescence of compound **81** (Φ_F = 0.6%) is greatly reduced as compared to Bodipy (Φ_F = 90%). The fluorescence lifetime was reduced to 1.67 ns for compound **81**, as compared with the lifetime of 3.86 ns for Bodipy.

The Gibbs free enegy changes ($\Delta G°_{CS}$) of the PET process of the **81** was calcualted 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 $\Delta G°_{CS}$ values were calculated as −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, as 2.15 eV, 1.81 eV and 1.71 eV in toluene, dichloromethane and acetonitrile, respectively. Note 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]



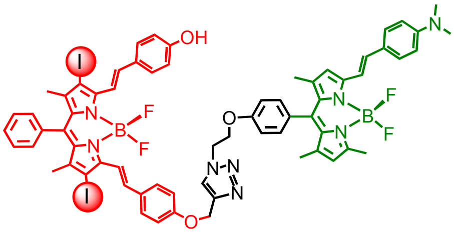
81 **82**

Fig. 50 Compounds used for comparison of the different quenching effect of DNBS on the singlet excited state (fluorescence. **81**) and the triplet state of Bodipy chromophore (**82**).[176]

On the other hand, we found that the PET in **82** is prohibited. For example, the $\Delta G°_{CS}$ values for **82** in toluene, dichloromethane and acetonitrile were calculated as +0.90 eV, +0.46 eV and + 0.33 eV (with triplet state of Bodipy as electron donor). The CTS energy level was also calculated for **82**. With the triplet state of Bodipy as the electron donor, the energy levels of the CTS are 2.42 eV, 1.98 eV and 1.85 eV. All these CTS enery levels are *higher* than the T_1 state energy levels of 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 $^1O_2$ quantum yield of **82** does not increase significantly upon cleavage of the DNBS (electron acceptor). For example, the Φ_Δ of **82** in acetonitrile is 74%, and it increases only slightly to 88% upon cleavage of the DNBS by thiols. Note the diiodoBodpy gives Φ_Δ of 79%.[87] This result is in stark contrast to the distinct switch-ON effect of the *fluorescence* in **81** upon cleavage of the DNBS moiety. In less polar solvents, such as toluene and dichloromethane, the Φ_Δ of **82** increase only slightly upon cleavage of the DNBS moiety by thiols.[176] It is only the triplet state lifetime of **82** increased from 24.7 μs to 86.0 μs (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 liftetime of **82** was determined as 166.6 μs and 168.1 μs, 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).

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 at singlet excited state and triplet excited state should be drastically different because 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 $\Delta G^{\circ}_{\mathrm{CS}}$ value will be different for the singlet excited state and the triplet excited state.[152]

We prepared a acid-responsive Bodipy-based dyad triplet photosensitizer **83** (Fig. 51), to study the modulation of the triplet by controlling FRET, as well as ICT.[189] In **83**, the diiododstyrylBodipy 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.



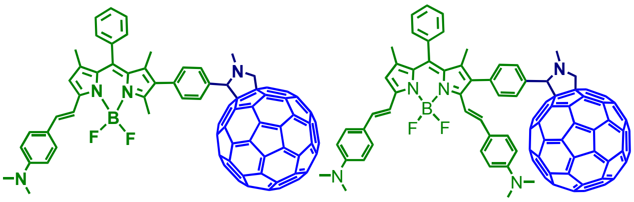
83

Fig. 51 Acid-responsive Bodipy based dyad triplet photosensitizer.[189]

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 dimethylaminosytyrlBodipy part, and this is a rare example in FRET that the singlet energy acceptor shows shorter absorption wavelength than the energy donor. Normally, the singlet energy acceptor in FRET gives longer absorption wavelength than the singlet energy donor.[2,67,191] As a prove of these postulations, the reference compound of the dimethylaminostyrylBodipy shows solvent-polarity-dependent fluorescence emission wavelength was studied.[189,190] The two units in **83** (the diiodoBodipy and the uniodinated Bodipy parts) give absorption at 586 nm and 663 nm, respectively. Upon addition of acid HCl (in mixed MeCN/H_2O, 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 with ns TA spectroscopy.[189] In toluene, triplet state localized on the diiodostyrylBodipy part was observed, with 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 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 oberved, as well as slight population of the protonated dimethylaminostyrylBodipy moiety (in mixed MeCN/H_2O, 9:1, v/v). Thus switching of the triplet state by acid was observed in polar solvents. The switching effect was demonstrated by $^1O_2$ photosensitizing. For **83**, the Φ_{Δ} is 6.0% (in mixed MeCN/H_2O, 9:1, v/v). Upon addition of acid, Φ_{Δ} increased to 59.2 % .

We also prepared styrylBodipy-C_{60} dyads for triplet excited state switching (**84** and **85**, Fig. 52).[192] The switching is based in either the acid-inhibited PET (**84**. with styrylBodipy as the energy donor and the C_{60} unit as the energy acceptor), or the acid-activated FRET-ISC-TTET cascade photophysical processes (**85**).



84 **85**

Fig. 52 Acid-responsive Bodipy-C_{60} dyad triplet photosensitizer.[192]

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 C_{60} unit is probable. In toluene, triplet state localized on the styrylBodipy part was observed (τ_T = 168.6 μs). In polar solvents such as dichloromethane, however, no triplet excited state signal was observed. This result is attributed to the electron transfer in dichloromethane (ΔG_{CS} = −0.10 eV), but not in toluene (ΔG_{CS} = +0.40 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 at 573 nm developed. Upon addition of acid, thus protonation of the dimethylamino group, triplet state was observed for **84** in polar solvents, with triplet state lifetime of 4.4 μs. 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 C_{60} moieties, as well as the ICT effect of the dimethylaminostyrylBodipy moiety.

For **85** (Fig. 52), the photophysical processes are different from that of **84**. Firstly, the S_1 state energy level of the antenna is *lower* than that of C_{60}. Thus even in non-polar solvents such as toluene, no triplet state was observed for **85**, note PET is prohibited for **85** in toluene (ΔG_{CS} = +0.31 eV), 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. Triplet state was observed for **85** upon protonation, even in polar solvent such as dichloromethane. The triplet state lifetime is τ_T = 74.8 μs.

3.3. Photoswitching of the triplet excited state of Bodipy

Besides the chemical-stimulated triplet state switching, light-switching is in 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 $^1O_2$ 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. 53).[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 S_1 state energy level of DTE-1(o) is 4.79 eV, and the S_1 state energy of the DTE-1(c) is 2.18 eV. Actually the T_1 state energy level of the DTE change substantially upon photocyclization/photoreversion.[195,204,205] The T_1 state energy of the DTE-1(o) is 1.97 eV, and it is 1.23 eV for the DTE-1(c).[195] Note the T_1 state energy level of diiodoBodipy is ca. 1.50 eV (Fig. 53).[85] Thus, the T_1 state of the diiodoBodipy is probably be able to be quenched by the DTE-(c), via intermolecular TTET (the long-lived triplet excited state of diiodoBodipy makes this process efficient), but not by DTE-(o) (Fig. 53). Since the DTE-(o) and DTE-(c) is reversibly transformed by UV/visible light irradiation, thus the T_1 state lifetime of diiodoBodipy can be reversibly reduced by light. Note 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]

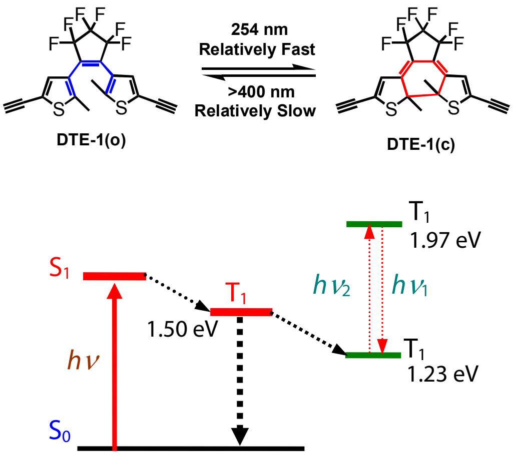
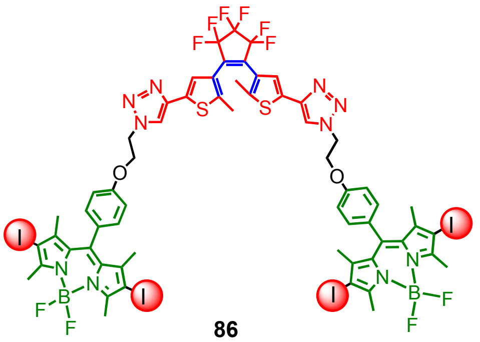


Fig. 53 Photoswitching of the triplet state of diiodoBodipy by using DTE, via intermolecular TTET.[203]

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

Note the success of using DTE-(c) as a quencher for the T_1 state of diiodoBodipy is due to the 'dark quencher' feature of DTE-(c). That is, photoreversion (closed form → open form of DTE) is with 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 T_1 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.



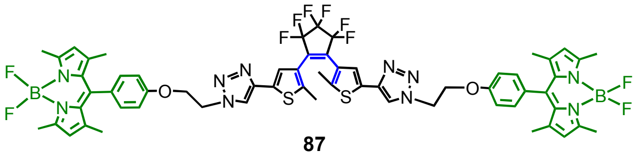
86

Fig. 54 Photoswitching of the triplet state of diiodoBodipy by using DTE, via *intramolecular* TTET.[206]

We also studied the photoswitching of the triplet state of 2,6-diiodoBodipy with the DTE moiety in a molecular triad (**86**. Fig. 54).[206] Upon photocyclization of the DTE unit, the triplet state lifetime of the diiodoBodipy unit in **86** is decreased from 105.1 μs to 40.9 μs. Calculation of the $\Delta G°_{CS}$ indicated that PET is thermodynamically prohibited for **86** with the DTE in either the open form or the closed form. Thus the reduce of the triplet state lifetime of the diiodoBodipy moiety is due to TTET. The formation of 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 of the diiodoBodipy part upon photocyclization of the DTE unit.[206]

It should be pointed out that a photostationary state (PSS) is always established for the photochromic compounds,[193,207] 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 lifeitme of the diiodoBodipy with the 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 $^1O_2$ production of the **86** with 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. 54), 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 the photocyclization was sensitized by the triplet state of the Ru(II) coordination centre.[195] Although it is a advantage that the photocyclization of DTE can be performed with visible light excitation via sensitizing, yet 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.



87

Fig. 55 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.[209]

Our group also developed a Bodipy-derived photoswitchable triplet energy acceptor (DTE-Bodipy triad) for application in TTA upconversion (**87**. Fig. 55).[209] The designing rational for **87** is to use the DTE unit to photoswitch the fluorescence of the Bodipy part, thus the TTA upconversion (with PdTPTBP as the triplet photosensitizer, because of its proper triplet state energy level. TPTBP = tetraphenyltetrabenzoporphyrin). As a triplet energy acceptor, the triplet state of the Bodipy units in **87** can also be quenched by the closed-form of DTE.

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	92600	519	0.006	–	–	176
82	533	91000	556	0.017	0.74	24.7	176
83	589/660	109000/ 56000	693	0.0046	–	–	189
84	573	120000	591	0.003	0.0019	168.6	192
85	627	109000	644	0.004	0.0011	–	192
86	535	132000	553	0.03/ 0.016	0.876/ 0.369	105.1/40.9	206
87	504	–	518	0.817	–	–	209

[a] For detail information, please refer to the maintext and the references.

Based on the nanosecond transient absorption spectra, it was found that **87** with DTE unit in the closed- form is a more efficient triplet acceptor than the **87** with the DTE unit in the opened form. This result also indicates that the 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 closded form, the effective triplet acceptor may be the DTE-c unit, which is with lower triplet state energy level than that of Bodipy, thus the driving force for the intermolecular TTET is larger. The bimolecular quenching rate constants are $k_q = 2.6 \times 10^7$ M^{-1} s^{-1} and $k_q = 6.6 \times 10^8$ M^{-1} 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 DTE moiety in open form, TTA uponversion may be observed. Based on our previous study, however, we proposed that the intramolecular TTET may quench the triplet state of the Bodipy moiety, thus the TTA upconversion will be switched off upon UV irradiation, with photocyclization of 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 photosensitizer.[209] 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 triplet excited state of Bodipy can be controlled by a competing FRET process. Chromophore conjugates with such a photophysical processes were rarely studied.[69] We constructed 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. 56).[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).

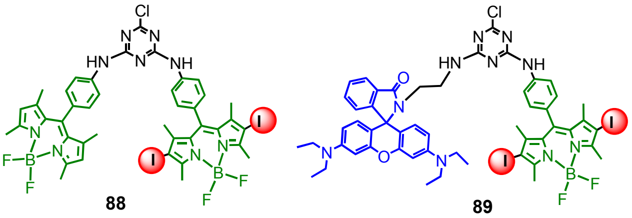


Fig. 56 Bodipy dyads **88** and **89** with cyanuric chloride linker.[211]

Without acid, triplet state localized on diiodoBodipy moiety in **89** was observed, with τ_T = 51.7 μs. 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 μs.

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

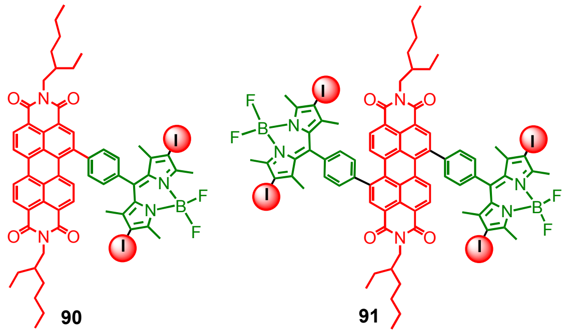


Fig. 57 DiiodoBodipy-PBI dyad **90** and triad **91**.[212]

PBI-diiodoBodipy (PBI = perylenebisimide) dyad and triad were prepared (Fig. 57).[212] Based on the spectral overlap of the two chromophores, FRET from the diiodoBodipy moiety to the PBI unit is assumed. In the dyad and triad, the fluorescence emission of the singlet energy acceptor was significantly quenched. 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 non-polar solvent such as toluene. The energy level of the CST is generally lower than the S_1 state of the PBI moiety.

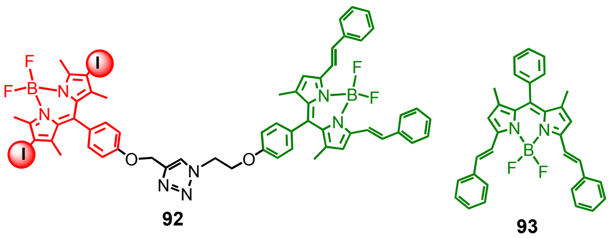
Triplet excited state localized on the PBI moiety was observed for both the dyad and the triad upon selective photoexcitation into the diiodoBodipy moiety. The triplet state lifetimes were determined as 150 µs and 148 µs, respectively. The Φ_Δ values of the dyad and the triad (Fig. 57) were determined as 80% and 78%, respectively. These results indicated that although the fluorescence of PBI in the dyad and 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 dyad and triad, we proved that the triplet state is unable to be produced by CR.

Femtosecond TA spectra indicated the FRET rate constant of **90** is $k_{EnT} = 5 \times 10^{10}$ s^{-1}, larger than the ISC of diiodoBodipy ($k_{ISC} = 7.7 \times 10^9$ s^{-1}), yet the triplet state yield of **90** is as high as 80% (approximated with the Φ_Δ). 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 the diiodoBodipy in the mixture, the transient absorption spectrum of the diiodoBodipy diminished. The triplet state of PBI was observed, which is produced by the intermolecular TTET.[212]

In order to achive a more significant spectra discrimination, we studied the competing FRET and ISC of diiodoBodipy-styrylBodipy dyad **92** (Fig. 58).[213]

Singlet energy transfer in **92** was confirmed by the fluorescence excitation spectrum. $\Delta G°_{CS}$ values indicate that PET is thermalbynamically allowed for **92** in polar solvents, which is in agreement with the fluorescence studies. Upon selective photoexcitation into the diiodoBodipy moiety, triplet state localized on the styrylBodipy was observed, with lifetime of 385.0 µs. This result indicated intramoelcular TTET. A Φ_T value of 36% was observed for **92**, as compared to **93** (for which the triplet state quantum yield is negligible). For 2,6-diiodoBodipy, $\Phi_\Delta = 0.85$. Thus, we proposed the ISC was efficiently competed by the FRET. Femtosecond transient absorption spectra indicate the FRET rate constant of $k = 6.9 \times 10^{10}$ s^{-1} ($\tau = 14.5$ ps), much faster than the ISC of the diiodoBodipy moiety.



92

93

Fig. 58 DiiodoBodipy-styrylBodipy dyad and a reference compound **93**.[213]

The slow intermolecular TTET between the reference diiodoBoidpy compound and the reference styrylBodipy compound was studied by nanosecond transient absorption spectroscopy (Fig. 59).[213]

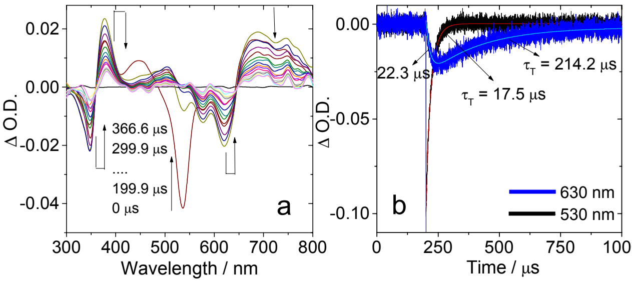


Fig. 59 (a) Intermolecular triplet−triplet energy transfer (TTET) from **8** to **93**, monitored by nanosecond transient absorption spectra of the mixture of **8** and **93**. The concentration of compound **8** was at $c = 1.0 \times 10^{-5}$ M, and the molar ratio of **8**:**93** was 1:1. (b) The 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 triplet excited state). In deaerated toluene. 20 °C. Reproduced with permission from Ref. 213.

Upon selective photoexcitation into the diiodoBodipy by 530 nm nanosecond pulsed laser, the featured triplet excited state absorption (ESA) of the diiodoBodipy appeared at 350 nm, as well as the significant bleaching band at 530 nm. With 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. 59a). The intermolecular TTET was monitored by following the transient absorbance at 530 nm and 630 nm (Fig. 59b). In the presence of the triplet energy acceptor **93** (Fig. 58), the decay of the diiodoBodipy ($\tau = 17.5$ µs) is much faster than the intrinsic decay of the diiodoBodipy alone ($\tau = 133$ µs). The intermolecular triplet state energy transfer rates are in the range from $k = 2.5 \times 10^4$ s^{-1} to $k = 6.0 \times 10^4$ 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]

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	102000/ 73400	523/552	0.071	–	130.6	211
89	534	71500	552/580	0.036/ 0.145	–	51.7/34.4	211
90	537	103000	566	0.0018	0.80	150	212
91	541	132000	597	0.0005	0.78	148	212
92	630/ 537	141000/ 98000	643	0.690	0.35/ 0.19	385	213
93	628	118000	641	0.590	–	–	213

[a] For detail information, please refer to the maintext and the references.

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 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-tripelt annihilation (TTA) upconversions.[40,47]

4.1. Photodynamic therepy (PDT)

Photodynamic therapy (PDT) is a noninvasive method for treatment of a variety of cancer by the combined use of visible or near-IR light with a photosensitizing drug. The principle is that upon photoexcitation of the triplet photosensitizer, triplet excited state will be populated, via ISC. Intermolecular TTET will produce the $^1O_2$, which is potent oxidant. Notably, the lifetime of $^1O_2$ is ca. 0.6 μs,[221] during which the $^1O_2$ can diffuse less than 0.1 μm. Thus PDT is a highly confined and selective treatment for cancer tissue.

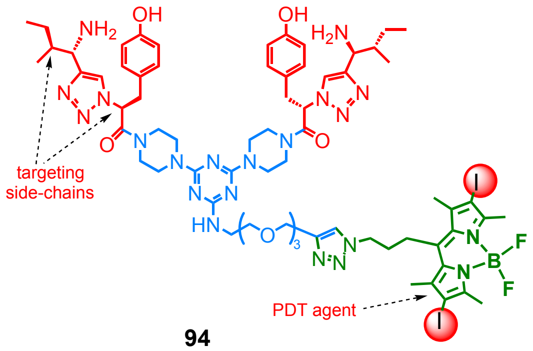
The conventional PDT reagents are the porphyrin derivatives.[23,89] These compounds are difficult to prepare and purify, as a result, some compounds are used as a mixture of the isomers. Concerning these aspects, the application of the Bodipy-derived triplet photosensitizers in PDT study is promising,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

As previously discussed, the 2,6-diiodoBodipy has been studied for 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. 46) was studied as triplet photosenstisizer for PDT application.[89] The absorption maxima varied from 600 nm to 700 nm. Light-induced cytotoxicity was studied with MRC5-SV40 cells. The EC_{50} value for **76d** is 1.4×10^{-8} M. With attachment of amino group to dibromo azaBodipy, acid-activatable PDT reagent was developed.[103]

In recent years, the development of activatable PDT reagents is in particular interest due to its 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. 49) was used as a GSH-activable PDT reagent, because the GSH concentration in carcer 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**, 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]

Targetted PDT reagents are in particular interest, because the treatment of the tumor tissue becomes more efficient and the 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 targetted PDT reagents.[77] For example, 2,6-diiodoBodipy module was connnected with a Tyr/Ile chains in **94** (Fig. 60), which is similar to the natural TrkC neurotrophin ligand NT3. These sides chain as targeting module toward the TrkC receptor, which is associated with some forms of cancer (e.g., neuroblastoma, medulloblastoma, and breast cancer) and with melanoma.[222]

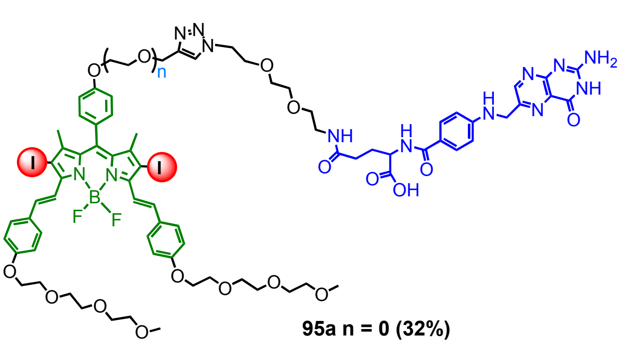


94

Fig. 60 Double-targeting PDT reagent **94** with the diiodoBodipy as the PDT module and Tyr/Ile side chains as the targeting module (the target is TrkC receptor).[222]

Compound **94** absorbs at 520 nm (Table 10). It has submicromolar 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 significantly less photocytotoxicity toward cells that do not express TrkC (NIH3T3-WT).

Folic acid receptor was usually over-expressed in tumor cells. Thus a PDT module can be connected with folic acid to prepare targeting PDT reagent (Fig. 61).[77]



95a n = 0 (32%)
95b n = 3 (27%)

Fig. 61 Targeting PDT reagent with the diiodostyrylBodpiy as the PDT module and folate as the targeting module.[77]

Two folate-conjugated diiododistyryl boron dipyrromethenes (**95a** and **95b**) were prepared and characterized with various spectroscopic methods (Fig. 61).[77] The two compounds show strong absorption in red spectral region (662 nm, ε = 61660 M^{-1} cm^{-1}), and low fluorescence quantum yields (Φ_F = 0.20). The Φ_Δ of these compounds were not reported.[77] However, previously we have shown the 2,6-diiodostyrylBodipy shows 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 phototoxcity 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 IC_{50} 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 subcellular 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 significant role in the development of new activatable PDT reagents.

4.2. TTA upconversion

TTA upconversion shows advantage of efficient harversting of the excitation light, high upconversion quantum yields, and supramolecular feature 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 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).

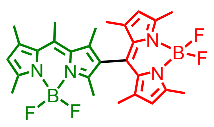
We also used the C_{60}-Bodipy dyads as the triplet photosensitizers for TTA upconversion.[90–92] Upconversion quantum yield of 7.0% was observed for the C_{60}-Bodipy dyads as triplet photosensitizer.[90]

Inspired by the previous finding that triplet state can be produced by Bodipy dimer,[95] we used hetero Bodipy dimers for TTA upconversion (Fig. 62).[149]

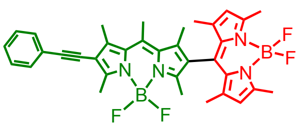
Note from **96** to **98**, the structures of the two components of the Bodipy dimer show more significant difference, such as the π-conjugation framework (Fig. 62). As a result, we observed a clear trend that the triplet state formation quantum yield of the compounds decreased from **96** to **98**. For example, the Φ_Δ of **96** is 64%, and it decreases to 42% for **97**, whereas for **98**, no $^1O_2$ photosensitizing ability was observed. For **96** and **97** the triplet state lifetimes were determined as 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 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/emitter in TTA upconversion (Fig. 63).[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 = tetraphenyltetrabenzoporphyrin).



96



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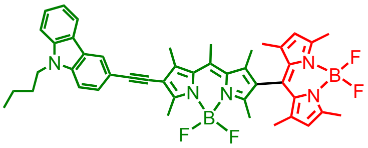
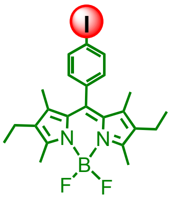


98

Fig. 62 HeteroBodipy dimers as heavy-atom-free triplet photosensitizers for TTA upconversion.[149]

Bodipy-derivatives **14** and **99** have been used as triplet acceptors for TTA upconversion (Fig. 63).[224,225] Note the iodine atoms are attached on 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 triplet photosensitizer, with 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 attaching of iodine atoms in **14** and **99** is *unnecessary*, althought the fluorescence quantum yields of **14** and **99** was not reduced by the presence of the iodine atoms in the molecules. As a prove of this postulation, we used non-iodinated Bodipy as triplet acceptor/emitter for TTA upconversion.[176,209]



99

Fig. 63 Bodipy derivative as triplet acceptor/emitter in TTA upconversion.[224]

In order to attain 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 $2E_{T1} > E_{S1}$ 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.

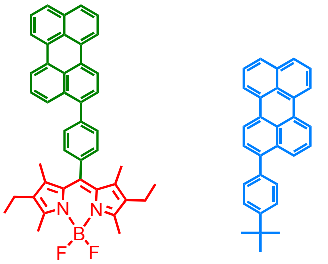

100 **101**

Fig. 64 Bodipy-perylene dimer for tuning of the excited state energy levels to optimize TTA upconversion.[226] The reference compound **101** is also presented.

For example, one of the popular triplet acceptors, perylene, is with T_1 state energy level of 1.53 eV, the S_1 state energy level of at least 2.78 eV, thus the requirement of $2E_{T1} > E_{S1}$ 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 connect with perylene moiety (Fig. 64) to tune the excited state energy level to improve the TTA. It was known that Bodipy is with S_1 state energy level of 2.35 – 2.45 eV, thus the $2E_{T1} > E_{S1}$ 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 of a mixture of different triplet acceptors (such as DPBF and DPA) leads to efficient hetero TTA process.[227]

We studied the detail photophysics of a similar Bodipy-perylene dyad, with the aim to optimize the energy levels further (**102**, Fig. 65).[228] We found that the TTA efficient of **102** is ca. 2-fold of that of peryelne. Moreover, we found that the PET is thermodynamically allowed in **102**, especially in polar solvents, such as dichloromethane and acetonitrile.

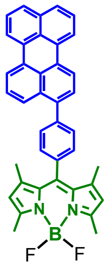

102

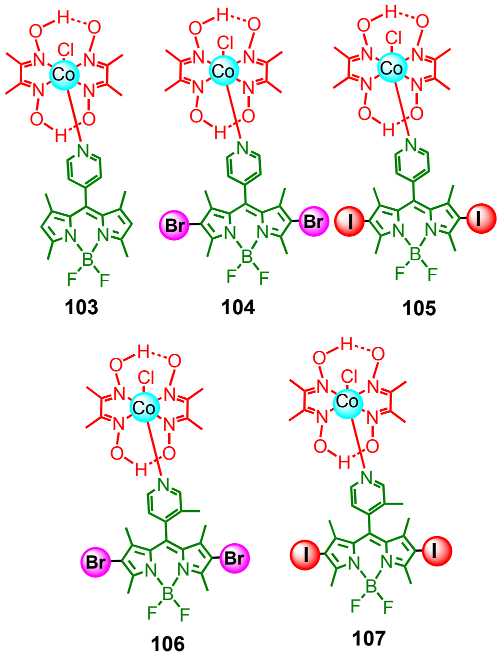
Fig. 65 Bodipy-perylene dimer to tune the excited state energy levels to optimize TTA upconversion.[228]

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] These informations 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. H_2 production

Re-newable energy attracted much attention in recent years, such as the photocatalytic hydrogen (H_2) production.[229–233] Usually a transition metal complex was used as the photosensitizer/electron donor, with a water reduction center (such as cobaloxime complexes), H_2 evolution was observed in the presence of sacrificail 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, thus the electron transfer process may be nonefficient. In order to improve the H_2 production, photosensitizers with strong absorption of visible light and long-lived triplet excited state are desired.

DiiodoBodipy or dibromoBodipy-binded Co(II) complex was prepared as a novel photocatalyst for H_2 evolution (Fig. 65).[234,235] The Bodipy moiety is the electron donor, and the cobaloxime moiety is the water reduction catalysts. The bromo- or the iodoBodipy unit show long-lived triplet excited state, thus the electron transfer to the water reduction centre (WRC) is supposed to be more efficient.


103 **104** **105**

106 **107**

Fig. 66 Bodipy−Cobaloxime Complexes as photocatalysts for H_2 evolution.[234]

Four cobaloxime catalyst complexes and three novel Bodipy chromophores are synthesized (Fig. 66).[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

H_2 per catalyst for the mesomethylpyridyl 2,6-diiodo Bodipy-sensitized cobaloxime complex **107**. It was proposed that accessing 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 H_2 generation. Without accessing the triplet state of the Bodipy chromophore, the singlet excited state of Bodipy (complex **103**, Fig. 66) only gives substoichiometric H_2.[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 concise and clean synthesis route, by formation of C−C or C−N bonds. For this kind of catalytic synthetic reactions, the photocatalyst (triplet photosensitizers) play the role of electron acceptor/donor, or triplet energy donor.[20] Thus, the photocatalytic activity will be improved by using triplet photosensitizers with strong absorption of visible light and 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 affect by other factors such as charge carrier mobility.

Popular triplet photosensitizers include the complexes such as $Ru(bpy)_3Cl_2$ and $Ir(ppy)_3$.[20] These transition metal complexes show only moderate or weak absorption in visible spectra range ($\varepsilon < 20000$ M^{-1} cm^{-1} in the spectral range beyond 400 nm. The absorption maximum is <500 nm), and the triplet state lifetimes of these complexes are short (less than 5 μs).[20,237] Therefore, the photocatalytic reactions efficiency is low and the reaction times are usually long. We propose that the weak absorption of these complexes in visible spectral region is due to the weakly allowed $S_0 \rightarrow {}^1MLCT$ transition because of its charge transfer character. The short triplet excited state is probably due to the strong heavy atom effect, which facilitate the $S_1 \rightarrow T_1$ ISC, but also the $T_1 \rightarrow S_0$ transition, thus the lifetime of the T_1 state is short.

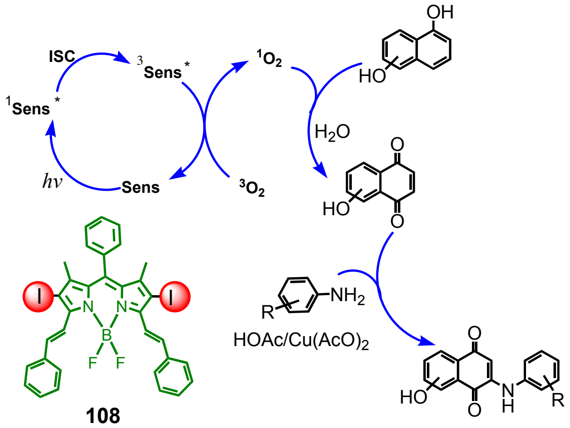


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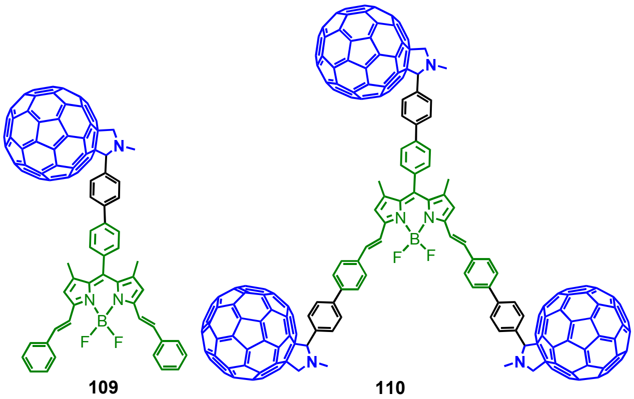
Fig. 67 Proposed one-pot reaction mechanism for the photooxidation with **8** and **108** as the organic photocatalysts to produce aminonaphthoquinone.[87]

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. 67).[87] The photocatalyzed reactions were mediated by singlet oxygen (${}^1O_2$), that is, the aerobic oxidative coupling of amines and the photooxidation of dihydroxylnaphthalenes, 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 Ru(II)/Ir(III) complexes.[87] Moreover, the organic photocatalysts show excellent photostability.



109 **110**

Fig. 68 Styryl Bodipy−C_{60} dyad and tetrad as photocatalysts for photooxidation of 1,5-dihydroxynaphthalene.[157]

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. Alone this line, we prepared C_{60}-StyrylBodipy conjugates **109** and **110** (Fig. 68), which show strong absorption of visible light ($\varepsilon = 65\ 000$ M^{-1} cm^{-1} at 650 nm), and long-lived triplet excited state (τ_T = 120 μs), to explore the potential of C_{60} for photocatalysis.[157] We used these organic triplet photosensitizers as photocatalysts for the photooxidation of 1,5-dihydroxynaphthalene to produce juglone, via photosensitization of ${}^1O_2$. The photocatalytic efficiency was compared with that of the conventional photocatalysts, such as $Ir(ppy)_2bpy$, methlyene blue, and C_{60}. It was found the photoreaction rates are 10-fold 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. 69). Previously $Ru(bpy)_3Cl_2$ was used as 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 O_2, and the electron transfer between the photocatalyst radical cations and the substrate (Fig. 69).[238] Concerning this aspect, C_{60} is a well-known electron acceptor, thus we used Bodipy-C_{60} conjugates **109** and **111** as new organic photocatalysts for the reactions (Fig. 70), and much higher catalytic efficiency was observed. For example, the reaction time required for photocatalyst $Ru(bpy)_3Cl_2$

is 4 h, and the yield is 37%. With the Bodipy-C_{60} dyads as the new photocatalysts, the reaction time is only 1 hour and the yield is up to 91%.[239]

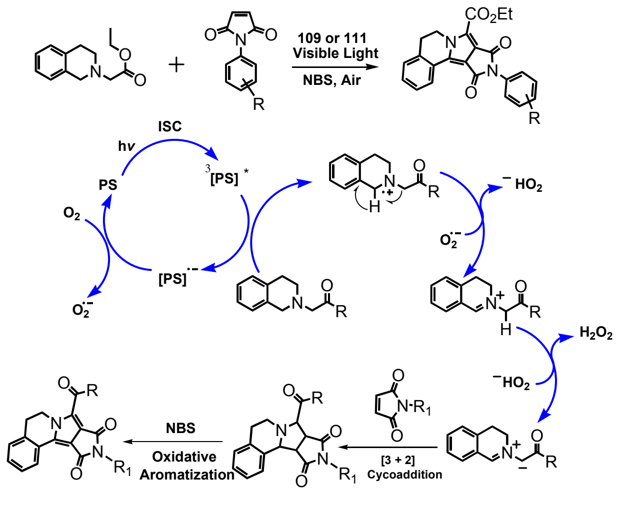
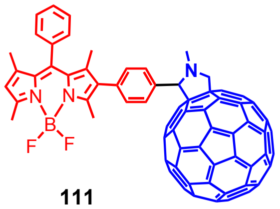


Fig. 69 Photocatalytic tandem oxidation/[3+2] cycloaddition reactions to prepare pyrrolo[2,1-*a*]isoquinoline.[239]



111

Fig. 70 Bodipy−C_{60} dyad as photocatalysts **111** for photocatalytic tandem oxidation/[3+2] cycloaddition reactions.[239]

We also used similar C_{60}-Bodipy conjugates for visible-light-induced aerobic oxidative hydroxylation of aryl boronic acids.[240] We found that C_{60}-Bodipy dyads can act as efficient electron-mediator between the sacrificial electron donor and the substrates.

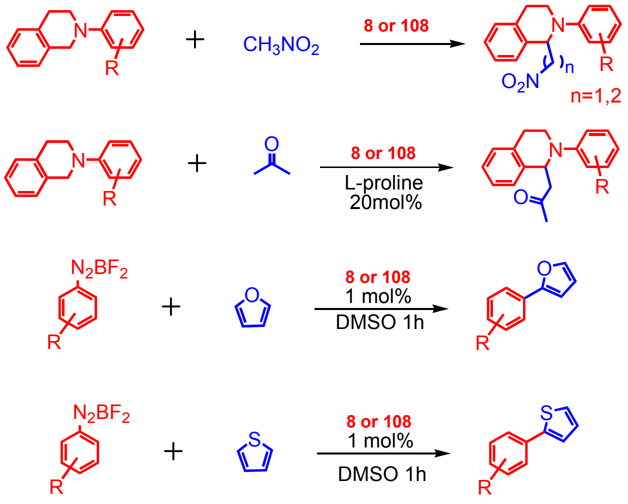


Fig. 71 The photoredox catalytic organic reactions catalyzed by compounds **8** and **108**. Photocatalytic tandem oxidation/[3+2] cycloaddition reactions to prepare pyrrolo[2,1-a]isoquinoline was not shown.[86]

Other photoredox catalytic organic reactions, such as the aza-Henry reaction of tetrahydroisoquinoline (Fig. 71),[241] and C–H arylation of heteroarenes with diazonium salts were also reported (Fig. 71).[242] Iodo-Bodipys were used as organic catalysts for these different photoredox catalytic organic reactions, (Fig. 71).[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 $Ru(bpy)_3[PF_6]_2$, $Ir(ppy)_3$, 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 $Ru(bpy)_3[PF_6]_2$ 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 ligth-absorbing Bodipy-diiodoazaBodipy **69** (Fig. 44) 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 tetrahydroisoquinolin as the substrates.[244] The photocatalytic reaction with the broadband visible light-absorbing organic triplet photosensitizers as the photocatalysts is generally more efficient than the normal triplet photosensitizers.[159,240,245]

Table 10. Photophysical properties of **94** – **111**.[a]

	λ_{abs}/nm	ε	λ_{em}/nm	Φ_F	Φ_Δ	τ_T/µs	Ref.
94	ca.540	–	ca.520	–	–	–	222
95a	662	48978	687	0.20	–	–	77
95b	662	61660	689	0.20	–	–	77
96	506	136000	527	0.022	0.64	115.6	149
97	509/541	87000 /58000	578	0.176	0.42	140.9	149
98	508/542	82000 /43000	644	0.023	–	–	149
99	505/518		548	0.78	–	–	224
102	504	62800	517	0.58	–	–	228
103	509	80300	–	–	–	–	234
104	541	73700	–	–	–	–	234
105	549	69100	–	–	–	–	234
106	540	68900	–	–	–	–	234
107	548	66000	–	–	–	–	234
108	630	77000	654	0.051	0.69	1.8	87
109	629	65300	644	0.01	0.82	71.5	157
110	657	64600	667	0.0009	0.85	123.2	157
111	517	76000	535	0.004	0.81	27.4	239

[a] For detail information, please refer to the maintext and the references.

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 the 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 10^6 times shorter than the *triplet* state of Bodipy.[86] The quenching constant of the isoquinolin substrate on the singlet excited state of Bodipy as $K_{SV} = 52.8$ 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 diiodoBodpy as $K_{SV} = 120$ M^{-1}. These results infer that the electron transfer beween the excited photocatalyst and the substrate (tetrahydroisoquinoline) may *not* be the rate-limiting step of this specific phtoocatalytic 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, etc). Moreover, new methods, such as with spin converter (e.g. C_{60}), or by charge recombination, exciton coupling and 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 vest 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 *different* rule, due to the difference 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 activatble photodynamic theraputic (PDT) reagents.

Applications of the triplet excited states of Bodipy in PDT, TTA upconversion, hydrogen (H_2) 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 with triplet photosensitizers which show strong absorption of visible light and long-lived triplet excited state. The triplet state of Bodipy derivatives fufill these requirements, and the Bodipy-derived triplet photosensitizers have been proved more efficient than the conventional triplet photosensitizers such as $Ru(bpy)_3Cl_2$ or $Ir(ppy)_3$ for photocatalytic hydrogen (H_2) production and TTA upconversion.

Despite of above developments, challenges as well as opportunities still exist. For example, singlet fission is being studied for efficient formation of triplet excited state (with quantum yield up to 200%) upon photoexcitation. But this strategy was not yet extended to Bodipy chromophore. Related research will foster new area and novel materials. On the other hand, designing of heavy atom-free triplet photosensitizer 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 orgnic chemists to design new molecules with matching 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 tackled 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 near future, because it is crucial for the fundamental photochemistry studies, and for the developments of the areas such as PDT, photocatalysis, 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
$^1O_2$	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 quanum 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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Notes and references

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Note: Colour was used for the molecular structures to discriminate different chromophores, especially for the dyads and triads, etc.

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