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Application of singlet energy transfer in triplet state formation: broadband visible light-absorbing triplet photosensitizers, molecular structure design, related photophysics and applications

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Conventional triplet photosensitizers usually contain a single visible light-harvesting chromophore, which is responsible for the dual-functionality of light-harvesting and intersystem crossing (ISC). These profiles render a few disadvantages, such as a single absorption band in the visible spectral range, low efficiency of harvesting broadband visible light (e.g., solar light); and it is difficult to design new triplet photosensitizers because the relation between molecular structure and ISC is unclear. In order to address these challenges, application of the Förster-Resonance-Energy-Transfer (FRET) and spin converter lead to a new molecular structure profile for triplet photosensitizers to attain the broadband visible light-absorption, and disintegrated functionality of visible light-harvesting and ISC. This review article summarized the triplet photosensitizers showing broadband visible light absorption, include the molecular design rationales, the photophysical processes involved in these photosensitizers, such as the FRET, ISC, the photo-induced electron transfer (PET) studied with nanosecond and femtosecond transient absorption spectroscopies. The application of the triplet photosensitizers in photoredox catalytic organic reactions and triplet-triplet annihilation upconversion were also discussed. We summarized the molecular structure-property relationship of these new photosensitizers, as well as the challenges in this emerging area.

1. Introduction

Triplet photosensitizers are versatile compounds which have been widely used in photodynamic therapy (PDT),\(^1\)\(^-\)\(^8\) catalytic hydrogen (H\(_2\)) production,\(^9\)\(^-\)\(^12\) and photoredox catalytic organic reactions,\(^13\)\(^-\)\(^17\) phosphorescent biological imaging,\(^18\)\(^-\)\(^22\) molecular logic gates,\(^23,24\) and more recently the triplet-triplet annihilation (TTA) upconversion.\(^25\)\(^-\)\(^30\) Triplet photosensitizers are compounds with triplet excited state efficiently populated upon photoexcitation, via intersystem crossing (ISC). Different from the application of singlet excited state, for which fluorescence is very often the purpose,\(^31\)\(^-\)\(^37\) the application of the triplet excited state of the triplet photosensitizers is usually to initiate intermolecular electron transfer or triplet-triplet-energy-transfer (TTET).\(^3\) Thus, the desired photophysical property of the triplet photosensitizers include strong absorption of visible light, high triplet state yields and long triplet excited state lifetimes.\(^8\) These properties exert significant influence on the performance of the triplet photosensitizers in the areas such as photocatalysis, and TTA upconversion. This scenario is different from that of the applications for which strong absorption of visible light is unnecessary, such as electroluminescence. Moreover,
triplet excited state lifetime of the electroluminescent materials must be short to avoid the saturation effect. Thus, the designing of the triplet photosensitizers is complicated by the above mentioned requirements, it may follow different rules of that for the electroluminescent materials, such as strong absorption of visible light and long-lived triplet excited state. Another major challenge in study of triplet photosensitizer is the difficulties in molecular structural designing of new triplet photosensitizers, especially to attain broadband visible light absorption. In the following section we will discuss the reasons for these prerequisite of the photophysical properties of triplet photosensitizers.

The desired photophysical property of strong absorption of visible light, high triplet state yield and long triplet state lifetime can be rationalized as following, exemplified with the TTET. The efficiency of the TTET can be evaluated quantitatively by the Stern-Volmer quenching of the triplet state of the energy donor by the triplet energy acceptor (the quencher), by Eq. 1:

\[ \frac{\tau_0}{\tau} = 1 + K_{SV}[Q] \]  
(Eq. 1)

where \( \tau_0 \) is the triplet state lifetime of the triplet photosensitizer, \( \tau \) is the quenched triplet state lifetime of the triplet photosensitizer in the presence of triplet acceptor, \([Q]\) is the concentration of the quencher (triplet energy acceptor), and \( K_{SV} \) is the Stern-Volmer constants. The larger the constant, the more efficient quenching (TTET) will be resulted. The \( K_{SV} \) can be broken down to Eq. 2:

\[ K_{SV} = k_q \tau_0 \]  
(Eq. 2)

where \( k_q \) is the bimolecular quenching constants, and \( \tau_0 \) is the intrinsic triplet state lifetime of the triplet photosensitizer. \( k_q \) is a value smaller than the diffusion controlled bimolecular collision constant \( k_0 \). In fluid solution, the \( k_q \) is a value close to \( k_0, f_0 \) is a value smaller than 1:

\[ k_q = f_0 \times k_0 \]  
(Eq. 3)

\( k_0 \) is a value defined by Eq. 4 and Eq. 5:

\[ k_0 = 4\pi RND/1000 = \frac{4\pi N}{1000} \left( R_i + R_e \right) \left( D_i + D_e \right) \]  
(Eq. 4)

\[ D = kT/6\pi \eta R \]  
(Eq. 5)

As discussed above, the quenching efficiency, or the TTET efficiency, is mainly dependent on the triplet state lifetime \( (\tau_0) \) of the triplet photosensitizer. Long triplet state lifetime is beneficial for efficient TTET. This postulation has been unambiguously confirmed by the application of triplet photosensitizers showing long triplet state lifetimes in TTA upconversion.\(^{41}\) On the other hand, most of the TTET process, and the ‘concentration’ of the triplet energy acceptor at the triplet excited state, is directly proportional to the ‘concentration’ of the excited photosensitizer. Thus, the visible light absorption (molecular absorption coefficient, \( \varepsilon \)) of the triplet photosensitizer is also crucial.

Most of the known triplet photosensitizers usually show weak absorption of visible light, short triplet excited state lifetimes, and the molecular structures are difficult to be modified or rationally designed.\(^{23,8,41-43}\) Recently we and other researchers developed new molecular structural designing approaches to address the above challenges (Fig. 1).\(^{8,41}\) For example, in order to attain strong absorption of visible light and efficient conversion of the photoexcitation energy into the triplet state manifold, direct metalation of organic chromophore, or selection of ligands and coordination center with matching singlet energy levels to ensure efficient energy transfer were employed.\(^{3,43,45}\) In order to design heavy atom-free organic triplet photosensitizers, spin converters, such as fullerene (C\(_{60}\)), were used for ISC thus formation of triplet state.\(^{5,8,45}\) Detail discussion of these molecular structure designing methods have been presented in a recent review.\(^5\)

Despite of these achievements, there is still another major challenge in the designing of triplet photosensitizers for efficient harvesting of broadband excitation light, such as solar light. Conventional triplet photosensitizers are usually based on a single light-harvesting chromophore, as a result, these is only one major absorption band in visible spectral region. The typical absorption spectra of a few triplet photosensitizers were presented in Fig. 2. For the mono-chromophore triplet photosensitizers, these is only one major absorption band in visible spectral region. Moreover, it is clear that the absorption of 9 in visible region is weak, and the absorption wavelength is only 450 nm (\( \varepsilon < 20000 \ M^{-1} \ cm^{-1} \)). The weak transition of the \( S_0 \rightarrow ^1 \text{MLCT} \) can be attributed to the charge transfer (CT) character of the transition.\(^{9,42}\) It should be noted that some Ru(II) complexes used for solar cells show longer absorption.

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wavelength and large ε values, however, the lifetime of the triplet excited states of these Ru(II) complexes are usually too short to ensure efficient intermolecular energy transfer.49,50

Concerning the application of the triplet photosensitizers, the conventional application is photodynamic therapy (PDT) studies.1−3 Recently new areas were developed, such as photoredox catalytic organic reactions,13 and TTA upconversion.26,28−30 Most of the photocatalysts used in the photoredox catalytic organic reactions are the conventional

Fig. 2 UV–vis absorption spectra of compounds (a) 9 and (b) 12.

Scheme 1 A simple schematic diagram for molecular design rationales of RET enhanced broadband visible light-harvesting triplet photosensitizers. RET stands for Resonance-Energy-Transfer, ISC stands for intersystem crossing, and EnT stands for energy transfer. D stands for energy donor and A stands for energy acceptor. Photoinduced electron transfer between the energy donor and the acceptor was omitted for clarity.

Fig. 1 The typical triplet photosensitizers, most are based on mono light-harvesting chromophore profile.
compounds, such as 3, 4, 33,4,53,55,9 and 10. More efficient triplet photosensitizers are desired for these applications, such as those triplet photosensitizers showing strong absorption of visible light and long-lived lifetime of triplet excited states.

In order to attain broadband visible light absorption, multichromophore dyads and triads triplet photosensitizers can be designed, based on fluorescence-resonance-energy-transfer (FRET) and spin converter for triplet state formation (Scheme 1).56-58 The photophysical processes of the FRET/spin converter based energy funneling broadband visible light-harvesting triplet photosensitizers are as following. Two (or more) different chromophores are linked together, via covalent bond or supramolecular interactions. Each of the chromophores show strong absorption of visible light, but at different wavelength.

The FRET energy donor will transfer the photoexcitation energy to the energy acceptor. The FRET energy acceptor is with ISC capability, thus the funneled photoexcitation energy is able to be efficiently transformed to the energy of triplet excited state. Thus triplet photosensitizers showing broadband visible light-absorption are obtained.59

It should be pointed out that FRET was widely used in singlet excited state-related compounds, such as fluorescent molecular arrays as light-absorbing antenna.60-63 However, this method was rarely used for production of triplet excited state upon excitation with broadband light source, such as solar light. This area witnessed significant progress in the past few years,58,59,60 and the application of these broadband visible light-absorbing triplet photosensitizers in photocatalysis and TTA upconversion is promising.58,64 This review will focus on introduction of these triplet photosensitizers, include the molecular designing rationales, the photophysical processes and the applications. Some of the photophysical processes involved in these multi-chromophore triplet photosensitizers are unique, for example, ping-pong energy transfer (forward singlet energy transfer and backward triplet energy transfer),65 and excited states equilibrium.66 These photophysical processes will be introduced with specific exemplars. The detail of the FRET mechanism was well established previously,60 and will not be discussed herein.

It should be pointed out that the alternative approach, i.e. to construct broadband visible light-absorbing triplet photosensitizers (dyads) by linking two triplet photosentizers was not studied. In this case intramolecular TTET will occur, and the triplet state will localize on one part of the dyad. This approach may be more synthetically demanding than the above mentioned FRET/ISC approach with only one part as spin converter.

2. Broadband visible light-absorbing multi-chromophore conjugates for triplet state formation

2.1. Covalent bond linked Bodipy-porphyrin conjugates

In 1998 Lindsey studied the energy transfer in Bodipy-porphyrin light-harvesting array 17–21 (Fig. 3).66 The linker between the Bodipy and the porphyrin moieties is rigid. Based on different structural profile (Fig. 3), different number of Bodipy antenna can be attached to the porphyrin core. There is no π-conjugation between the Bodipy and porphyrin moieties, otherwise the molecule is no longer a supramolecular system, and the excited states collapsed into that of one chromophore, no significant broadband absorption can be resulted.

The Soret band of porphyrin is strong (419 nm), the absorbance at longer wavelength, e.g. 514 nm, however, is only 5% of the absorbance at 419 nm (Fig. 4). Bodipy shows strong absorption at 516 nm, which is complementary to the absorption of porphyrin. Bodipy antenna can be attached at the para position of the phenyl ring on the porphyrin, thus more Bodipy antenna can be introduced to the molecule.

The Bodipy moieties in 17–21 show low fluorescence quantum yields (ФF = 5%), which is much lower than the parent Bodipy without any substituents on the meso position (ФF = 30–80%).63,64 The low fluorescence quantum yields of the Bodipy building blocks in the conjugates 17–21 is actually due to the free rotor effect of the phenyl ring at the meso position of the Bodipy chromophore,63 a property was later utilized to develop fluorescent viscosity molecular sensors.68,69 As a proof, introducing methyl substituent at 1,7-position of the Bodipy core increase the fluorescence quantum yield dramatically, because the free rotation of the phenyl ring is hindered.1,32,70-73

The decay of the singlet excited state of the Bodipy moieties in 17, 18, 20, 21 is faster than the normal Bodipy derivative showing high fluorescence quantum yield. Biexponential decay of the singlet excited state were found for the Bodipy building block in the conjugates in 17–21, as 15 ps and 500 ps, which are assigned to the singlet excited states with different conformations (generated by the different dihedral angles between the Bodipy core and the 5-phenyl ring). It should be pointed out that using of such Bodipy building blocks, rather than the Bodipy units with methyl groups at 1,7-position to hinder the free rotation of the phenyl ring at the meso position.1,32,71 is probably detrimental to the light harvesting effect, due to the fast non-radiative decay of the singlet excited states of the antenna, a process which is competitive to the FRET process (may take a few ps or even longer time).62 Fortunately, the FRET in the Bodipy-porphyrin conjugates (Fig. 3) is fast. The decay of the Bodipy unit become much faster in the arrays (2 and 20 ps, respectively). This time scale can be treated as the rate of FRET.
Based on the steady state and the femtosecond time-resolved transient absorption spectroscopy, it was proposed that the energy transfer mechanism is mainly through-bond-energy-transfer (TBET). This conclusion is derived from the following considerations. The rates of energy transfer are essentially the same for arrays in which the connections of the Bodipy unit are at the meta-versus para-position on the meso-aryl ring of the linker to the porphyrin core. If the Förster through-space mechanism exclusively applied for the energy transfer in the conjugates, observable differences in the energy-transfer rates and efficiencies for the different architectures would be expected. However, such differences in the FRET kinetics were not observed.

The free base of porphyrin actually show efficient ISC (ΦT = 90%). Thus, following the funneling of the photoexcitation energy from the Bodipy antenna to the porphyrin core of the molecular conjugates (Fig. 3), triplet excited state may be produced via the ISC of the porphyrin moiety, given the process is not inhibited by any photo-induced electron transfer (PET), or charge separation (CS). However, the photophysical property of the Bodipy-porphyrin arrays was not studied with the nanosecond transient absorption spectroscopy, or singlet oxygen (O2) photosensitizing experiments. Thus no information concerning the triplet excited state of the array was presented. It should be pointed out the femtosecond transient absorption spectrometer is not suitable for study of the triplet excited state, which are usually with much longer lifetimes than the singlet excite states, due to the limitation of the optical delay line in the femtosecond transient absorption spectrometer (only for a few ns).

2.2. Bodipy-tetraphenyltetrabenzoporphyrin conjugates

In 2011, Thompson et al reported the Bodipy-tetraphenyltetrabenzoporphyrin (TPBP) Pt(II) bichromophoric complex (22) (Fig. 5). The designing of this molecular is with a clear goal, i.e. to prepare a broadband visible light-absorbing triplet photosensitizer, based on the energy transfer between Bodipy chromophores and the benzoporphyrin-Pt coordination center. It should be pointed out that the fast non-radiative decay channel still exist for the Bodipy chromophore selected for the conjugates (Fig. 5). However, as discussed earlier, this fast decay channel does not necessarily mean an inhibition of FRET effect, given the latter (FRET process) is faster.

The absorption of the Bodipy moiety is complementary to the absorption of complex 24, i.e. the Bodipy moiety shows strong absorption at 514 nm (Fig. 6). With four Bodipy antenna, the complex shows an absorption at 514 nm which is comparable to the Soret band of the complex 24 at ca. 425 nm. Phosphorescence at 770 nm was observed, which is attributed to the Pt(II) coordination center, and Bodipy units do not contribute directly to the phosphorescence emission.

The phosphorescence excitation spectrum demonstrated the efficient singlet energy transfer from the Bodipy moiety to the Pt(II) coordination center (Fig. 6). The phosphorescence lifetime of the complex is 67 μs, which is much longer than the unsubstituted complex 24 (30 μs). Thus the Bodipy chromophore exerted substantial influence on the excited state of the complex 24.

The ultrafast transient absorption spectrum of the complex was recorded upon selective photoexcitation into the Bodipy part (Fig. 7). Upon femtosecond pulsed laser excitation, bleaching band at 515 nm were observed, which are due to the depletion of the ground state of the Bodipy moiety. At the same time, bleaching bands at 450 nm and 620 nm were also observed, which are due to the depletion of the ground state of the coordination center of complex 22. With longer delay, the bleaching band at 515 nm diminished, while the bleaching bands at 450 nm and 620 nm grows over ca. 10 ps. Thus singlet energy transfer in the complex 22 was confirmed. Fitting the curves give a singlet energy transfer time of 1/kET = 1.29 ± 0.11 ps.

After 10 ps, the transient spectrum is identical to the triplet state of complex 22 (Fig. 8), because it was shown the ISC of the complex 24 takes only about 400 fs. Therefore the singlet excited...
state of the Pt(II) coordination center won’t be accumulated, due to the fast draining channel of ISC. At longer delay time, however, the bleaching bands at 450 nm and 620 nm diminished, and the bleaching band at 515 nm grows in Fig. 8. These changes indicated the backward triplet-triplet-energy transfer (TTET) from the Pt(TPBP) coordination center to the Bodipy moiety. The rate constant is $k_{\text{TTET}} = 1.0 \times 10^{10}$ s$^{-1}$. It should be pointed out that this kind of ping-pong energy transfer and the backward triplet energy transfer, was not observed with the fluorescent FRET molecules.$^{62,83-84}$

$25$ Fig. 7 Ultrafast transient absorption spectra of 22 in toluene after excitation at 508 nm (0.2–10 ps). Reproduced with permission from Whited et al.$^{65}$

$26$ Nanosecond transient absorption spectroscopy of complex 22 was studied.$^{65}$ Three bleaching bands at 430 nm, 515 nm, 620 nm were observed promptly upon nanosecond pulsed laser excitation. These bleaching bands indicated the triplet state is delocalized on the Bodipy and the Pt(TBTP) moieties, in other words, there is triplet state equilibrium in conjugate 22. All the transient signals in the spectra decay with the same kinetics, the triplet state lifetime (and the phosphorescence lifetime) is 67 μs, which is much longer than the 30 μs lifetime of the unsubstituted complex 24. This extension of the triplet state lifetime is attributed to the energy resivor effect of the Bodipy chromophore.$^{65}$

$25$ Fig. 8 (a) Ultrafast transient absorption spectra of 22 after excitation at 508 nm (10–300 ps). (b) Transient absorptions at 515 nm (BODIPY) and 620 nm (porphyrin) with predicted traces based on kinetic parameters for the system. Reproduced with permission from Whited et al.$^{65}$

$27$ The photophysical processes of complex 22 is summarized in Fig. 9. Selective photoexcitation of the Bodipy antenna by 510 nm pump produces the singlet excited state of Bodipy. Then the FRET will lead to the formation of the singlet excited state of Pt(TPBP) moiety. The ultrafast ISC of Pt(TPBP) moiety produce the triplet excited state of the Pt(TPBP) moiety. Then the TTET produce the triplet state of Bodipy, and an triplet state equilibrium was established. Based on the relationship between the TTET rate constant and the number of the intervening phenylene units, the authors propose the TTET is a phenylene linker–mediated superexchange mechanism.

$28$ Fig. 9 Jablonski diagram summarizing the excited-state behaviour of complex 22 upon selective photoexcitation into the BODIPY or benzoporphyin units. Reproduced with permission from Whited et al.$^{65}$

$33$ 2.3. Bodipy-containing Pt(II)(diimine)(dithiolate) complexes

As a typical photophysical feature, the visible light-absorption of normal triplet photosensitizers is actually weak.$^{8}$ For example, Pt(II)(diimine)(dithiolate) complexes have been demonstrated to be able to inject electron into titanium oxide, thus the complexes are useful for photovoltaics. These complexes have also been used in photocatalytic hydrogen (H$_2$) production. However, these complexes show only moderate absorption of visible light at ca. 550 nm ($\varepsilon < 10^4$ M$^{-1}$ cm$^{-1}$), which is at least one order of scale smaller than the typical organic dyes such as Bodipy, which show absorption in visible spectral region with $\varepsilon$ value up to $8 \times 10^4$ M$^{-1}$ cm$^{-1}$.85

$34$ Eisenberg et al used Bodipy ligand to preparation of Pt(II) diimide(dithiolate) complexes (Fig. 10). The Bodipy chromophore is either attached on the bipyridine ligand (complexes 25 and 26), or on the dithiolate ligand (complex 27).86 The Bodipy moiety shows absorption at 527 nm (with $\varepsilon = 70000$ M$^{-1}$ cm$^{-1}$), and the Pt(II) coordination center shows absorption band at ca. 600 nm ($\varepsilon = 8000$ M$^{-1}$ cm$^{-1}$). Both the
Upon selective photoexcitation into the 1Bodipy singlet excited state, the singlet energy transfer takes place, which lead to the formation of MMLL'CT singlet excited state. The ultrafast ISC (<1 ps) of the Pt(II) coordination center produces the triplet excited state (3MMLL'CT). Then the intramolecular TTET leads to the formation of the triplet excited state of Bodipy. Based on these photophysical processes, both the fluorescence of the Bodipy moiety and the phosphorescence of Pt(II) coordination center should be quenched, which is in agreement with the experimental results.

Fig. 11 Femtosecond transient absorption spectra of the complex 26 obtained with a 530 nm pump pulse. The 530 nm excitation directly excites the ππ* absorption band of the Bodipy moiety. Reproduced with permission from Lazarides et al.

Femtosecond transient absorption spectra of the complex 26 was recorded to reveal the photophysical processes (Fig. 11). Upon selective excitation into the Bodipy ligand (530 nm), the spectra show the ground state bleaching band of Bodipy moiety at 530 nm, and the stimulated emission (SE) band at ca. 600 nm. The ground state bleaching band decrease significantly within 2–30 ps, with decrease of the excited state absorption (ESA) at 350 nm. This process is the 1Bodipy→3MMLL'CT singlet energy transfer process. The bleaching basically did not change during the following 2–6 ps, during which the ISC of 3MMLL'CT→3MMLL'CT took places. Then the bleaching band increased again, with the increasing of the ESA at 425 nm (which is the featured ESA of the Bodipy triplet state), the process takes 6–8 ps (Fig. 12), which is attributed to the 3MMLL'CT→1Bodipy TTET process.

Fig. 12 Kinetics of 26 at probe wavelengths of 500 and 489 nm, following excitation at 530 (green symbols) or 600 or 615 nm (red symbols). The kinetics at these probe wavelength are indicative of the bleach of the Bodipy ππ* absorption band. Reproduced with permission from Lazarides et al.

The photophysical processes of 26 can be summarized in Fig. 13. Upon selective photoexcitation into the 1Bodipy singlet excited state, the singlet energy transfer takes place, which lead to the formation of MMLL'CT singlet excited state. The ultrafast ISC (<1 ps) of the Pt(II) coordination center produces the triplet excited state (3MMLL'CT). Then the intramolecular TTET leads to the formation of the triplet excited state of Bodipy. Based on these photophysical processes, both the fluorescence of the Bodipy moiety and the phosphorescence of Pt(II) coordination center should be quenched, which is in agreement with the experimental results.

Analysis of the spectral overlap and the dipole moments orientation in dyad 26 predict a slow singlet energy transfer (710 ps). However, the experimental value for the singlet energy transfer time is 0.6 ps. Thus it was proposed that electron exchange is responsible for the ultrafast singlet energy transfer in 26, not the Förster mechanism (FRET). Moreover, it was proposed the electron exchange play the major rule for the triplet energy transfer. However, the triplet excited state lifetime of the complexes 26 and 27 were not disclosed.

Concerning of visible light-harvesting and formation of triplet excited state, the designing of the molecular structures of dyads 26 and 27 is successful to large extent. However, the triplet excited state is no longer localized on the Pt(II) coordination center, rather, it is re-located to the Bodipy moiety, which may change the excited state redox property, thus the photocatalysis may be affected.

Fig. 14 Pt(II) diimine dithiolate complex (28, 29) containing Bodipy antenna. The mixed-metal-ligand-to-ligand' charge transfer (3MMLL'CT) state is with lower energy level than the Bodipy triplet excited state.

To address this problem, the same group modified the molecular structure, electron withdrawal groups were attached on the bpy ligand, thus the energy level of the mixed–metal–ligand-to–ligand’ charge transfer (3MMLL'CT) state become lower than that of the Bodipy triplet state, thus the T1 state of the dyads 28 and 29 is localized on the Pt(II) coordination center, not on Bodipy antenna. This tuning of the confinement of the excited state may be beneficial to the catalytic activity.

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2.4. Bodipy-Porphyrin conjugates with C_{60} as electron acceptor

In multichromophore conjugates, besides the desired energy transfer, electron transfer is very often the process involved. In some cases the formation of triplet excited state can be inhibited by formation of charge transfer state (CTS). However, in some cases the charge recombination (CR) may produce the triplet state.\(^8\)

A representative charge separation Bodipy-Porphyrin-C_{60} pentad (30) was reported.\(^9\) The Bodipy antenna shows absorption at 504 nm, and the Zn porphyrin coordination center gives absorption at 434 nm. The emission of the Bodipy antenna in compound 31 was quenched as compared with that of the free Bodipy. Moreover, the fluorescence of the Zn(II) porphyrin coordination center was not quenched, and the fluorescence excitation spectrum of 7 shows a band at ca. 504 nm, therefore singlet energy transfer was confirmed for 31, with Bodipy as the singlet energy donor and the Zn(II) porphyrin coordination center as the singlet energy acceptor. For pentad 30, however, the fluorescence of the Zn(II) porphyrin coordination moiety was quenched, and no fluorescence of the C_{60} moiety was observed (expected to be at 720 nm). Thus, PET was proposed for pentad 30.

![Diagram](image-url)  
**Fig. 15** Bodipy-porphyrin-C_{60} pentad (30) with the FRET and PET process (with Zn(II) porphyrin as electron donor and C_{60} as the electron acceptor). Compound 31 was used as a reference for study of the photophysical properties.\(^8\)

Femtosecond transient absorption spectra of compound 31 indicates the singlet excited state of the Bodipy moiety was produced upon selective excitation into the Bodipy part (\(^1\)BDP\(^*\)). Then the \(^1\)ZnP\(^*\) grows in within 400 ps, which was attributed to the FRET with rate constant of \(k = 2.7 \times 10^{10} \text{s}^{-1}\). For the pentad 30, however, the femtosecond transient absorption spectra indicated the production of the singlet excited state of porphyrin was followed by the formation of the radical ion pair (BDP\(^*_2\)-ZnP\(^*_2\)-C\(_{60}\))\(^−\), indicated by the characteristic absorption of the C\(_{60}\) radical anion at 1000 nm.

![Diagram](image-url)  
**Fig. 16** Proposed photochemical events in supramolecular Fe–(C\(_{60}\)*)–Im(1ZnP)–BODIPY (32) tetrad featuring a zinc porphyrin (ZnP) as primary electron donor, Bodipy as energy-transferring antenna, ferrocene (Fc) as charge stabilizing HS agent, and fullerene (C\(_{60}\)) as terminal electron acceptor. Abbreviations: EnT = excited energy transfer, ET = excited electron transfer, HS = hole shift, and CR = charge recombination.\(^9\)

Different from the covalent bond profile for attachment of visible light-harvesting Bodipy antenna to the porphyrin chromophore, a novel photosynthetic-antenna–reaction-center model compound, comprised of BF\(_2\)-chelated dipyrrmethene (Bodipy) as an energy-harvesting antenna, zinc porphyrin (ZnP) as the primary electron donor, ferrocene (Fc) as a hole-shifting agent, and phenylimidazole-functionalized fulleropyrrolidine...
(C₆₀Im) as an electron acceptor, has been synthesized and characterized (Fig. 16). Selective photoexcitation of Bodipy resulted in efficient singlet energy transfer to the ZnP moiety. Electron transfer from the Sn(IV) porphyrin framework is helpful to improve the light-harvesting ability of the complex in the visible spectral region, and broadband visible light absorption is resulted. The Bodipy antenna was quenched, but the emission of the Sn(IV) porphyrin moiety was mainly quenched by PET process in complex 33. For the array 34, however, upon selective excitation into the Bodipy moiety, the fluorescence emission of the Sn(IV) porphyrin moiety was not quenched. Thus electron transfer is not significant in array 34. Moreover, band attributed to the Bodipy moiety was observed in the fluorescence excitation spectra of 34, thus, no significant PET exists in array 34, and the quenching is due to singlet energy transfer from the Bodipy antenna to the Sn(IV) porphyrin moiety.

2.5. Supramolecular Bodipy-porphyrin, phthalocyanine or subphthalocyanine conjugates

In a similar way, Guldi et al prepared conjugates with Bodipy antenna axially bound to a Sn(IV) porphyrin via a phenolate or benzoate bridge (Complex 33 and 34, Fig. 17).

The difference between complexes 33 and 34 is that the bridge between the Sn(IV) and the Bodipy antenna, it is phenolate in complex 33, and it is benzoate in complex 34. The complexes 35 and 36 were used as reference for study of the photophysical properties (Fig. 17). It should be pointed out that although the absorption of Sn(IV) porphyrin coordination center is strong at 425 nm, but the Soret and Q bands at 560 nm and 600 nm are very weak. Thus attaching of Bodipy antenna to the Sn(IV) porphyrin framework is helpful to improve the light-harvesting ability of the complexes in the visible spectral region, and broadband visible light absorption is resulted.

The array 33 shows strong absorption at 425 nm and 500 nm, which are attributed to the Sn(IV) porphyrin coordination moiety and the Bodipy antenna, respectively. The absorption of the array is the sum of the components, thus there is no significant interaction between the chromophores in the array at the ground state. The electrochemical data support this conclusion as well.

The fluorescence emission of the Bodipy antenna was significantly quenched in array 33, which indicates singlet energy transfer, or electron transfer. The emission of Sn(IV) porphyrin moiety is weak. The reference compound 35, which is without any Bodipy antenna, also shows much weaker emission as compared with that of axially OH-coordinated Sn(IV)-porphyrin complex, thus it was concluded that the fluorescence of the Sn(IV) porphyrin moiety was mainly quenched by PET process in complex 33. For the array 34, however, upon selective excitation into the Bodipy moiety, the fluorescence emission of the Sn(IV) porphyrin antenna was quenched, but the emission of the Sn(IV) porphyrin moiety was not quenched. Thus electron transfer is not significant in array 34. Moreover, band attributed to the Bodipy moiety was observed in the fluorescence excitation spectra of 34, thus, no significant PET exists in array 34, and the quenching is due to singlet energy transfer from the Bodipy antenna to the Sn(IV) porphyrin moiety.

Femtosecond transient absorption spectra of the complexes were studied. For array 34, upon selective excitation into the Bodipy antenna, the singlet state of the antenna decay with much faster kinetics 3.5 ± 1 ps, as compared with the Bodipy reference, for which the decay time of the singlet excited state is 3.5 ± 0.5 ns. The product of the decay is the singlet excited state of the Sn(IV) porphyrin moiety, indicated by the minima at 435, 560, 600, and 660 nm as well as a broad maximum between 445 and 600 nm. Then the singlet excited state of the Sn(IV) porphyrin undergoes the ISC to produce triplet excited state.

For the array 33, however, the photophysical processes are different. Upon selective excitation into Bodipy antenna in array 33, firstly the singlet excited state of the Bodipy antenna was produced. Then the singlet excited state of the porphyrin moiety was produced by a fast energy transfer (2.0 ± 0.5 ps). Then a charge transfer state (CTS) was formed with a kinetic of 4 ± 2 ps, indicated by the absorption at 460, 485, 545, 585, 615, and 645 nm, which resemble the one-electron-reduced porphyrin anion. The charge recombination (CR) takes ca. 450 ± 50 ps.
The energy transfer mechanism was proposed to be via the Förster mechanism, based on the match of the calculated Förster energy transfer rate constant and the experimental results. However, the triplet state property of the arrays was not studied in detail, for which the nanosecond transient absorption spectroscopy is required. Moreover, the arrays were not studied for any applications. But we envision that the complexes are interesting for applications in photocatalytic hydrogen (H₂) production, or other photocatalysis. The photophysical processes involved in arrays 33 and 34 can be summarized in Fig. 18.

Similar approach was also used for preparation of Bodipy-subphthalocyanine arrays, with the Bodipy antenna axially bound to the B atom of SubPc (Fig. 19). The subPc unit gives strong absorption at 563 nm (log ε = 4.96), and the Bodipy unit gives absorption at 502 nm (log ε = 5.06). The styrylBodipy in 38 gives absorption at 562 nm (log ε = 5.02). Thus singlet energy transfer from the Bodipy to the SubPc unit was observed in array 37, whereas in array 38 the single energy transfer is from subPc to the styrylBodipy moiety. The energy transfer process was not studied with femtosecond transient absorption. Although the triplet excited state was not studied, formation of triplet excited state, especially in array 37, is expected since it is known that subPc undertakes efficient ISC (triplet state quantum yield is up to Φ₆ = 70%). For dyad 38, however, the ISC may be in competition with the FRET to the styrylBodipy unit.

Similarly BODIPY–phthalocyanine conjugates were prepared, with the Bodipy antenna axially bound to the Si atom (Fig. 20). In these triads, the Bodipy antenna show strong absorption at 502 nm (log ε = 5.31), whereas the phthalocyanine gives strong absorption at 683 nm (log ε = 5.44). The styrylBodipy units in triad 40 gives absorption at 571 nm (log ε = 5.40). For triad 39, the singlet energy transfer from the Bodipy unit to the phthalocyanine unit is predominant, whereas for triad 40, the electron transfer is significant. Phthalocyanine part (energy acceptor) in triad 39 gives fluorescence quantum yield of 60%, whereas in triad 40 the phthalocyanine part gives fluorescence quantum yield of only 0.3%.

The triplet excited state of the triads were not studied. Study of the triplet state property of triad 39 will be interesting, since it was reported that phthalocyanine derivatives show efficient ISC. Besides the energy transfer, phthalocyanine was also used for construction of molecular arrays for photoinduced charge transfer.

The molecular arrays discussed in the above sections show broadband visible light absorption. However, it should be pointed out that most of the above chromophore conjugates were not designed as triplet photosensitizers. In most of the cases, the triplet state, especially in array 39 and 40, states were not studied in detail with the nanosecond transient absorption spectroscopy. Based on the widely used FRET approach for attaining broadband visible light absorption in the areas of fluorescent molecule sensors, we designed organic chromophore conjugates to attain broadband visible light absorption. Moreover, the singlet energy acceptors in these chromophore conjugates play the role of spin converter, i.e. for triplet state formation.

2.6. Broadband visible light-absorbing chromophore conjugates as triplet photosensitizers

![Fig. 20 Broadband visible light-absorbing subphthalocyanine triads 39 and 40](image)

![Fig. 21 Bodipy-diodoBodipy dyads as triplet photosensitizers (41, 42, 43)](image)

We designed the dyads with Bodipy and iodoBodipy moieties (Fig. 21). In 41, 42 and 43, Bodipy moiety gives shorter absorption wavelength, and its emission band overlaps with the absorption of the diiodoBodipy moiety. FRET is ensured for this dyad and the similar dyads 42 and 43. Moreover, the diiodoBodipy moiety in 41 is the spin converter, since efficient ISC was observed for the diiodoBodipy moiety previously. The absorption wavelength range of 41, 42 and 43 is broader than the diiodoBodipy (12) (Fig. 22a).
Interestingly, we found that the triplet excited state of photosensitizers, the nanosecond transient absorption spectra of \( \text{41, 42 and 43} \) were studied (examplified with \( \text{41} \) in Fig. 22b). In order to study the triplet excited states of the dyad triplet photosensitizers, the nanosecond transient absorption spectra of \( \text{41, 42 and 43} \) were studied (examplified with \( \text{41} \) in Fig. 22b). Time-dependent DFT (TDDFT) computations indicated that the \( T_3 \) and \( T_5 \) states of 41, which is confined on the two chromophores, respectively, are degenerated (with same energy levels). Herein forward singlet energy transfer from the Bodipy moiety to the iodoBodipy moiety occurs, and followed by the backward triplet energy transfer from the iodoBodipy to the Bodipy moiety, i. e. the ping-pong energy transfer and triplet state equilibrium was established. To the best of our knowledge, this is the first time that such photophysical processes were observed for an organic molecular conjugate.

It should be pointed out that the intramolecular triplet state energy transfer in 41 is fast (\( k > 10^8 \text{ s}^{-1} \)). We also studied the intermolecular triplet energy transfer between the iodoBodipy and Bodipy. The results show that the intermolecular TTET is much slower (Fig. 23). Moreover, no triplet state equilibrium was observed, and the TTET is uni-directional.

The dyad triplet photosensitizers, \( \text{41, 42 and 43} \) were used for photosensitizing singlet oxygen \( (\text{^{1}O_2}) \), with broadband photoexcitation (white light from a xenon arc lamp). The results show that the \( \text{^{1}O_2} \) photosensitizing of the dyad triplet photosensitizers are more efficient than the iodoBodipy. These results show that broadband visible light-absorbing triplet photosensitizers are more efficient than the mono-chromophore based triplet photosensitizers.

In order to obtain broader visible light-absorption band, and to explore more diverse molecular structure for the triplet photosensitizers based on FRET effect, we used Bodipy, or carbazole-conjugated Bodipy as energy donor (for variable absorption wavelength), and diido-azaBodipy at the energy acceptor and the spin converter to prepare triplet photosensitizers, thus triad \( \text{44 and 45} \) were prepared, with 46 as the reference compound (Fig. 24).

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Fig. 22 (a) The UV–vis absorption of 41 and the energy donor and energy acceptor reference compounds (12 and Bodipy), in toluene, \( c = 1.0 \times 10^{-5} \text{ M} \). (b) The nanosecond transient absorption of 41 in deaerated toluene, \( \lambda_{ex} = \lambda_{em} = 532 \text{ nm}, c = 1.0 \times 10^{-4} \text{M}, 20^\circ \text{C} \).

Fig. 23 Intermolecular triplet-triplet-energy-transfer (TTET) observed with nanosecond transient absorption spectra. (a) \( c \) [Bodipy] = \( 5.0 \times 10^{-4} \text{ mol/L} \), \( c \) [bodipy] : c[12] = 5:1, (b) The decay trace at 500 nm, (c) \( c \) [Bodipy] = \( 1.0 \times 10^{-4} \text{ mol/L} \), c[Bodipy]: c [12] = 1:1. (d) The decay trace at 500 nm, \( \lambda_{em} = 535 \text{ nm} \). In Toluene, 20 °C.

Fig. 24 Diido-AzaBodipy derived broadband visible light-absorbing triplet photosensitizers 44, 45, 46 and 47.
Fig. 25 (a) UV–vis absorption spectra of 44, 45 and 46. (b) Comparison of the fluorescence excitation spectrum with the UV–vis absorption spectrum of 45 (λem = 760 nm). (c) = 1.0 × 10^{-5} M in toluene, 20°C.58

It should be pointed out that the singlet energy transfer such as FRET was usually evaluated by the quenching of the fluorescence of the energy donor. However, this is not a realiable method because photophysical processes other than the FRET can also quench the fluorescence of the energy donor, such as photo-induced electron transfer (PET). This scenario was demonstrated by the quenching of the fluorescence of the energy donor in 45 (Fig. 26). It is obvious that the fluorescence of the energy donor was almost completely quenched. Quantitative EnT will be postulated based on the quenching study. Calculation of the Gibbs free energy transfer of 45 indicated that PET is also possible for the quenching of the energy donor’s fluorescence.

Fig. 26 Fluorescence emission spectra of 47 and the triplet photosensitizer 45, λem = 490 nm, c = 1.0 × 10^{-5} M in toluene 20°C.58

In order to study the triplet excited state property of the Bodipy-azaBodipy triads, the nanosecond transient absorption spectra of the triads were studied (Fig. 27). Upon nanosecond pulsed laser excitation at 355 nm (both Bodipy and iodo-
AzaBodipy are photoexcited), bleaching band at 668 nm was observed. Interestingly, no bleaching band at 503 nm was observed. These results indicate that the T1 excited state of 45 is exclusively confined on the diiodoAzaBodipy moiety, and the Bodipy moiety makes no contribution to the T1 state of 45. This result is due to the lower T1 state energy level of the azaBodipy (1.22 eV)17 as compared with that of the Bodipy moiety (1.69 eV)78,117. Similar results were observed for 44.58

The singlet energy transfer process in 45 was studied with the femtosecond transient absorption spectra (Fig. 28). Upon femtosecond pulsed laser excitation at 504 nm, where the absorption is dominated by the Bodipy moiety (energy donor), the bleaching band at 505 nm decreased, at the same time, the bleaching band at 680 nm grows. This process indicates the singlet energy transfer in 45. The energy transfer rate constant is k_{ET} = (4.3 ± 0.3) × 10^{10} s^{-1}. In comparison, the singlet energy transfer of 44 is with a fast kinetics, k_{ET} = (5.1 ± 0.4) × 10^{11} s^{-1}. The faster singlet energy transfer in 44 is attributed to the larger spectral overlap integral for 44. We confirmed that the broadband visible light-absorbing 44 and 45 is more efficient than 46 in 1O2 photosensitizing.

Fig. 27 (a) Nanosecond transient absorption spectra of 45. (b) The decay process was monitored at 430 nm. After pulsed excitation at 355 nm (c = 2.0 × 10^{-5} M, in deaerated toluene, 20°C).58

Fig. 28 (a) Femtosecond transient absorption spectra of dyad 45 upon pulsed laser excitation (λex = 504 nm) in toluene; (b) Decay trace at 505 and 680 nm. 20°C.17

Fig. 29 Rhodamine-diiodo-styrylBodipy dyad triplet photosensitizers (48, 49, 50 and 51) which give broadband visible light-absorption.17
Rhodamine is a well known visible light-absorbing chromophore, and has been widely used in preparation of FRET molecular dyads, mainly concerning singlet excited state manifold, i.e. fluorescence, as well visible light-harvesting molecular assemblies and molecular probes. However, no application of rhodamine in construction of organic triplet photosensitizers was reported.

On the other hand, rhodamine derivatives usually contain carboxylic moiety, which may complicate the photophysical property due to the reversible spirolactam-opened amide transformation. The spirolactam form gives no visible light-absorption and the opened amide form give strong absorption at ca. 570 nm. In order to eliminated this complicity, we used rhodamine moiety which is without the carboxylx moiety for construction of broadband visible light absorbing triplet photosensitizers 48 and 49 (Fig. 29).

In 48 and 49, rhodamine was used as energy donor and diiodostyrilBodipy was used as energy acceptor, as well as spin converter. The UV-vis absorption of 48 (Fig. 30) indicated that there is no strong interaction between the components at ground state. Fluorescence quenching of the rhodamine part in 48, and the comparison of the fluorescent excitation spectrum and the UV-vis absorption spectrum of 48 supports the singlet energy transfer process.

![Fig. 30 UV-vis absorption of 48, 50 and 51. c = 1.0 × 10⁻³ M, in CH₂Cl₂, 20 °C. Reproduced with permission from Ma et al.](image)

![Fig. 31 (a) Nanosecond transient absorption spectra of 48 (λex = 532 nm). (b) Decay curve of 48 at 630 nm, c = 1.0 × 10⁻³ M, in deaerated CH₂Cl₂, 20 °C. Reproduced with permission from Ma et al.](image)

The nanosecond transient absorption spectroscopy shows that the T₁ state of 48 is confined on the diiodostyrilBodipy moiety (Fig. 31). The triplet state lifetime is 1.53 µs (Fig. 31b). Note the uniodinated styrylBodipy shows much longer triplet exited state lifetime, for example in styrylBodipy-C₆₀ dyad (71.5 µs). The triplet formation with 49 is weak in polar solvents, such as acetonitrile. This effect may be attributed to the quenching of the triplet state by intramolecular charge transfer (ICT) in the styrylBodipy part in 49.

The dyad triplet photosensitizers were used for photoredox catalytic organic reactions (Fig. 32), i.e. oxidation/[3 + 2] cycloaddition/aromatization tandem reaction with tetrahydroisoquinoline derivatives.

![Fig. 32 Oxidation/[3 + 2] cycloaddition/aromatization tandem reaction with tetrahydroisoquinoline derivatives catalyzed by organic triplet photosensitizers 48 and 50. Reproduced with permission from Ma et al.](image)

The reaction mechanism were studied with electron spin resonance (ESR) spectroscopy. It was supposed that the triplet excited state of 48 acts as electron acceptor, the isetetrahydroquinoline is the electron donor (Fig. 33). Upon photoexcitation of the 48, and the following intermolecular electron transfer, iminium was formed. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were employed as scavengers for O₂⁺ and •O₂, respectively. Therefore the electron transfer from the amine substrate to the organic triplet photosensitizer is confirmed, i.e. the photocatalytic reaction proceeds with O₂⁺ as one of the crucial species, not •O₂ (Fig. 33). Upon white light photoexcitation (broadband light source), the photocatalytic efficiency of R-1 is higher than that of B-1, which demonstrated that the broadband visible light-absorbing triplet photosensitizer is superior to the mono-visible light-harvesting chromophore triplet photosensitizers. It should be pointed out application of the efficient new triplet photosensitizers as photocatalysts in photoredox catalytic organic reactions is still in the very early age. We envisage that more tripletphotosensitizers will be witnessed.

Recently a polymeric broadband visible light-adsorbing triplet
photosensitizer was designed (Fig. 34). In the polymer backbone, the fluorene and Bodipy units were copolymerized as the singlet energy donor, as well as the UV-green light-harvesting units. Diiodo-StyrylBodipy units were dangled on the fluorene unit, as the singlet energy acceptor and the spin converter. As a result the polymer shows broadband absorption in the range of 400–700 nm. It was confirmed the polymeric triplet photosensitizer is more efficient than the diiodostyrylBodipy alone for photosensitizing of $^{1}$O$_2$.

Fig. 34 Polymeric broadband visible light-absorbing triplet photosensitizer (52). Reproduced with permission from He et al.121

2.7. C$_{60}$ as the Spin converter in broadband visible light-absorbing heavy atom–free triplet photosensitizers

Up to now most of the triplet photosensitizers are dependent on heavy atom effect, with which the ISC is facilitated. The same hold for the broadband absorbing triplet photosensitizers such as 52, in which the spin converter is diiodoBodipy derivatives. Previously it was reported that for oligothiophene and azaBodipy antenna dyads with C$_{60}$, population of triplet excited state was observed upon photoexcitation (Fig. 35). In some cases it was attributed to the CR process. However, it is well known that C$_{60}$ shows efficient ISC (close to unity), thus a cascade singlet energy transfer and ISC of the C$_{60}$ moiety may play the role for triplet production with these dyads.

Fig. 35 AzaBodipy-C$_{60}$ (53) and PBI-C$_{60}$ dyads (54) with triplet excited state populated upon photoexcitation.

Recently we proposed to use the ISC capability of fullerene C$_{60}$ for preparation of heavy atom free triplet photosensitizers (Fig. 36). These heavy-atom-free triplet photosensitizers were used for TTA upconversion, and photoredox catalytic organic reactions, and the efficiency of these organic heavy atom-free triplet photosensitizers is satisfactory. High $^{1}$O$_2$ quantum yields ($\Phi_{\Delta} = 0.85$) and TTA upconversion quantum yield were observed. Using of a C$_{60}$ unit as the spin converter is better than using a spin converter which is dependent on the heavy atom effect, because ISC may not be facilitated by heavy atoms if the intrinsic decay of the S$_1$ state of the chromophore is ultrafast. In other words, attaching heavy atoms to chromophore does not always guarantee efficient ISC.

Fig. 36 Representative C$_{60}$-Bodipy heavy atom-free triplet photosensitizers (55, 56, 57, 58, 59).46,125,126

In order to attain broadband visible light absorption, we used C$_{60}$ as spin converter and more than one Bodipy unit as light-harvesting antenna for preparation of heavy atom-free broadband
visible light-absorbing triplet photosensitizers (Fig. 37). The strategy is to attach different antenna to C₆₀ to attain broadband absorption visible light, and the harvested photoexcitation energy can be funneled to the C₆₀ moiety. The ISC of C₆₀ moiety will convert the photoexcitation energy to triplet state. We selected Bodipy as the principle chromophore due to the feasible derivatization.

In compound 60, the two Bodipy moieties are with different conjugation frameworks, thus the absorption wavelength of the two Bodipy moieties are at 517 nm and 629 nm, respectively. Note the S₁ state energy level of C₆₀ is 1.75 eV, thus singlet energy transfer from the two Bodipy moieties to the C₆₀ moiety is possible. At least with the antenna alone, we confirmed the FRET effect, although the detail photophysics of 60 were not studied with femtosecond transient absorption spectroscopy.

The triplet excited state of the triad was studied with nanosecond transient absorption spectra (Fig. 38), upon selectively excitation into the Bodipy antenna, the triplet excited state is confined on the styrylBodipy moiety, neither on the C₆₀ moiety or Bodipy moiety. This result can be rationalized by the different triplet state energy levels of the three moieties. These results indicate that ping-pong energy transfer occurred for 60, i.e. the forward singlet energy transfer from the Bodipy moieties to the C₆₀ moiety, and the backward fast triplet energy transfer from the C₆₀ moiety to the styrylBodipy moiety (rate constants > 10⁸ s⁻¹).

Fig. 38 Nanosecond transient absorption spectra of 60. (a) Transient absorption spectra and (b) the decay trace of the ground state bleaching at 630 nm.

We found that the Bodipy-C₆₀ broadband visible light-absorbing triplet photosensitizers are efficient ¹O₂ sensitizers (with Φₐ up to 81–92%). Moreover, the compounds were used as electron donor to produce superoxide radical anion (O₂⁻) in the presence of sacrificial electron donor such as N,N-diisopropylthylamine. Thus these compounds were used as photocatalyst for photocatalytic aerobic oxidation of aromatic boronic acids to produce phenols. The reaction times are much shorter as compared with that of the conventional photocatalyst such as Eosin Y (3). Thus the Bodipy-C₆₀ triads can be used as dual functional photocatalysts, either as ¹O₂ photosensitizer, or as electron donor to produce superoxide radical anion (O₂⁻) for aerobic oxidation of aromatic boronic acids to produce phenols.

2.8. Pt(II) complexes show broadband visible light absorption

Previously broadband visible light-harvesting transition metal complexes were reported. However, much room is left for preparation of Pt(II) complexes with feasibly derivatizable molecular structures. Concerning this aspect, the trans bis(trialkylyphosphine) Pt(II) bisacetylide complexes are in particular interest, because different alkyln ligands can be induced by a stepwise approach. Thus we envisaged to prepare trans bis(phosphine) Pt(II) bisacetylide complexes which show broadband visible light absorption (Fig. 39).

Fig. 39 The broadband visible light-absorbing trans bis(tributylphosphine) complexes 66 and 67. The complexes 64, 65 and 68 containing a mono visible light-absorbing ligand were used as reference complexes.

The design rationals for complexes 66 and 67 is that the bismetalated 2,6-diethylnylBodipy will show red-shifted absorption as compared with that of the mono-metalated 2-ethylnBodipy ligand. Thus 66 will show broad band visible light absorption. Moreover, it is expected that the ISC of the central coordinated Bodipy ligand is efficient, therefore the broadband visible light photoexcitation energy harvested by 66 can be efficiently funneled to the triplet state manifold. The lowest-lying triplet excited state (T) of 66 is confined on the central coordinated Bodipy ligand. The same design rational was applied for 67. In 67, however, the peripheral coordinated Bodipy ligand will show absorption at ca. 500 nm because the coordinated center is not attached to the π-core of the Bodipy. Thus more distinct absorption bands will be observed for 67 as compared to that of 66.

The UV–vis absorption spectra of the complex show that 66 shows broadband absorption in the range of 500–700 nm, whereas 67 shows absorption bands in the range of 450–700 nm, and the two absorption bands of 67 are almost baseline-separated (Fig. 40). For 66, the two absorption bands are almost merged. Quenching of the energy donor and the comparison of the luminescence excitation and UV–vis absorption spectra indicated the singlet energy transfer process in 66 and 67.
The FRET process was confirmed by the femtosecond transient absorption spectroscopy (Fig. 41). Upon selective excitation into the energy donor, two bleaching bands were observed at 505 nm and 650 nm. Along with the decrease of the bleaching band at 505 nm, the bleaching band at 650 nm grows. These processes indicated the FRET process in 67. The rate constants of the singlet energy transfer process was calculated as $k_{\text{ET}} = 4.0 \times 10^{10}$ s$^{-1}$.

In order to study the triplet excited state of the triad 66 and 67, nanosecond transient absorption spectra were studied. The results show that the T$_1$ states of 66 and 67 are confined on the central coordinated Bodipy ligands. The T$_1$ state energy level of the centrally coordinated Bodipy ligand can be approximated as $1.50$ eV by the phosphorescence emission, which is lower than the peripheral Bodipy ligands, for which the T$_1$ state energy level is $1.69$ eV. The results of the nanosecond transient absorption spectroscopy indicated that the ISC rate constant of 67 is at least $1 \times 10^8$ s$^{-1}$, and that there is no triplet state equilibrium.

The advantage of using trans bis(tributylphosphine) Pt(II) bisacetylide complexes is that different light-harvesting ligands can be easily introduced to the complex. Different ligands pairing may exert significant impact on the intramolecular energy transfer or electron transfer process, and the property of the triplet excited state may vary substantially. Following this line, we prepared a Bodipy-NDI dyad (69, Fig. 42). Complexes 70 and 71, which contain only one visible light-harvesting chromophore, were used as reference complexes in the studies.

The UV–vis absorption spectrum of 69 is the sum of that of 70 and 71 (Fig. 43). Thus there is no $\pi$-conjugation between the NDI and the Bodipy chromophores in 71 across the Pt(II) coordination center. In other words, the Franck-Condon state is localized on the respective chromophores. Previously it was proposed that the Franck-Condon state may be de-localized. Application of heteroleptic ligands giving drastically different absorption in the complexes is helpful for elucidate the issue.

Comparison of the luminescence excitation spectra with the UV–vis absorption spectra indicates the singlet energy transfer from the Bodipy unit to the NDI unit. Nanosecond transient absorption spectroscopy shows that intramolecular TTET occurred for 69, since selective photexciitation into the energy donor (the Bodipy unit) mainly produce the NDI-localized triplet excited state. Intermolecular TTET between 70 and 71 was also studied.

2.9. Switchable triplet excited state of broadband visible light-absorbing triplet photosensitzers

Different from the study on singlet excited state (such as fluorescence), for which many switching or modulation
mechanisms have been developed,31 the study on switching of the triplet excited state is rare. Switching of the singlet excited state leads to vast functional molecules, such as fluorescent molecular probes,31,131 and light-harvesting arrays.81 etc. Switching of the triplet excited state will also give important compounds such as activatable PDT reagents,7,114 and molecular machines or logic gates with \( O_2 \) as a novel output.32

Recently we prepared Bodipy-derived broadband visible light-absorbing triplet photosensitizers which show tunable triplet excited state, either by the solvent polarity or protonation (Fig. 44).115 In 72, the Bodipy unit is the singlet energy donor, and the dimethylaminostyrylBodipy is the singlet energy acceptor and the spin converter. In 73, the uniodinated Bodipty part is the singlet energy acceptor, and the iodinated Bodipy part is the singlet energy donor.

![Figure 44](image_url) Broadband visible light-absorbing Bodipy Dyads (72 and 73) with tunable triplet excited state.115

Compound 72 shows strong absorption band at 497 nm and 639 nm due to the uniodinated Bodipy part and the iodinated Bodipy unit (Fig. 45), respectively. For 72 alone, the emission intensity was greatly reduced in polar solvents. By comparison with the reference compounds, we proved that the emission of 73 is due to the iodinated Bodipy part, the uniodinated Bodipy unit in 73 is the singlet energy acceptor. Hence, 73 is a rare example that the chromophore showing shorter absorption wavelength acts the singlet energy acceptor in the FRET process.83 This is due to the large Stokes shift of the uniodinated Bodipy part in 73.

![Figure 45](image_url) Variation of the UV–vis absorption spectra and the fluorescence emission spectra upon protonation with addition of aqueous HCl. (a) Compound 72 with increasing amount of HCl was added and (b) the corresponding emission spectra changes of compound 72 (λ<sub>ex</sub> = 540 nm) upon addition of the HCl. The aliquots of the HCl solution (1 M) added are 1 μL, 2 μL, 3 μL, 4 μL, 5 μL, 10 μL, 20 μL, 30 μL, 50 μL and 100 μL. In MeCN/H<sub>2</sub>O = 9:1(v/v), (c = 1.0 × 10<sup>−5</sup> M, 20 °C).115

The singlet oxygen (\( O_2 \)) photosensitizing ability of the compounds were evaluated with a \( O_2 \) scavenger, 1,3-diphenylisobenzofuran (DPBF). In neutral solution (CH<sub>3</sub>CN: H<sub>2</sub>O 9:1, v/v), no formation of triplet excited state was observed, and the \( O_2 \) photosensitizing is negligible (ΦΔ = 7%). Upon addition of acid, thus protonation of the amino group, the \( O_2 \) photosensitizing quantum yield (ΦΔ) increased to 73.8%.

Broadband visible light-absorbing C<sub>60</sub>-Bodipy dyads were also prepared for study of the triplet excited state switching (76 and 77), 74 and 75 were used as reference compounds (Fig. 46).137 In these triads, the Bodipy chromophores are the visible light-harvesting antenna and singlet energy acceptor. C<sub>60</sub> unit is the singlet energy acceptor and the spin converter. Moreover, the Bodipy units are also the electron donor. The visible light-harvesting antenna were selected in such a way that the S<sub>1</sub> state of the styrylBodipy in 75 and 77 is lower than that of C<sub>60</sub>, thus singlet energy transfer from the Bodipy moiety to C<sub>60</sub> is inhibited. On the other hand, singlet energy transfer may occur for 74 and 76, the triplet state of the dimethylaminostyrylBodipy may be produced by the backward triplet-triplet-energy-transfer (TTET). However, as we discovered earlier, the triplet state of the dimethylaminoStyrylBodipy will be quenched in polar solvents such as dichloromethane. Thus, the triplet state property of the C<sub>60</sub>-Bodipy triads can be switched via a few approaches, such as electron transfer, singlet energy transfer and intra-antenna charge transfer.

For 74, the absorption band is centered at 622 nm, and the fluorescence emission band is at 660 nm. Thus the S<sub>1</sub> state energy level of the Bodipy antenna in 74 is higher than C<sub>60</sub> (1.75 eV).78,124 As a result, singlet energy transfer from the Bodipy antenna to C<sub>60</sub> is possible in 74. Indeed the triplet state of the Bodipy antenna in 74 can be observed in non-polar solvent, such as toluene (τ<sub>T</sub> = 168.6 μs, Φ<sub>T</sub> = 1.9%). But no triplet state was observed for 74 in polar solvents such as dichloromethane. In this case the formation of triplet state is either inhibited by the electron transfer from Bodipy to C<sub>60</sub> or by the intra-antenna charge transfer. Upon addition of TFA, thus protonation of the amino group, the absorption band is blue-shifted to 573 nm, and triplet excited state localized on the Bodipy antenna was observed even in polar solvent (in dichloromethane. τ<sub>T</sub> = 4.4 μs, Φ<sub>T</sub> = 73%).
For 75, the absorption is at 712 nm, and the fluorescence emission is at 770 nm. Thus the S1 state energy level of the Bodipy antenna (1.61 eV) is close or lower than that of C60. Thus singlet energy transfer from the Bodipy antenna to C60 in 75 is inhibited. As a proof of this postulation, no significant formation of triplet excited state was observed for 75, even in non-polar solvent such as toluene (ΦΔ = 1.1 %). It is known that photo-induced electron transfer will be inhibited to large extent in nonpolar solvents.62,124 With addition of TFA, the absorption and fluorescence emission of 75 are blue-shifted to 627 nm and 644 nm, respectively. Thus singlet energy transfer in the protonated 75 become possible. Triplet excited state was observed for 75 upon addition of acid (in dichloromethane. τT = 74.8 μs, ΦΔ = 26%). Similar results were observed for 76 and 77, except that broadband visible light absorption was observed for 76 and 77.

For the above compounds or the broadband visible light-absorbing triplet photosensitizers with triplet state switched, the emission is at 770 nm. Thus the S1 state energy level of the 75 increased up to 88.5%.

Fig. 46 Broadband visible light-harvesting C60-Bodipy triads (76 and 77. 74 and 75 are reference compounds).137

![Diagram](https://example.com/diagram.png)

Fig. 47 Acid-activatable Rhodamine-C60 dyad triplet photosensitizers (78, 79).138

2.10. Broadband visible light-absorbing triplet photosensitizers with competing ISC and FRET

Up to date the molecular structural designing rational of the broadband visible light-absorbing triplet photosensitizers is based on the desired profile, i.e. the singlet energy acceptor plays the role of the spin converter. Thus the FRET process is followed by ISC, and this cascade process is beneficial for funneling of the photoexcitation energy for formation of triplet excited state. The alternative profile, i.e. the singlet energy donor as the spin converter, for which a competing ISC and FRET will be established, has never been studied. In order to study the photophysics of the broadband visible light-absorbing triplet photosensitizers with competing ISC and FRET, we prepared dyads 82 and triad 83 (Fig. 48),102 in which competing ISC and FRET is expected.

In 82 and 83, the iodoBodipy part is the singlet energy donor, and the PBI part is the singlet energy acceptor. Fluorescence of the PBI unit (the singlet energy acceptor) is substantially quenched, thus PET is proposed, and it was supported by the calculation of the Gibbs free energy changes (ΔG°) of the PET process.62,78,102

It is known that PBI is with T1 state energy level of ca. 1.2 eV, which is much lower than Bodipy (ca. 1.69 eV). Thus the T1 state of the dyad 82 and triad 83 is assumed to be located on the PBI moiety. It should be pointed out that the PBI moiety shows only week ISC ability, thus significant population of the PBI-localized triplet excited state will indicate intramolecular TTET. The nanosecond transient absorption spectroscopy show that the triplet state of the dyad and triad is localized on the PBI moiety, even with selective photoexcitation into the diiodoBodipy unit (Fig. 49). An exceptionally long-lived triplet excited state lifetime ca. 150 μs was observed (Fig. 49b). Previously with heavy atom effect of Pt(II) the PBI triplet state lifetime was found to be much shorter (less than 1 μs).139 The intramolecular TTET process is assumed to be fast because the TTET process
cannot be monitored by the nanosecond transient absorption spectrometer.

![Fig. 48](image)

**Fig. 48** Broadband visible-light-harvesting PBI-Bodipy dyad 82 and triad 83 with competing ISC and FRET process. Dyad 80 and triad 81 were prepared as reference compounds.102

With femtosecond transient absorption spectroscopy, the singlet energy transfer rate constant was determined as \(5 \times 10^{10}\) s\(^{-1}\). Previously it was reported that the intersystem crossing rate constants of 2,6-diiodoBodipy is \(7.7 \times 10^{9}\) s\(^{-1}\). Thus the ISC of the diiodoBodipy moiety should be significantly quenched by the FRET. In other words, the triplet state formation quantum yield (\(\Phi_T\)) of the dyad 82 and the triad 83 should be low, due to the competition of FRET on the ISC. To our surprise, the triplet state yield of the dyad and the triad (approximated with the singlet oxygen quenem yield, \(\Phi_D\)), which were determined as 80% and 78%, respectively. Thus we propose the singlet excited state of the diiodoBodipy in 82 and 83 was trapped somehow, although the faster decay channel of FRET exists.

In order to add modularity to triplet photosensitizers with such novel photophysical properties, we propose that the reversible transformation of rhodamine between the spirolactam and the opened amide structures can be used to switch the triplet excited state as well (Fig. 50).140 The two structures show drastically different photophysical properties, such as visible light absorption, the \(S_1\) state energy level, as well as the \(T_1\) state energy level. The electron donating ability may also change accompanying the spirolactam→opened amide structure transformation. The spirolactam structure of rhodamine shows no visible light absorption ability, the \(S_1\) state is with high energy level (2.63 eV). The \(T_1\) state energy level is also high (3.36 eV). The electron donating ability is presumably strong. For the opened amide structure, strong absorption at ca. 560 nm emerges, intense fluorescence emission at 580 nm develop, and the \(S_1\) state energy level is ca. 2.13 eV. The \(T_1\) state energy level is 1.73 eV.

![Fig. 49](image)

**Fig. 49** Nanosecond transient absorption spectra of 12, 82 and 83. (a) Transient absorption spectra of 82 and (b) the decay trace of 82 at 470 nm. (c) Transient absorption difference spectra of 83 and (d) the decay trace of 83 at 470 nm. (e) Transient absorption difference spectra of 12 and (f) Decay trace of 12 at 520 nm. \(\lambda_{ex}=532\) nm (nanosecond pulsed laser), \(c=1.0 \times 10^{-5}\) M in deaerated toluene. 20°C.102

![Fig. 50](image)

**Fig. 50** Spirolactam-Opened amide structure transformation of Rhodamine.140 Based on these spectral property changes, we assume that the spirolactam/opened structural transformation of rhodamine can be used to modulate the triplet excited state of triplet photosensitizers. This structural transformation has been widely used for designing fluorescence molecular chemosensors, i.e. for modulation of singlet excited states, but it was not used for modulation of triplet excited states. Thus we designed RB-NDI and RB-NI dyads for switching of the triplet excited state (Fig. 51).140

In the absence of acid, compound 84 shows a moderate absorption band at 537 nm, which is due to the 2-bromo-6-amino-NDI (\(\varepsilon=10800\) M\(^{-1}\) cm\(^{-1}\)). The fluorescence of 84 is
weak as compared with that of NDI, thus electron transfer may be responsible for the quenching of the fluorescence of NDI moiety. Upon addition of acid, intense absorption band at 557 nm emerged, which is attributed to the opened amide rhodamine ($\varepsilon = 64400$ M$^{-1}$ cm$^{-1}$). With optically matched solution, we found that the emission of RB-NDI (84)/TFA is half of the emission intensity of RB+TFA. Thus the PET in the RB-NDI (84)/TFA is not significant, otherwise the fluorescence of the rhodamine part may be quenched.

No triplet excited state was observed for compound 84 in polar solvents (DCM:MeOH = 9:1, v/v). This lack of the formation of the triplet excited state may be due to the PET in compound 84, with RB (spirolactam structure) as the electron donor and the NDI part as the electron acceptor, based on the electrochemical property of the compounds.140

In the presence of acid (TFA), triplet signal was observed for compound 84 in the presence of TFA (100 $\mu$L), $c = 2.0 \times 10^{-5}$ M; (b) decay trace at 450 nm. $c = 1.0 \times 10^{-5}$ M. Excited with 532 nm nanosecond pulsed laser. In deaerated DCM/MeOH (9/1,v/v), 20 °C.140

The triplet state lifetime was 9.89 $\mu$s. The observation of the triplet state is due to addition of acid. Based on these conjugates showing competing FRET and ISC, we found that the ISC of the singlet energy donor is unable to be completely quenched by FRET. In some cases, the PET plays the major role for triplet state quenching.

It is still in the very early age for the studying of the broadband visible light-harvesting triplet photosensitizers. Molecular designing strategies for these photosensitizers need to be developed to reduce the synthetic demandings, to repress the PET process (clearly this is a undesired side-photophysical process), to ensure efficient FRET and high triplet state yield.

Although there are some reports on preparation of such triplet photosensitizers, the application of these novel compounds is rare. Applications of such photosensitizers in $1O_2$ production and photocatalytic organic reactions were reported, but the enhancement of the photosensitizing efficiency is not always satisfactory. Detail kinetic modeling concerning these photophysical processes will help to elucidate the situation, but at present such studies are left to be done. These studies will be helpful to the areas such as photocatalysis and photovoltaics, as well as fundamental photochemistry studies.

3. Conclusion

In summary, the molecular design methods for broadband visible light-absorbing triplet photosensitizers are summarized. Conventional triplet photosensitizers usually contain a single visible light-harvesting chromophore, thus show only a single...
Notes and references

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Graphical Abstract:

Application of singlet energy transfer in triplet state formation: broadband visible light-absorbing triplet photosensitizers, molecular structure design, related photophysics and applications

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The molecular structure designing, photophysical properties and the application of the broadband visible light-absorbing triplet photosensitizers were summarized.