Triplet–Triplet Energy Transfer Study in Hydrogen Bonding Systems

Zhijia Wang, Jianzhang Zhao*, and Song Guo

Abstract: The 2,6-diiodoBodipy–styrylBodipy hydrogen bonding system was prepared to study the effect of hydrogen bonding on the triplet–triplet-energy-transfer (TTET) process. 2,6-DiiodoBodipy linked with *N*-acetyl-2,6-diaminopyridine (**D-2**) was used as the triplet energy donor, and the styrylBodipy connected with thymine (**A-1**) was used as triplet energy acceptor, thus the TTET process was established upon photoexcitation. The photophysical processes of the hydrogen bonding system were studied with steady-state UV-vis absorption spectroscopy, fluorescence spectroscopy, fluorescence lifetime measurement and nanosecond time-resolved transient absorption spectroscopies. The TTET of the intramolecular/hydrogen bonding/intermolecular systems were compared through nanosecond transient absorption spectroscopy. The TTET process of the hydrogen bonding system is faster and more efficient ($k_{TTET} = 6.9 \times 10^4$ s^{-1}, $\Phi_{TTET} = 94.0\%$) than intermolecular triplet energy transfer ($k_{TTET} = 6.0 \times 10^4$ s^{-1}, $\Phi_{TTET} = 90.9\%$), but slower and less efficient than intramolecular triplet energy transfer ($k_{TTET} > 10^8$ s^{-1}). These results are valuable for designing self-assembly triplet photosensitizers and for the study of the TTET process of hydrogen bonding systems.

Keywords: Bodipy · Hydrogen bond · Intermolecular/Intramolecular TTET · Supramolecular

Introduction

Supramolecular chemistry has attracted much attention due to its wide application in molecular recognitions,[1–4] separation techniques,[5–8] chemical syntheses,[9–11] and supramolecular materials.[12–14] It is a chemistry that investigates the non-covalent interactions between two or more molecules, which are highly ordered and exhibit specific function.[15] Compared with covalent compounds, supramolecular systems are more controllable, reversible and easier to synthesize.

Among a variety of supramolecular interactions, such as π–π stacking, electrostatic forces, strong dipole–dipole association, hydrophobic forces and steric repulsion,[16] the hydrogen bond remains the most widely used and investigated supramolecular interaction due to its high directionality and tunable strength.[17] Hydrogen bonding is widely applied in molecular sensors,[18–22] crystal engineering,[23] biological macromolecular building blocks,[24] *etc.* Since hydrogen bonding is crucial in organisms (DNA and proteins are composed of a large number of hydrogen bonds), various studies about the hydrogen bond have been carried out. However, the study of energy transfer in hydrogen bonding system is scarce. Singlet energy transfer between an energy donor and an energy acceptor unit linked by a hydrogen bond has been studied previously,[25,26] but triplet energy transfer in hydrogen bonding systems was rarely investigated,[27,28] though triplet energy transfer is fundamental for photosynthesis,[29] photoredox catalytic organic reactions,[30–32] and in photodynamic therapies.[33,34] Previously, our group synthesized a Bodipy-C$_{60}$ triple hydrogen bonding assembly and studied the fluorescence resonance energy transfer (FRET) and TTET processes of the hydrogen bonding system.[35] Herein the energy donor unit (diiodoBodipy) is quite different from the previous work with C$_{60}$. Due to the weak absorption of C$_{60}$ in the visible region, the hydrogen bonding system has only one major absorption band in the visible spectral region. Hydrogen bonding systems with broadband visible light-harvest ability have rarely been designed before. Moreover, to the best of our knowledge, the TTET of the intramolecular/hydrogen bonding/intermolecular systems have never been compared and studied systematically, thus much room is left to fully explore the triplet energy transfer of hydrogen bonding systems.

In order to study the effect of the formation of hydrogen bond on TTET, herein we prepared Bodipy compounds for the study of supramolecular triplet photosensitizers (PSs) (**D-1**, **D-2**, **A-1**, **B-1**, **9**, **10**, **11**, Scheme 1). The assembly process was driven by the diamidopyridine-thymine three-point hydrogen bonding interactions,[36–41] where the 2,6-diiodoBodipy linked with *N*-acetyl-2,6-diaminopyridine and the styrylBodipy connected with thymine were used as the triplet energy donor and triplet energy acceptor, respectively. Thus a hydrogen bonding system can be built with the pair **D-1/A-1**, and the pair **D-2/A-1** (Scheme 2); intermolecular triplet energy transfer will be investigated by the mechanically mixed compounds **9** and **10**; intramolecular triplet energy transfer will be studied with the dyad **B-1**, where 2,6-diiodoBodipy and styrylBodipy are linked by covalent bonding by click chemistry. The photophysical processes of the compounds were studied with steady state UV-vis absorption spectroscopy, fluorescence spectroscopy and nanosecond transient absorption spectroscopy.

Experimental Section

General Methods

UV-vis absorption spectra were taken on a HP8453 UV-vis spectrophotometer.

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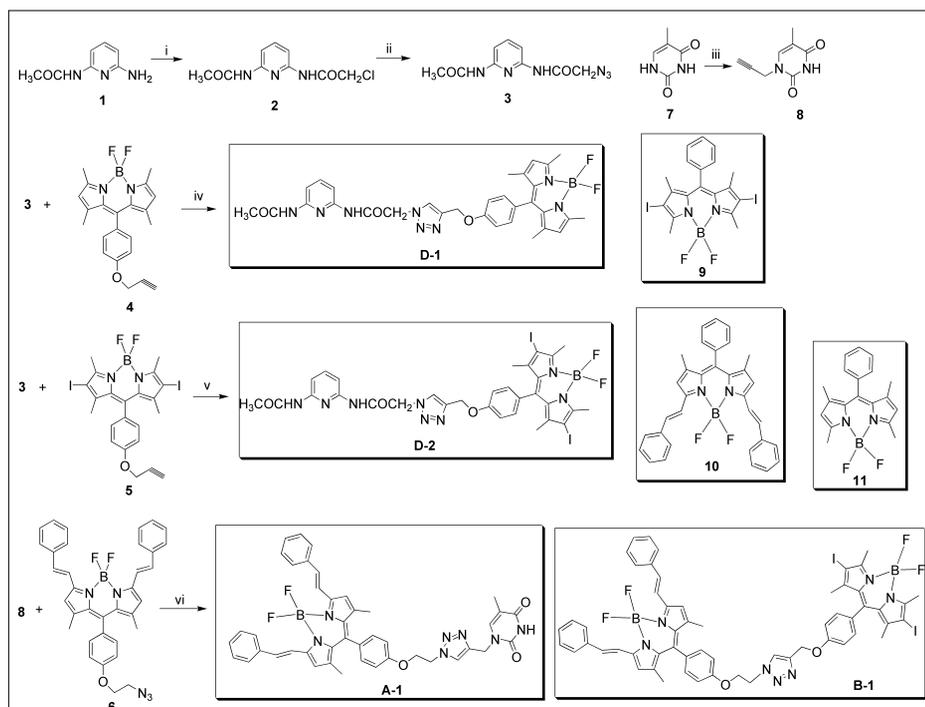
Scheme 1. Synthesis of the triplet photosensitizers **D-1**, **D-2**, **A-1**. (i) 2-Chloro-acetyl chloride, dry CH₂Cl₂, 25 °C, 2 h in Ar, 50%. (ii) NaN₃, DMF, 70 °C, 5 h, 80%. (iii) Propargyl bromide, K₂CO₃, DMF, rt, Ar, 10 h, 80%. (iv) Sodium ascorbate, CuSO₄, rt, Ar, 24 h, 55%. (v) Sodium ascorbate, CuSO₄, rt, Ar, 24 h, 50%. (vi) Sodium ascorbate, CuSO₄, rt, Ar, 24 h, 60%.

Fluorescence spectra were recorded on Shimadzu RF-5301PC spectrofluorometer. Luminescence lifetimes were measured on a OB920 fluorescence/ phosphorescence lifetime instrument (Edinburgh instruments, U.K.).

Synthesis and Characterization

Synthesis of Compound **D-1**

Under N_2 atmosphere, compound **3** (20 mg, 0.08 mmol) and **4** (50 mg, 0.08 mmol) were dissolved in CHCl₃/EtOH/H₂O (23 mL, 10:0.8:0.8, v/v), then the mixture was stirred at room temperature (RT). One drop of Et₃N was added and the mixture was stirred for 5 min. Then sodium ascorbate (10 mg, 0.048 mmol) and CuSO₄·5H₂O (6 mg, 0.024 mmol) were added. The mixture was stirred at RT for 24 h. Then water was added, and the mixture was extracted with DCM. The organic layers were combined and washed with saturated sodium chloride solution, and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure. The crude product was purified using column chromatography (silica gel, dichloromethane) to give a orange solid. Yield: 28 mg (55%). ¹H NMR (400 MHz, DMSO-D₆): δ = 10.61 (s, 1H), 10.15 (s, 1H), 8.30 (s, 1H), 7.77–7.73 (m, 3H), 7.31–7.23 (m, 4H), 6.17 (s, 2H), 5.49 (s, 2H), 5.25 (s, 2H), 2.45 (s, 6H), 2.12 (s, 3H), 1.41 (s, 6H). ESI-HRMS (C₃₁H₃₁BF₂N₈O₃ + Na⁺): calcd. *m/z* = 635.2478; found *m/z* = 635.2463.

Synthesis of Compound **D-2**

Under N_2 atmosphere, compound **3** (20 mg, 0.08 mmol) and **5** (mg, 0.08 mmol) were dissolved in CHCl₃/EtOH/H₂O (23 mL, 10:0.8:0.8, v/v), then the mixture was stirred at room temperature (RT). One drop of Et₃N was added and the mixture was stirred for 5 min. Then sodium ascorbate (10 mg, 0.048 mmol) and CuSO₄·5H₂O (6 mg, 0.024 mmol) were added. The mixture was stirred at RT for 24 h. Then water was added, and the mixture was extracted with DCM. The organic layers were combined and washed with saturated sodium chloride solution, and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure. The crude product was purified using column chromatography (silica gel, dichloromethane) to give a red solid. Yield: 24 mg (50%). ¹H NMR (400 MHz, DMSO-D₆): δ = 10.61 (s, 1H), 10.15 (s, 1H), 8.31 (s, 1H), 7.77–7.74 (m, 3H), 7.34–7.25 (m, 4H), 5.49 (s, 2H), 5.27 (s, 2H), 2.54 (s, 6H), 2.12 (s, 3H), 1.41 (s, 6H). MALDI-HRMS (C₃₁H₂₉BF₂N₈O₃I₂): calcd. *m/z* = 864.0513; found *m/z* = 864.0555.

Synthesis of Compound **A-1**

Under N_2 atmosphere, compound **8** (11 mg, 0.07 mmol) and **6** (40 mg, 0.07 mmol) were dissolved in CHCl₃/EtOH/H₂O (23 mL, 10:0.8:0.8, v/v), then the mixture was stirred at room temperature (RT). One drop of Et₃N was added and the mixture was stirred for 5 min. Then sodium ascorbate (10 mg, 0.048 mmol) and CuSO₄·5H₂O

(6 mg, 0.024 mmol) were added. The mixture was stirred at RT for 24 h. Then water was added, and the mixture was extracted with DCM. The organic layers were combined and washed with saturated sodium chloride solution, and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure. The crude product was purified using column chromatography (silica gel, dichloromethane) to give a dark solid. Yield: 30 mg (60%). ¹H NMR (400 MHz, CDCl₃): δ = 8.73 (s, 1H), 7.95 (s, 1H), 7.76 (d, 2H, *J* = 16.0 Hz), 7.65 (d, 4H, *J* = 8.0 Hz), 7.42–7.26 (m, 11H), 7.02 (d, 2H, *J* = 8.0 Hz), 6.64 (s, 2H), 4.96 (s, 2H), 4.80 (s, 2H), 4.43–4.40 (m, 2H), 1.88 (s, 3H), 1.46 (s, 6H). MALDI-HRMS (C₄₃H₃₈BF₂N₇O₃): calcd. *m/z* = 749.3097; found *m/z* = 749.3120.
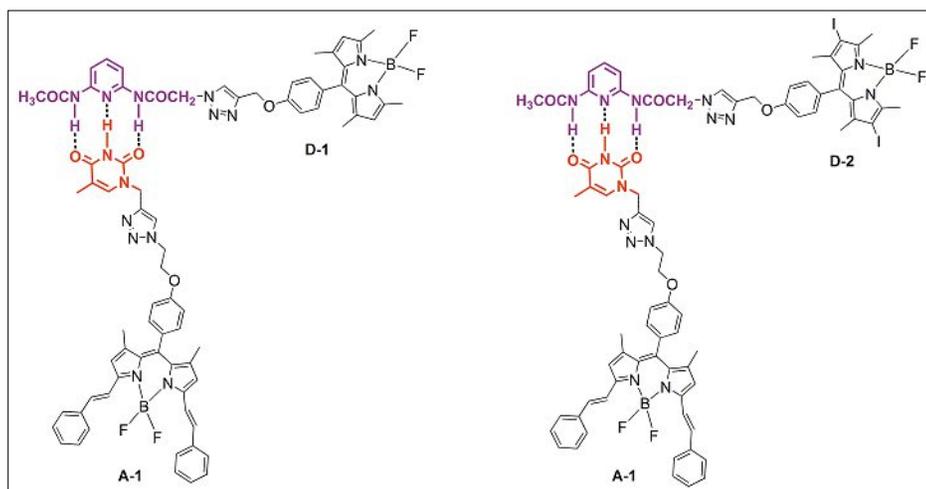
Nanosecond Transient Absorption Spectroscopy

Nanosecond time-resolved transient difference absorption spectra were recorded on a LP920 laser flash photolysis spectrometer (Edinburgh Instruments, UK). The solutions were purged with N_2 or argon for 30 min before measurement. The samples were excited with a nanosecond pulsed laser (OPOLette 355II, wavelength tunable in the range of 410–2400 nm), and the transient signals were recorded on a Tektronix TDS 3012B oscilloscope.

Results and Discussions

Molecular Design

The hydrogen bonding system is established based on the *N*-acetyl-2,6-diaminopyridine-thymine structure.[35] Bodipy is selected as the basic unit for its good photophysical properties and ease of functionalization.[42–49] DiiodoBodipy is used as a triplet energy donor while styrylBodipy is used as a triplet energy acceptor. To add hydrogen bonding capacity, 2,6-diiodoBodipy is functionalized with *N*-acetyl-2,6-diaminopyridine (**D-2**) and styrylBodipy is connected to thymine (**A-1**) (Scheme 2). The non-iodization Bodipy part connected to *N*-acetyl-2,6-diaminopyridine unit (**D-1**) is prepared for comparison, which has no intersystem crossing (ISC) ability, thus the hydrogen bonded pairs **D-1/A-1** and **D-2/A-1** are prepared.

The 2,6-diiodoBodipy and the styrylBodipy parts are also connected by a Cu(I) catalyzed click reaction to give the dyad **B-1**, thus the intramolecular TTET can be investigated. Moreover, 2,6-diiodoBodipy (**9**) and styrylBodipy (**10**) can be mechanically mixed to study the intermolecular TTET. The preparation of the compounds is based on the routine methods developed for the Bodipy chromophore (Scheme 1).

Scheme 2. Structure of the hydrogen-bonding assemblies (**D-1/A-1** and **D-2/A-1**).

formation of hydrogen bonds. **D-2** alone shows fluorescence at 554 nm. Upon addition of **A-1**, the fluorescence intensity of **D-2** quenched significantly, and a new band appeared at 660 nm, which is ascribed to the fluorescence of **A-1** (Fig. 2b). When 10 equiv. of **A-1** is added, the fluorescence intensity of **D-2** is reduced by 80% and reaches saturation (Fig. 2c). Given that **D-2** and **A-1** interact by H-bonds, the distance between the **D-2** and **A-1** is reduced, thus singlet energy transfer from **D-2** to **A-1** is established. As a result, the fluorescence of **D-2** is quenched and a new fluorescence band of **A-1** appears. Similar results are found for the pair **D-1/A-1** (Fig. 2a).

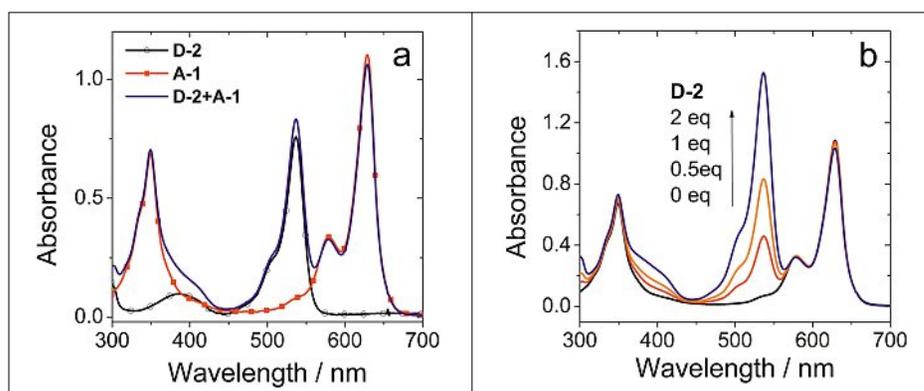In order to further confirm the formation of hydrogen bonds between donors

UV-vis Absorption and Photoluminescence Spectroscopy

All compounds are obtained with moderate to satisfactory yields.

The UV-vis absorption spectroscopy of the hydrogen bonding system was studied in solution (Fig. 1 and Table 1). The absorption of energy donor **D-2** gives intense absorption at 537 nm, while the absorption of energy acceptor **A-1** is located at 629 nm. The UV-vis absorption of the pair **D-2/A-1** is the sum of **D-2** and **A-1** (Fig. 1a), which indicates that, in the hydrogen bonding system, there is no significant interaction between the two moieties in the ground state.[50] This conclusion was also supported by a absorption spectral titration experiment (Fig. 1b). Similar results were observed for the pair **D-1/A-1** (Supplementary Data, Fig. S7). It is noted that this hydrogen bonding system is a broadband visible light-absorption system (two major bands at 537 nm and 629 nm in the visible region), which is very different from the Bodipy-C$_{60}$ hydrogen bonding system previously studied (only one major band in the visible region).[35]

The fluorescence titration experiments have also been conducted to verify the

Fig. 1. UV–vis absorption spectra of (a) **D-2**, **A-1** and the mix **D-2/A-1** (1/1); (b) **A-1** solution with increasing amount of **D-2**. *c* = 1.0 × 10⁻⁵ M in toluene, 20 °C.

Table 1. Photophysical parameters of the compounds

	λ_{abs}/nm[a]	ε[b]	λ_{em}/nm[c]	τ_F/ns[d]
D-1	503	0.87	517	3.7
D-2	537	0.75	554	0.2
A-1	630	1.10	642	5.0
9	538	0.92	556	0.2
10	628	1.18	641	4.9
11	503	0.88	515	3.4

[a]Maximal UV/vis absorption wavelength in toluene (1.0 × 10⁻⁵ M). [b]Molar absorption coefficient at absorption maxima. ε: 10⁵ M⁻¹ cm⁻¹. [c]Maximal emission wavelength in toluene (1.0 × 10⁻⁵ M). [d]The fluorescence life time, in toluene (1.0 × 10⁻⁵ M).
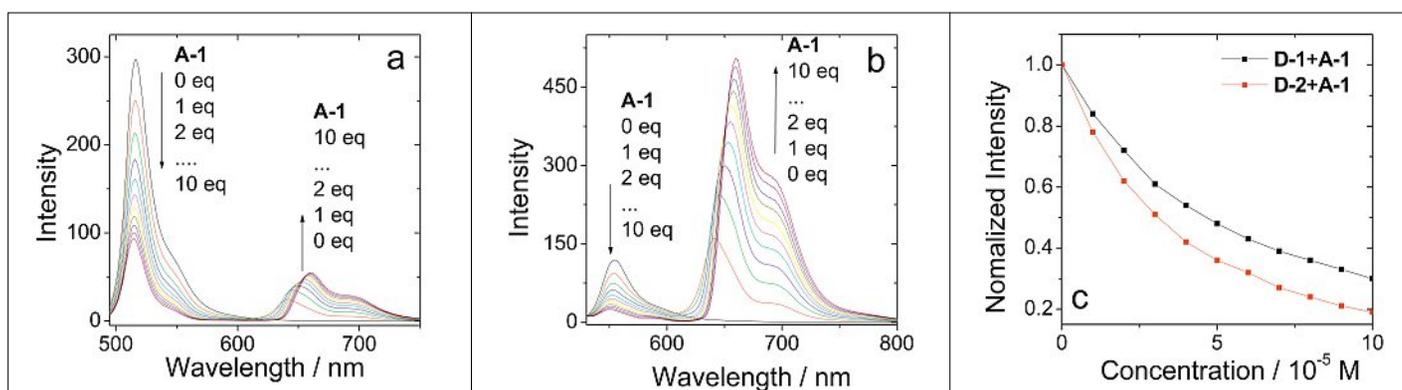

Fig. 2. Fluorescence of (a) **D-1**(λ_{ex} = 485 nm) and (b) **D-2**(λ_{ex} = 505 nm) solution (1.0 × 10⁻⁵ M) in toluene quenched by **A-1** solution in toluene. (c) Emission intensity of **D-1** at 516 nm (*c* = 1.0 × 10⁻⁵ M in toluene) and **D-2** at 554 nm (*c* = 1.0 × 10⁻⁵ M in toluene), versus increasing concentration of **A-1** following excitation at 485 nm and 505 nm, respectively.

and acceptors, fluorescence recovery experiments were carried out using hexafluoroisopropanol (HFIP), a compound that can destroy the hydrogen-bonded network between **D-1/A-1** and **D-2/A-1**. For the pair **D-2** and **A-1**, the fluorescence is recovered upon addition of HFIP (Fig. 3a), while for the control pair **9** and **10**, no significant change is observed (Fig. 3b). The recovery experiments demonstrate that hydrogen bonds are formed in the **D-2/A-1** pair. Similar observations are made for the **D-1/A-1** pair in the presence of HFIP (Supplementary Data, Fig. S8).

The fluorescence lifetime of the energy donors (**D-1** and **D-2**) was measured upon addition of the energy acceptor (**A-1**). The fluorescence lifetime is nearly constant (3.5 ns – 3.6 ns for **D-1** and 0.19 ns – 0.2 ns for **D-2**) and not related to the concentration of **A-1** (Table 2). These results suggest that the fluorescence quenching may be a static, rather than a dynamic quenching mechanism.[51]

Nanosecond Transient Absorption Spectroscopy

Nanosecond time-resolved transient absorption spectra of the hydrogen bonding assemblies were investigated, thus the formation of the hydrogen bond between **D-2/A-1** was further confirmed and the triplet-triplet energy transfer (TTET) of intramolecular/hydrogen bonding/intermolecular systems were compared (Fig. 4).

The TTET in the dyad **B-1** was first studied. DiiodoBodipy (compound **9**) alone gives a characteristic band at 538 nm (Fig. 4a), the triplet state lifetime is 132.8 µs (Fig. 4b), while styrylBodipy (compound **10**) alone is short of ISC ability.[52] For dyad **B-1**, where compounds **9** and **10** are linked by a covalent bond, a bleaching band at 623 nm is observed upon selective photoexcitation through the iodoBodipy unit (Fig. 4c). The triplet state lifetime is 385.0 µs (Fig. 4d). The bleaching band and the long triplet state lifetime are in accordance with our previous study,[52] thus we can conclude that the triplet state is located at the styrylBodipy unit. It is noted that no bleaching band at 530 nm is observed, which indicates a high efficiency of the intramolecular triplet state energy transfer.

Intermolecular triplet state energy transfer between compounds **9** and **10** was investigated for comparison (Figs 5a and 5b). Upon 536 nm pulsed laser photoexcitation, different from dyad **B-1**, the mixture of compounds **9** and **10** gives two major bleaching bands at 538 nm and 623 nm, which are ascribed to the diiodoBodipy unit and styrylBodipy unit, respectively. This phenomenon is rationalized in terms of a longer distance between the triplet energy donor and triplet energy acceptor
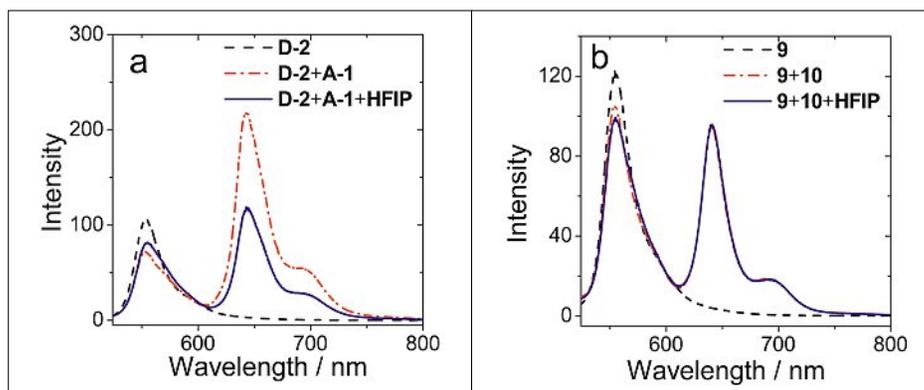

Fig. 3. Fluorescence of (a) **D-2**, **D-2** + **A-1**, **D-2** + **A-1** + 100 µL HFIP (λ_{ex} = 514 nm), (b) **9**, **9** + **10**, **9** + **10** + 100 µL HFIP (λ_{ex} = 514 nm), in toluene at 20 °C.

Table 2. Luminescence lifetimes of **D-1** and **D-2** with addition of different amounts of **A-1** (ns)[a]

	0 M **A-1**	1.0×10^{-5} M **A-1**	1.5×10^{-5} M **A-1**	2.0×10^{-5} M **A-1**
D-1	3.69	3.61	3.55	3.54
D-2	0.19	0.20	0.20	0.25

[a]c = 1.0×10^{-5} M with different amounts of **A-1** at 20 °C. λ_{ex} = 470 nm.
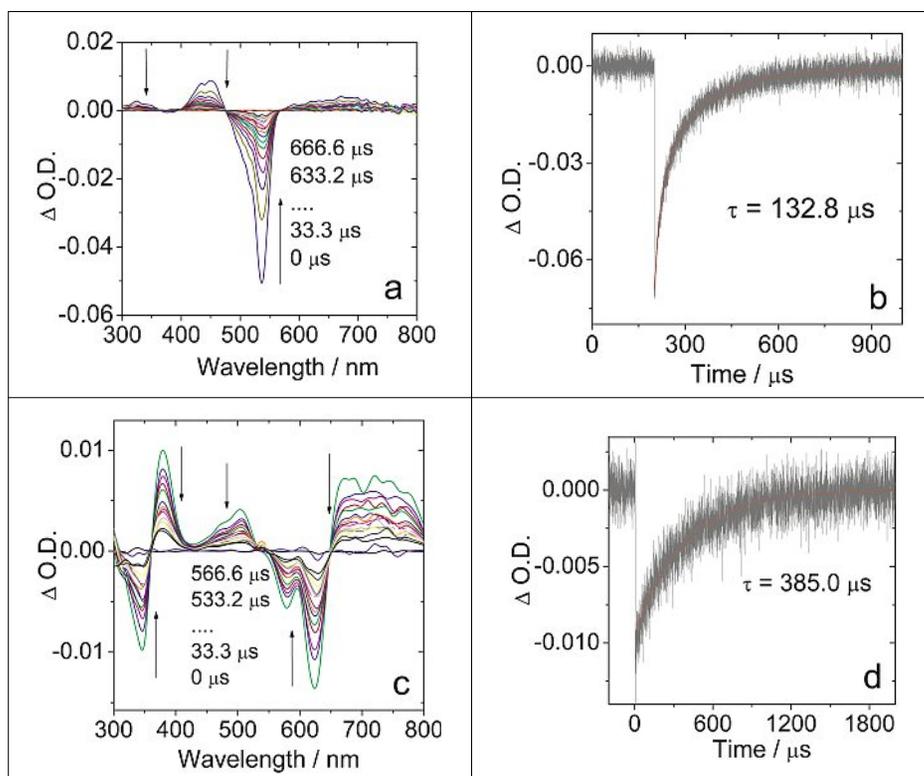

Fig. 4. Nanosecond time-resolved transient absorption spectra of **B-1** and compound **9**. (a) **9** upon pulsed laser excitation (λ_{ex} = 536 nm) and (b) decay trace of **9** at 530 nm; (c) **B-1** upon pulsed laser excitation (λ_{ex} = 536 nm) and (d) decay trace of **B-1** at 630 nm. c = 1.0×10^{-5} M in toluene, 20 °C.

units in the mixture, which overall leads to lower intermolecular triplet state energy transfer efficiency. As to the mixture of **D-2** and **A-1**, the relative population of the triplet excited states localized on the energy donor and acceptor sites, obtained from the optical density (OD) value at the bleaching band, appears to be smaller than that of the **9** and **10** mixture (Fig. 5c), which suggests a more efficient TTET for the hydrogen

bonding system over the intermolecular system. If the upside of the decay trace at 630 nm is approximately regarded as the triplet energy transfer process, we can conclude that the mixture of **D-2** and **A-1** experienced a faster triplet energy transfer than the **9** and **10** mixture (11.3 µs for the mixture of **D-2** and **A-1**, and 15.2 µs for the mixture of **9** and **10**). However, when hexafluoroisopropanol (HFIP) is added to

the mixture of **D-2** and **A-1**, the ratio of the donor triplet and the acceptor triplet increases, and the process of triplet energy transfer becomes slower (15.3 μs, the value is exactly the same with 15.2 μs for the mixture of **9** and **10**). All these results illustrate the hydrogen bonding assembly between **D-2** and **A-1**.

Compared with the Bodipy–C_{60} hydrogen bonding system that we previously studied,[35] the diiodoBodipy–styrylBodipy hydrogen bonding system shows different properties. The biphasic decay trace is obvious in our diiodoBodipy–styrylBodipy hydrogen bonding system, while the increasing phase cannot be observed in the Bodipy–C_{60} system. This may be due to the lower efficiency of the hydrogen bond formation for diiodoBodipy–styrylBodipy system than the Bodipy–C_{60} system, or the slower TTET for diiodoBodipy–styrylBodipy hydrogen bonding system as compared to the Bodipy–C_{60} hydrogen bonding system.

The intramolecular/hydrogen bond/intermolecular triplet energy transfer was also compared quantitatively (Table 3). For the mixture of **9** and **10**, which stands for intermolecular triplet energy transfer, the ratio of OD value at 530 nm to 630 nm is 1.66. While for the mixture of **D-2** and **A-1**, the ratio becomes much smaller (1.15), indicating a higher triplet energy

transfer efficiency for the hydrogen bonding assembly. However, when HFIP is added to destroy the hydrogen bonded system, the ratio of OD value at 530 nm to 630 nm is recovered and reached a value of 1.86, similar to the value observed for the intermolecular triplet energy transfer between **9** and **10**.

The TTET rate constants and the TTET efficiency were calculated based on Eqns (1) and (2).[53] The TTET rate constants for the pair **9** and **10** is 6.0×10^4 s^{-1}, and the TTET efficiency is calculated at 90.9%. While the value for the pair **D-2** and **A-1** is 6.9×10^4 s^{-1} and 94.0%, respectively. Upon addition of HFIP to the mixture **D-2** and **A-1**, these values decrease to 4.7×10^4 s^{-1} and 91.4% (Table 3).

$$k_{ET} = (1/\tau_2) - (1/\tau_1) \qquad (1)$$

$$\Phi_{ET} = 1 - \tau_2/\tau_1 \qquad (2)$$

Where τ_1 is the triplet state lifetime of the triplet energy donor in the absence of energy acceptor; τ_2 is the triplet state lifetime of the triplet energy donor in the presence of energy acceptor.

However, either for the pair **9** and **10** (intermolecular triplet energy transfer), or the pair **D-2** and **A-1** (hydrogen bond triplet energy transfer), the triplet energy

Table 3. Kinetics of the triplet state energy transfer[a]

Mixture components[b]	$\tau_{530\ nm}$[c] / μs	$\tau_{630\ nm}$[d] / μs	$\tau_{630\ nm}$[e] / μs	k_{TT} / s^{-1}	Φ_{TT}
9+10	15.3	15.2	167.7	6.0×10^4	90.9%
D-2+A-1	13.7	11.3	173.0	6.9×10^4	94.0%
D-2+A-1+HFIP	19.6	15.3	194.5	4.7×10^4	91.4%

[a]Determined with nanosecond time-resolved transient difference absorption spectroscopy.
[b]The mole ratio of **9**:**10** and D-2:A-1 are both 1:1.66 in toluene. The amount of HFIP is 100 μL.
[c]Lifetime monitored at 530 nm. Upon pulsed excitation at 536 nm. [d]The lifetime for the first phase of the trace at 630 nm. [e]The lifetime for the second phase of the trace at 630 nm.
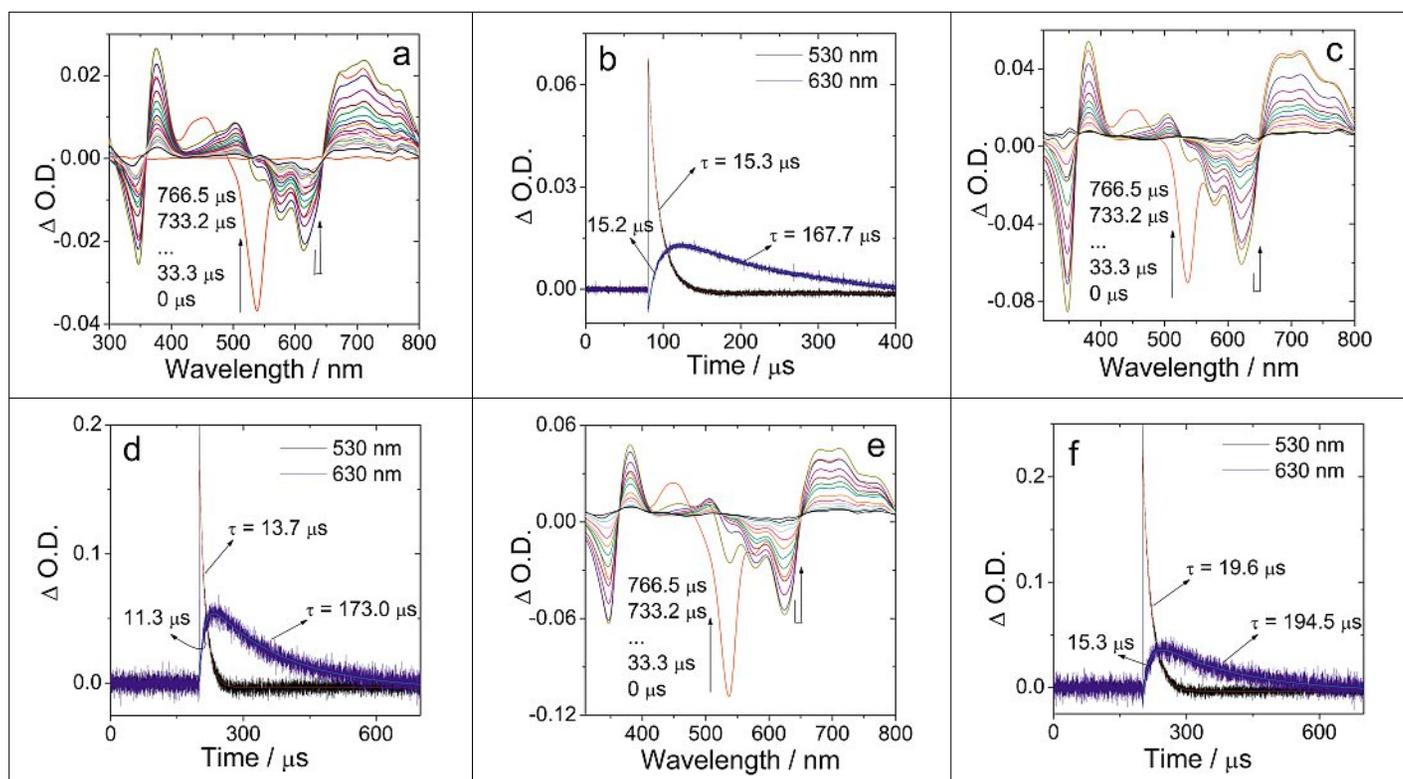

Fig. 5. Nanosecond time-resolved transient absorption spectra. (a) mixture of **9** ($c = 1.0 \times 10^{-5}$ M) and **10** ($c = 1.66 \times 10^{-5}$ M) upon pulsed laser excitation (λ_{ex} = 536 nm) and (b) decay trace of the mixture of **9** ($c = 1.0 \times 10^{-5}$ M) and **10** ($c = 1.66 \times 10^{-5}$ M) at 530 nm and 630 nm; (c) mixture of **D-2** ($c = 1.0 \times 10^{-5}$ M) and **A-1** ($c = 1.66 \times 10^{-5}$ M) upon pulsed laser excitation (λ_{ex} = 536 nm) and (d) decay trace of the mixture of **D-2** ($c = 1.0 \times 10^{-5}$ M) and **A-1** ($c = 1.66 \times 10^{-5}$ M) at 530 nm and 630 nm; (e) mixture of **D-2** ($c = 1.0 \times 10^{-5}$ M) and **A-1** ($c = 1.66 \times 10^{-5}$ M) and HFIP upon pulsed laser excitation (λ_{ex} = 536 nm) and (f) decay trace of the mixture of **D-2** ($c = 1.0 \times 10^{-5}$ M) and **A-1** ($c = 1.66 \times 10^{-5}$ M) and HFIP at 530 nm and 630 nm.

transfer is incomplete, as compared to **B-1** (*intramolecular* triplet energy transfer). For **B-1**, no diiodoBodipy (triplet energy donor) bleaching band was observed.

Above all, the intermolecular/hydrogen bond/intramolecular triplet energy transfer was compared, which was rarely investigated previously. The intramolecular triplet energy transfer has the highest efficiency, while the intermolecular triplet energy transfer efficiency remains low. The triplet energy transfer efficiency of the hydrogen bonded system is midway between the two.

Conclusions

In summary, a 2,6-diiodoBodipy–styrylBodipy hydrogen bonding system with broadband visible light-harvest ability was designed (**D-2** and **A-1**). 2,6-DiiodoBodipy unit was used as a triplet energy donor and the styrylBodipy as a triplet energy acceptor, thus TTET process was established. Hydrogen bond formation was proved with steady state UV-vis absorption and fluorescence quenching spectra, as well as nanosecond transient absorption spectroscopy. The effect of hydrogen bond on TTET was investigated with nanosecond transient absorption spectroscopies. Intramolecular, hydrogen bonding assembly, and intermolecular triplet energy transfer were compared. The intramolecular triplet energy transfer is the fastest ($k_{TTET} > 10^8$ s^{-1}) and most efficient. The intermolecular triplet energy transfer is the slowest and the least efficient (Φ_{TTET} = 90.9%, k_{TTET} = 6.0 × 10^4 s^{-1}), while the TTET process of the hydrogen bonding system is between the two (Φ_{TTET} = 94.0%, k_{TTET} = 6.9 × 10^4 s^{-1}). These studies will be useful for designing supramolecular triplet photosensitizers, as well as for a deeper understanding of the TTET process of hydrogen bonding systems.

Supplementary Data

Molecular structure characterization and additional spectra are available free of charge as Supplementary Data and *via* the Internet at *http://dx.doi.org*.

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