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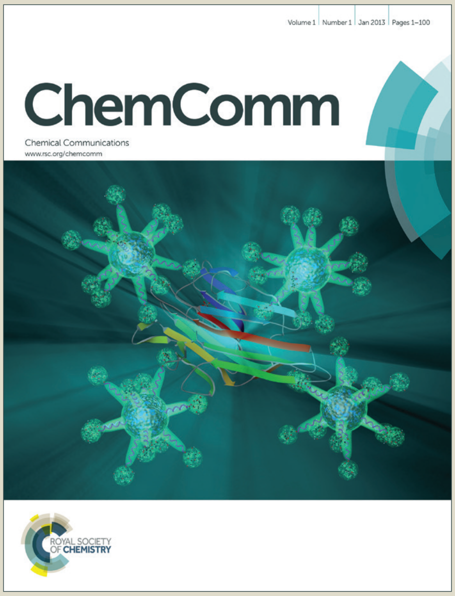

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COMMUNICATION

Photoswitching of triplet-triplet annihilation upconversion showing large emission shifts with photochromic fluorescent dithienylethene-Bodipy triad as triplet acceptor/emitter †

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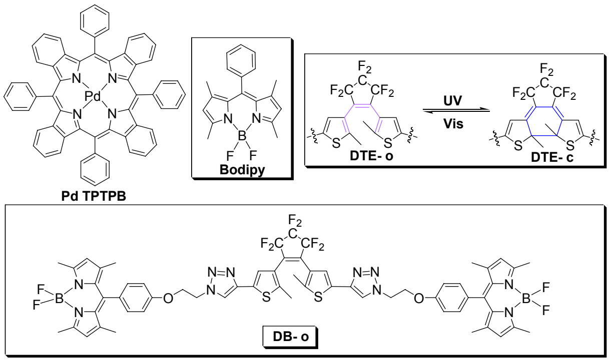
Photoswitchable fluorescent triad based on dithienylethene and Bodipy was used as triplet acceptor/emitter for reversible photoswitching of triplet-triplet-annihilation upconversion (with Pd(II) tetraphenyltetrabenzoporphyrin as triplet photosensitizer) which shows green/near IR emission changes with emission energy difference of 0.79 eV ($\Delta\lambda = 268$ nm).

Triplet-triplet-annihilation (TTA) upconversion has attracted much attention, due to the advantages of low-photoexcitation power density requirement (solar light is sufficient), strong absorption of visible light, and high upconversion quantum yields (up to 20–30%).[1–5] TTA upconversion has been widely used in luminescent bioimaging,[6] photovoltaics,[7,8] and photocatalysis.[9] External-stimuli responsive luminescent molecules will offer additional moduality and application dimensions for the luminescent materials, such as molecular probes,[10a-d] activatable photodynamic therophy,[10e] or the super-resolution fluorescence microscopy.[11] Concerning this aspect, external-stimuli responsive, such as photoswitching of TTA upconversion is in particular interest but it was rarely studied. Previously we achived photoswitching of TTA upconversion with a mechanical mixture approach with triplet photosensitizer, triplet acceptor/emitter and a photochromic compound dithienylethene (DTE).[12] The energy difference of the switched emission is 0.55 eV. The contrast of the color change is not significant (green/blue. $\Delta\lambda$ = 110 nm).[12] Photochromic triplet photosensitizer was also used for photoswitching of TTA upconversion, but the system is with similar emission wavelength variation ($\Delta\lambda$ = 110 nm).[13]

In order to address the above challenges, such as to achive distinctive emission color changes and large $\Delta\lambda$ values, herein we used a DTE-Bodipy triad (**DB**, Scheme 1) as the photoswitchable triplet acceptor/emitter for photoswitching of TTA upconversion. The fluorescence of the Bodipy moieties in the triad **DB** is in ON state with the DTE moiety in the opened form (DTE-o), but the fluorescence is able to be quenched with the DTE in the closed form (DTE-c).[13] It is known that the photocyclization/ photoreversion of DTE-o and DTE-c show good fatigue-resistance, distinctively different absorption feature and excited state energy levels.[14–18] The photocyclization/ photoreversion is reversibly controllable with alternative UV and visible light irradiation.[19] Pd(II) tetraphenyltetrabenzoporphyrin (**PdTPTBP**) was used as triplet photosensitizer, which is excitable with red light (635 nm).[20a] Heavy atom effect is essential for this complex to produce triplet state upon photoexcitation.[20b,c] Thus photoswitching of TTA upconversion with photo-responsive triplet acceptor/emitter were achieved. The corresponding emission wavelength variation of the system is distinctively different ($\Delta\lambda$ = 268 nm).

Previously it was reported that **PdTPTBP**/Bodipy TTA upconversion system gives a large anti-Stokes shift.[20a] Moreover, it was found that the fluorescence of Bodipy is able to be efficiently switched by DTE.[21] Thus we prepared a DTE-Bodipy triad as the photoswitchable triplet acceptor/emitter (**DB-o**, Scheme 1).[13] Flexible linker is used for connection of the DTE and the Bodipy moieties in the triad to ensure fast intramolecular singlet/triplet energy transfer, which is essential for the efficient quenching of the fluorescence of Bodipy part.



Scheme 1. Triad **DB-o** based on dithienylethene (DTE) and Bodipy was used as triplet acceptor/emitter in the photoswitching of TTA upconversion. The photochromism of **DB-o** is illustrated with DTE-o and DTE-c. **PdTPTPB** is the triplet photosensitizer, Bodipy, **DB-o** and **DB-c** are the triplet energy acceptor/emitter of the TTA upconversion.

Firstly the photoswitching of the UV/Vis absorption of triad was studied (Fig. 1).[13] **DB-o** shows strong absorption at 504 nm, which is assigned to the Bodipy moiety in **DB-o**. DTE-o moiety does not give absorption band in visible spectral region. Upon UV light irradiation (λ = 254 nm), a new absorption band at 580 nm developed (Fig. 1a), which is attributed to the product of photocyclization, i.e. DTE in closed form.[14,22,23] Since the absorption wavelength of the DTE-c moiety overlaps with the fluorescence emission of the Bodipy moiety, thus fluorescence-resonance-energy-transfer (FRET) is ensured, with Bodipy part as the energy donor and the DTE-c moiety as the energy acceptor (quencher).[24,25] Note the weak absorption band of **DB-c** does not necessarily mean inefficient energy transfer.

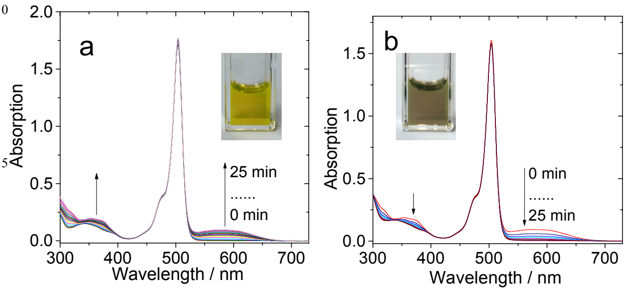


Fig. 1 The UV/Vis absorption changes of **DB-o/c** upon alternative UV/visible light irradiation. (a) Upon photoirradiation by UV light at 254 nm (1.0 mW/ cm^2); after establishment of the PSS, then (b) Upon photoirradiation by visible light at 635 nm (15.0 mW/ cm^2). Inset: the photographs of the solution at different photostationary states (c = 1.0 × 10^{-4} M in toluene). c = 1.0 × 10^{-5} M in toluene; 20 °C.

Ater establishment of the photostationary state (PSS) with 254 nm irradiation, the photoreversion upon 635 nm laser excitation was studied (Fig. 1b). Upon 635 nm irradiation, the absorption band at 580 nm was reduced gradually, indicated the reversible photocyclization/photoreversion processes.[14] Note the absorption band of the Bodipy moiety did not give any variation thus the photostablity of the photoswitchable fluorophore is satisfactory.

The kinetics of the photocyclization and photoreversion processes were studied (see ESI †, Fig. S1). It was found that significant photocyclcization was observed within 10 min and the photoreversion is finished within about 5 minutes. The quantum yield of the photocyclization ($\Phi_{o\to c}$) and the photoreversion processes ($\Phi_{c\to o}$) were determined as 32.0% and 3.2%,[13] respectively. The components of the opened and the closed form **DB** at the photostationary state (PSS, established upon 254 nm photoirradiation) is 92.7% and 7.3%, respectively.[13]

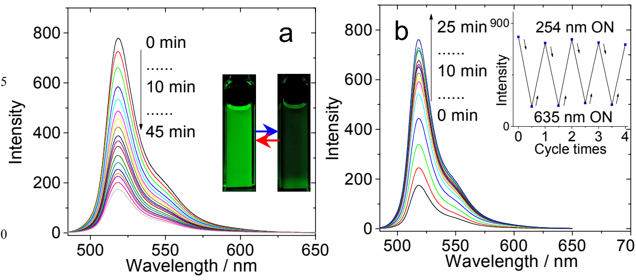


Fig. 2 The fluorescence emission changes of **DB-o/c** upon alternative UV/visible light photoirradiation. (a) The fluorescence emission was switched off by irradiation at 254 nm (1.0 mW/ cm^2); after establishment of the PSS, then (b) The recovery of the fluorescence emission upon visible light irradiation at 635 nm (15.0 mW/ cm^2). The inset in (a) shows the photographs of the emission changes of the solution upon photoswitching; the inset in (b) shows the reversibility of the fluorescence emission intensity during the photocyclization/ photoreversion. c = 1.0 × 10^{-5} M in toluene, 20 °C.

The photoswitching of the fluorescence of triad **DB** was studied (Fig. 2). For **DB-o**, strong green fluorescence was observed (Φ_F = 81.7%). Upon UV light irradiation at 254 nm, the fluorescence emission at 518 nm was decreased. At PSS, the emission intensity was reduced to 22.4% of the initial value (Φ_F = 18.3%). The residual fluorescence may be due to the presence of **DB-o** at PSS.[21] Detail elucidation of this residual emission can be achived by isolation of the closed and the open isomers.[17c] Upon 635 nm excitation, the fluorescence emission at 518 nm was fully recovered (Fig. 2b). No significant fluorescence lose was observed after four cycles of photocyclization/photoreversion (inset of Fig. 2b).

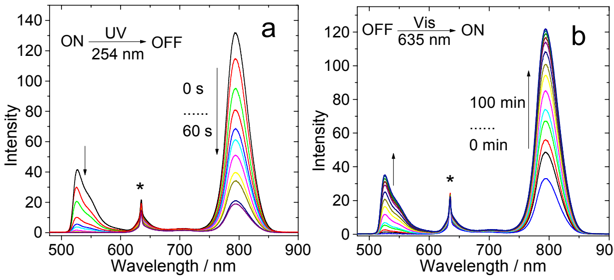


Fig. 3 Photoswitching of the TTA upconversion with **PdTPTBP** as triplet photosensitizer and **DB-o/c** as the photoswitchable triplet energy acceptor/emitter. (a) The upconversion intensity was switched OFF by UV light irradiation at 254 nm (1.0 mW/ cm^2); and then (b) the upconversion was recovered by irradiation at 635 nm (15.0 mW/ cm^2). Upconversion was performed upon excitation with a 635 nm continuous laser (power density is 15.0 mW/cm^2). c [**PdTPTBP**] = 1.0 × 10^{-5} M, c [Acceptor] = 2.0 × 10^{-4} M in toluene, 20 °C.

The fluorescence of the triad **DB** can be reversibly switched (Fig. 2), thus photoswitching of TTA upconversion with **PdTPTBP** as triplet photosensitizer and **DB** as triplet acceptor/emitter was envisaged.[12] With **DB-o**, strong TTA upconversion was observed (Fig. 3a). Note the phosphorescence of **PdTPTBP** is at 794 nm, and the upconverted emission is at 526 nm. Thus the energy difference of the switched emission bands is up to 0.79 eV ($\Delta\lambda$ = 268 nm). The TTA upconversion quantum yield was determined as 4.4%. Upon UV light photoirradiation (254 nm), the TTA upconversion intensity was reduced, as well as the phosphorescence of **PdTPTBP** (Fig. 3a). The quenching of the **PdTPTBP** phosphorescence indicates that an additional triplet quenching channel was activated upon UV irradiation of **DB-o**, thus we envisage that the photocyclization product, i.e. the **DTE-c** moiety, is responsible for the quenching of the **PdTPTBP** phosphorescence.[26] It was shown that the **DTE-c** moiety is with a very low T_1 state energy level.[26] At the photostationary state, the TTA upconversion was completely quenched (Fig. 3a). It should be pointed out that it is unnecessary for a complete photocyclization of all the **DB-o** molecules to **DB-c** to induce a significant quenching of the TTA upconversion.[27] Surpassing a threshold of quenching will eliminate the TTA upconversion completely.

Upon photoexcitation of the upconversion solution at 635 nm, the photoreversion **DB-c**→**DB-o** take places, correspondingly, recovery of the TTA upconversion was observed (Fig. 3b). At the same time, the phosphorescence of **PdTPTBP** recovered, indicating the triplet state quenching channel was inhibited with the photoreversion.[28] The photoswitching of the TTA upconversion is reversible (Fig. 4a). It should be pointed out that 635 nm irradiation of the upconversion mixture is able to facilitate the closed form→open form transformation of the DTE moiety, but this undesired side effect is minimized under our experimental conditions (see ESI †, Fig. S3. Note the $\Phi_{c\rightarrow o}$ quantum yield is low).

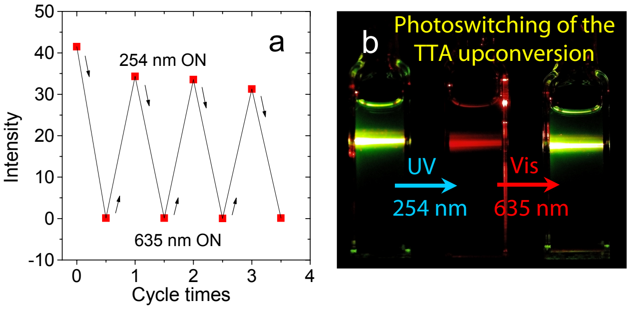


Fig. 4 (a) The reversibility of the photoswitching of TTA upconversion with **DB-o/c** as the photoswitchable triplet energy acceptor/emitter; (b) The photographs of the photoswitching of TTA upconversion. Upconversion was performed upon excitation with a 635 nm continuous laser (power density is 15.0 mW/cm^2). *c* [sensitizer] = 1.0 × 10^{-5} M and *c* [DB] = 2.0 × 10^{-4} M in toluene, 20 °C.

After three cycles of photoswitching of the TTA upconversion, no significant lose of the TTA upconversion was observed (Fig. 4a). Moreover, distinct color change of the photoswitching of TTA upconversion was observed (Fig. 4b). With the upconversion is in the ON state, green emission was observed upon 635 nm laser excitation (red laser). The CIE coordinates are (0.33, 0.65). Upon 254 nm photoirradiation, the TTA upconversion was switched off, the emission color of the solution turns from the green to red, the CIE coordinates are (0.71, 0.29). Then upon 635 nm photoirradiation again, thus the photoreversion of **DB-c** to **DB-o**, the TTA upconversion is switched ON again and the emission turns to green (Fig. 4b). Such a distinct luminescence wavelength variation ($\Delta\lambda = 268$ nm) is unprecedented and will be useful for applications in the area of luminescence bioimaging and super-resolution fluorescence microscopy.[11]

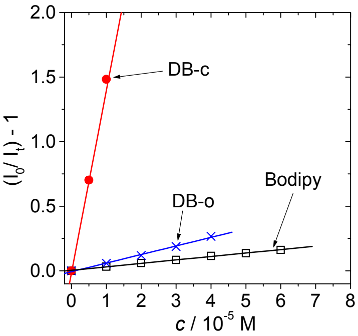


Fig. 5 Stern–Volmer plots generated from phosphorescence-quenching of **PdTPTBP** (λ_{ex} = 635 nm) with **DB-o**, **DB-c**, and **Bodipy** as quencher. More data points are available (see ESI †, Table S2). *c* [**PdTPTBP**] = 1.0 × 10^{-5} M in toluene, 20 °C.

In order to study the mechanism of photoswitching of the TTA upconversion with **DB** as photoswitchable triplet acceptor/emitter, quenching of the phosphorescence of **PdTPTBP** with **DB-o**, **DB-c** and the reference compound **Bodipy** as the triplet quencher were studied (Fig. 5). The results show that **DB-c** is more efficient to quench the phosphorescence (i.e. the triplet excited state) of **PdTPTBP** than **DB-o** and **Bodipy** does. In Fig. 2 we demonstrated that the fluorescence of the **Bodipy** moiety was quenched by the **DTE-c** part. Therefore, we propose that both the intermolecular triplet energy transfer from the **PdTPTBP** to **DB-c**, and the intramolecular quenching of the singlet excited state of the **Bodipy** units (fluorescence) are responsible for switching off the TTA upconversion (Fig. 3a).[12]

The parameters related to the photoswitching of the TTA upconversion were summarized in Table 1. It is shown the TTA upconversion quantum yield with **DB-o** is similar to that with **Bodipy**. In order to study the quenching efficiency of the triplet excited state of **PdTPTBP** with **DB-o** and **DB-c**, the Stern-Volmer quencing constants (K_{SV}), the bimolecular quenching constants (k_Q), the diffusion-controled bimolecular quenching constant (k_0) and the collision quenching efficiency (f_Q) were calculated (Table 1).[29]

Table 1. Upconversion-related photophysical parameters. **PdTPTBP** as the photosensitizer. [a]

	DB-o	**DB-c**	**Bodipy**
Φ_{UC} (%) [b]	4.4%	0.0%	4.6%
K_{SV}/M^{-1} [10^3] [c]	5.8	148	3.2
k_q/M^{-1} s^{-1} [10^7] [d]	2.6	66.2	1.4
k_0/M^{-1} s^{-1} [10^{10}] [e]	2.1	2.5	6.3
f_Q [f]	0.12%	2.70%	0.02%

[a] In deaerated toluene. [b] Upconversion quantum yields measured with **Pd TPTBP** as the standard (Φ_L = 16.7 % in toluene). [c] Stern–Volmer quenching constants. [d] Bimolecular quenching constants. $K_{SV} = k_q\tau_L$, τ_L = 223.7 μs. [e] Diffusion-controlled bimolecular quenching rating constants. [f] The quenching efficiency.

Based on the quenching of the phosphorescence of **PdTPTBP**, the K_{SV} value of **DB-c** is larger than that of **DB-o** and **Bodipy**, indicated that the quenching of the triplet excited state of **PdTPTBP** is significant with **DB-c** as the triplet energy acceptor (quencher). The bimolecular quenching constant (k_q) of **DB-c** is also much larger than the corresponding values with **DB-o** and **Bodipy**.

The diffusion-controlled bimolecular quenching rating constants (k_0) were calculated with the Smoluchowski equation (Eq. 1),[29]

$$k_0 = 4\pi RND/1000 = \frac{4\pi N}{1000}\left(R_f + R_q\right)\left(D_f + D_q\right) \qquad \textbf{(Eq. 1)}$$

D is the sum of the diffusion coefficients of the energy donor (D_f) and quencher (D_q), N is Avogadro's number. R is the collision radius, the sum of the molecule radii of the energy donor (R_f) and the quencher (R_q). Diffusion coefficients can be obtained from Stokes-Einstein equation:[29]

$$D = k\mathrm{T}/6\pi\eta R \qquad \textbf{(Eq. 2)}$$

k is Boltzmann's constant, η is the solvent viscosity, R is the molecule radius. **DB-o**, **DB-c** and **Bodipy** as triplet energy acceptor were calculated as 2.1×10^{10} M^{-1} s^{-1}, 2.5×10^{10} M^{-1} s^{-1} and 6.3×10^{10} M^{-1} s^{-1}, respectively. Thus the larger molecular size will reduce the k_0 value. However, the quenching efficiency (f_Q) of

DB-c is larger than that of **DB-o** and Bodipy, indicating that the large molecular size of a quencher does not necessarily reduce the quenching efficiency.

In summary, a Bodipy-dithienylethene (DTE) based triad was used as a photoswitchable triplet energy acceptor/emitter for photoswitching of triplet-triplet-annihilation (TTA) upconversion. With the DTE moiety in the open form (DTE-o), the fluorescence of the Bodipy moiety in the triad was not disturbed. Upon 254 nm photoirradiation, thus the photocyclization of the DTE moiety to the closed form (DTE-c), the fluorescence of the Bodipy moiety was quenched by fluorescence-resonance-energy-transfer (FRET). TTA upconversion was observed with Pd(II) tetraphenyltetrabenzoporphyrin as the triplet photosensitizer (excited at 635 nm, upconverted emission is at 526 nm) and the triad as triplet energy acceptor/emitter. Upon 254 nm irradiation of the upconversion system, the TTA upconversion was quenched. The emission of the solution turns to deep red/near IR (phosphorescence of PdTPTBP). The photoswitching of the TTA upconversion is reversible, and the switched emission energy difference is as large as 0.79 eV ($\Delta\lambda$ = 268 nm). Both the *intermolecular* quenching of the triplet excited state of the photosensitizer and the *intramolecular* quenching of the singlet state of the emitter (Bodipy unit) are responsible for the switching OFF of the TTA upconversion. This photoswitching TTA upconversion with distinct luminscence wavelength change may be beneficial for applications in switchable luminescence bioimaging and super-resolution fluorescence microscope.

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† Electronic Supplementary Information (ESI) available: molecular structural characterization and other information. See DOI: 10.1039/b000000x/

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