

# Reversible Photoswitching of Triplet–Triplet Annihilation Upconversion Using Dithienylethene Photochromic Switches

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**S** Supporting Information

**ABSTRACT:** Reversible photoswitched triplet–triplet annihilation upconversion (TTA UC) was demonstrated with dithienylethene (DTE) derivatives as the photochromic units, 2,6-diiodobodipy as the triplet photosensitizer, and perylene as the triplet acceptor/emitter. The TTA UC is undisturbed by the open-form DTE but can be switched OFF upon photoirradiation of the mixture of the three components at 254 nm, i.e., by the closed-form DTE. Subsequent visible light irradiation restores the TTA UC. By studying the competitive triplet-state energy-transfer processes with nanosecond time-resolved transient difference absorption and fluorescence spectroscopy, we confirmed that the quenching of the perylene triplet excited state by closed-form DTE is dominant among the four possible quenching processes.

Triplet–triplet annihilation upconversion (TTA UC) has attracted much attention due to its advantages of strong harvesting of the non-coherent and low-power-density excitation light, high UC quantum yield, and tunable excitation/emission wavelength.<sup>1–5</sup> To date, great efforts have been devoted to the preparation of new efficient triplet photosensitizers<sup>2,6,7</sup> or new triplet acceptors<sup>8,9</sup> and the study of the kinetics of the photophysical processes.<sup>10–12</sup> Applications of TTA UC in luminescence bioimaging and solar cells have also been studied.<sup>13–18</sup> However, an external stimuli-responsive or switched TTA UC protocol has never been reported, although this kind of controllable TTA UC would offer unprecedented spatial and temporal resolution, for example, in luminescence bioimaging.

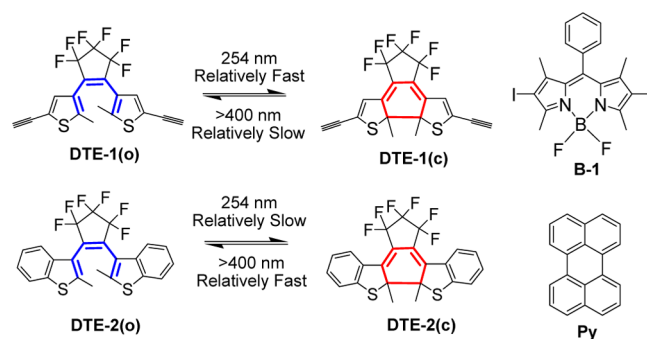
Herein for the first time we demonstrate that the TTA UC can be photoswitched. Dithienylethene (DTE) was selected as the photochromic unit due to its fatigue resistance, thermal stability of the two metastable states, and feasibly derivatizable molecular structures.<sup>19–23</sup> DTE has been used to switch the fluorescence or electron transfer of organic fluorophores<sup>24–28</sup> and the triplet excited state or nonlinear optical properties of Ru(II), Os(III), Pt(II), and Ir(III) complexes,<sup>29–31</sup> and recently to control the production of singlet oxygen (<sup>1</sup>O<sub>2</sub>) by a porphyrin complex.<sup>26</sup> However, it has never been used for photoswitching of UC. Here a new protocol of photoswitched TTA UC is devised with DTE as the photochromic unit, 2,6-diiodobodipy as the organic triplet photosensitizer, and perylene as the triplet acceptor/emitter.<sup>32</sup>

The rationale for the current photoswitchable TTA UC protocol is that the open-form DTE (DTE-(o)) gives a high T<sub>1</sub>-state energy level (ca. 1.97 eV);<sup>33</sup> thus, the triplet-state-related TTA UC photophysical processes will not be inhibited, because both B-1 and perylene show much lower T<sub>1</sub>-state energy levels (ca. 1.69 and 1.53 eV, respectively) than DTE-(o).<sup>1,34</sup> Upon UV irradiation, DTE-(o) will be reversibly transformed to the closed-ring form (DTE-(c)), which has a very low T<sub>1</sub>-state energy level (1.23 eV; see the Supporting Information (SI) for the time-dependent density functional theory calculations of T<sub>1</sub>-state energy levels).<sup>26</sup> As such, the triplet states involved in the TTA UC will be quenched by the DTE-(c), and TTA UC will be switched OFF. By visible light irradiation, DTE-(c) will be switched back to DTE-(o), and the TTA UC will be recovered. With nanosecond time-resolved spectroscopy, we confirmed that the singlet excited states of DTE played a negligible role in switching the TTA UC.

Two DTE units were investigated for photoswitching of TTA UC, i.e., DTE-1 and DTE-2 (Scheme 1). DTE-1 has ethynyl moieties; thus, further molecular derivatization is feasible.

First, the intrinsic photochromism of DTE-1 and DTE-2 was studied (Figure 1). The open forms of both compounds give absorption bands only in the UV region (259 and 257 nm, respectively). Upon photoirradiation with monochromic light

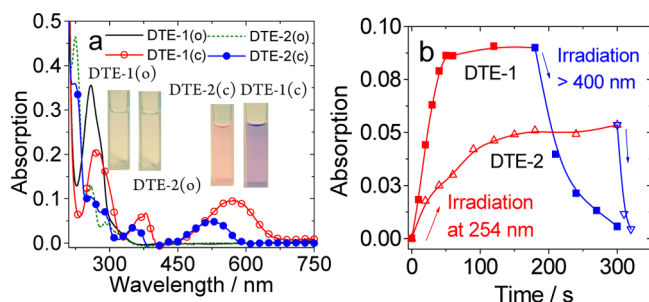
**Scheme 1. Dithienylethene Derivatives (DTE-1 and DTE-2) Used in the Photoswitching of TTA UC<sup>a</sup>**



<sup>a</sup>B-1 is the triplet photosensitizer, and perylene (Py) is the triplet energy acceptor and emitter of the TTA UC. DTE-1(c) and DTE-2(c) are triplet quenchers to photoswitch the TTA UC.

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**Figure 1.** (a) UV-vis absorption spectra of DTE-1, DTE-2, and the photostationary state produced with 254 nm irradiation ( $1.0 \times 10^{-5}$  M). Inset: Photographs of the solutions taken at  $5.0 \times 10^{-5}$  M. (b) Kinetics of photoconversion of DTE-1 (absorbance at 570 nm) and DTE-2 (absorbance at 525 nm) with 254 nm and visible light irradiation:  $[\text{DTE-1 or DTE-2}] = 1.0 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ , 20 °C.

at 254 nm (hand-held UV lamp), new absorption bands appeared at 570 and 525 nm, respectively. Correspondingly the solution turned from colorless to blue and pink. The process is reversible; that is, upon subsequent visible light irradiation (>400 nm), the open form was recovered.

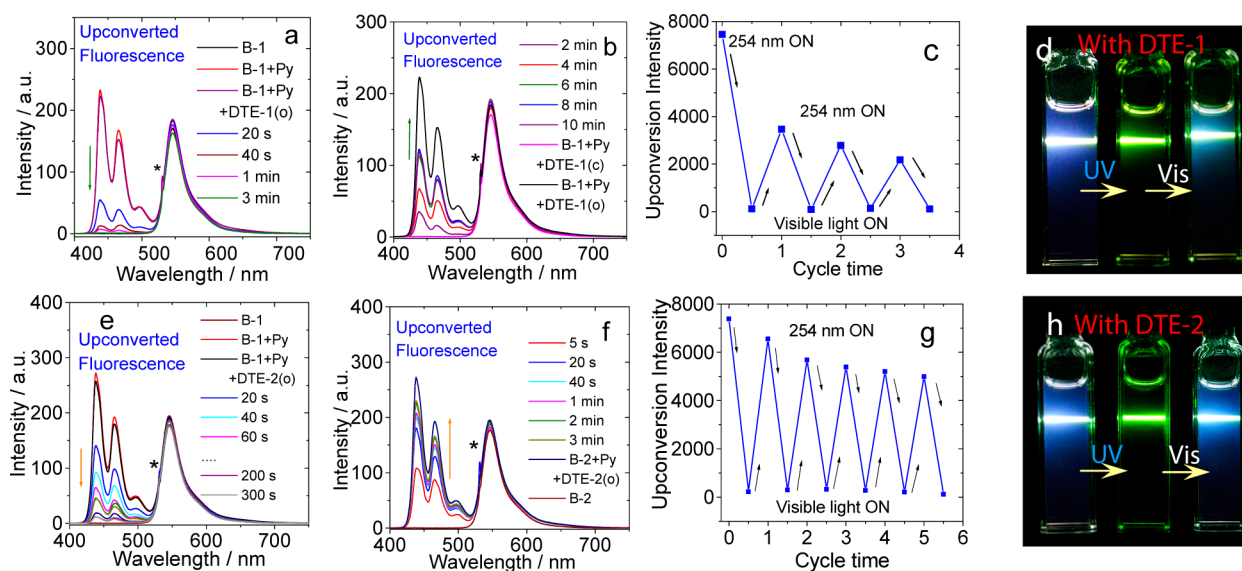
Interestingly, we found that the photochromism kinetics of the two compounds are complementary (Figure 1b). DTE-1 gives relatively faster photocyclization, DTE-1(o)  $\rightarrow$  DTE-1(c), as compared with that of DTE-2 (Figure 1b). However, DTE-1(c) gives relatively slower photoreversion kinetics, DTE-1(c)  $\rightarrow$  DTE-1(o), than DTE-2(c). The fast photocyclization of DTE-1 may be due to the antiparallel geometry of the molecules, indicated by the  $^1\text{H}$  NMR spectrum (SI, Figures S1 and S3).<sup>19,33</sup> These complementary photochromic kinetics may offer an additional dimension for the photoswitch concerning temporal and spatial resolution or contrast.<sup>35</sup> The open/closed ratios of the two isomers at the photostationary state (PSS) were determined with HPLC as 7:93 and 44:56 for DTE-1 and

DTE-2, respectively. These values are close to previously reported values obtained by  $^1\text{H}$  NMR (Figures S9 and S10).<sup>29b,c</sup> The quantum yields of the photochromism of DTE-1 and DTE-2 were measured with a chemical actinometer (SI). For DTE-1,  $\Phi_{\text{O} \rightarrow \text{C}} = 0.299$  and  $\Phi_{\text{C} \rightarrow \text{O}} = 0.045$ ; for DTE-2,  $\Phi_{\text{O} \rightarrow \text{C}} = 0.267$  and  $\Phi_{\text{C} \rightarrow \text{O}} = 0.223$ .

Next, the photoswitching of TTA UC was studied with the mixture of DTE-1 (or DTE-2), 2,6-diiodoBodipy, and perylene (Figure 2). In the presence of DTE-1 (o), the TTA UC of 2,6-diiodoBodipy/perylene was not inhibited (Figure 2a). Upon UV irradiation of the mixed solution at 254 nm, however, the TTA UC emission intensity decreased sharply, and the TTA UC was completely quenched after 3 min of 254 nm photoirradiation. The residual fluorescence of 2,6-diiodoBodipy was almost not decreased, indicating that the quenching is via the triplet-state manifold, not the singlet excited state of Bodipy. Subsequent visible light (>400 nm) photoirradiation will recover the TTA UC (Figure 2b). Similar photoswitching of the TTA UC was observed with DTE-2 (Figure 2e,f). The present photoswitching protocol may find applications with microcapsules (liquid core/solid shell).<sup>14</sup>

The reversibility of photoswitching was studied (Figure 2c,g). With DTE-1, substantial loss of UC intensity was observed for the first cycle (which may be attributed to the establishment of PSS, thus the persistent presence of the closed-form DTE); thereafter, the reversibility did not change significantly (Figure 2c). For DTE-2, no such loss of reversibility was found (Figure 2g). Considering that the photoswitch efficacy, that is, the UC emission contrast ratio between the ON and OFF states, is substantial—as high as 20–50—the minor loss of reversibility will not compromise any application of the current protocol.

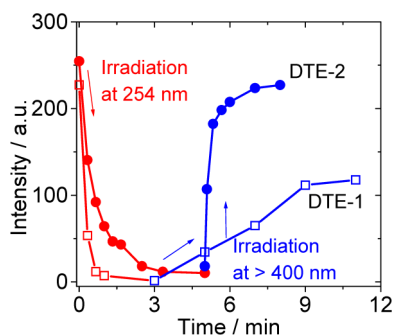
The reversible switching of TTA UC can be seen with unaided eyes (Figure 2d,h). Such highly visible reversible photoswitching TTA UC will be useful in many areas, such as luminescence bioimaging. Such a photoswitched TTA UC



**Figure 2.** Photoswitching of the TTA UC with B-1 as photosensitizer and perylene as acceptor by using (a–d) DTE-1 or (e–h) DTE-2 for the switch. (a,e) Upconversion was observed in the presence of open-form DTE-1 or DTE-2 and was switched off by irradiation of the mixture at 254 nm. (b,f) Upconversion was recovered by subsequent visible light irradiation at >400 nm. (c,g) The reversibility of the photoswitching of TTA UC with DTE-1 and DTE-2; (d,h) The photographs of the photoswitching of TTA UC. Upconversion was performed upon excitation with a 532 nm continuous laser (power density is  $24.5 \text{ mW cm}^{-2}$ ; asterisks in a, b, e, and f are the scattered laser):  $[\text{B-1}] = 1.0 \times 10^{-5}$  M,  $[\text{Py}] = 4.0 \times 10^{-5}$  M, and  $[\text{DTE-1 or DTE-2}] = 1.0 \times 10^{-5}$  M in deaerated  $\text{CH}_3\text{CN}$ , 20 °C.

will work well in microcapsules, etc.<sup>13</sup> UV irradiation may be a disadvantage, which can be overcome by using sensitized photochromism so that visible-light-induced photochromism of DTE can be performed.<sup>33</sup>

We found that the complementary photochromic kinetics of DTE-1 and DTE-2 was transduced to the photoswitching of the TTA UC (Figure 3). The switching OFF process of TTA

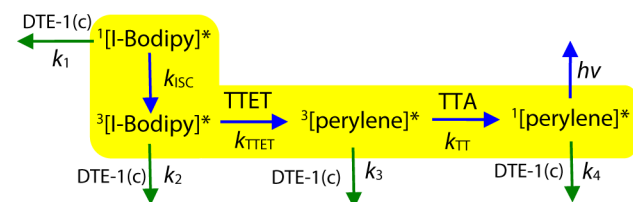


**Figure 3.** Kinetics of the photoswitching of upconverted fluorescence intensity with DTE-1 and DTE-2 as the photochromic units. The UC emission intensity was monitored at 438 nm against the irradiation time (254 nm or visible light). Data taken from Figure 2.

UC with DTE-1 is faster as compared with that of DTE-2. However, thereafter the switching ON process with DTE-1(c) is much slower than that with DTE-2 (Figure 3). These results may offer additional switching dimensions to control the TTA UC with higher spatial or temporal resolution by using different DTE derivatives.<sup>19</sup>

Multiple photophysical processes are involved in TTA UC, such as intersystem crossing (ISC) of the triplet photosensitizer, triplet–triplet energy transfer (TTET), annihilation of the triplet acceptor, and radiative decay of the triplet acceptor (perylene, Scheme 2).<sup>1–8,36</sup> The possible mechanisms

#### Scheme 2. Mechanism of Photoswitching TTA UC, Exemplified with DTE-1(c)<sup>a</sup>



<sup>a</sup>Quenching (with DTE-1 as quencher) is denoted with rate constants of  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$ . The rate constants for the photophysical processes involved in TTA UC are denoted with  $k_{ISC}$  (intersystem crossing),  $k_{TTET}$  (triplet–triplet energy transfer), and  $k_{TT}$  (triplet–triplet annihilation rate constant). The TTA UC pathway is highlighted with yellow background.

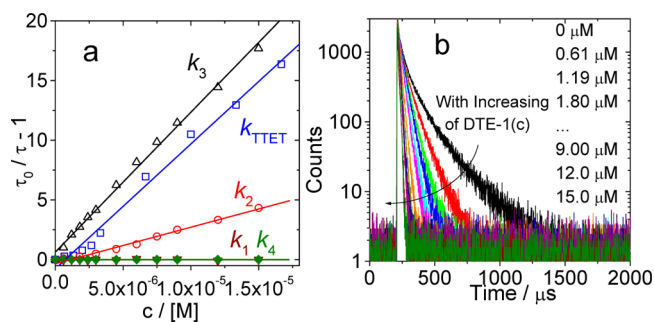
of photoswitching of the TTA UC with DTE-1(c) include quenching the triplet state of the photosensitizer, quenching the triplet state of the triplet energy acceptor, and quenching the singlet state of the perylene (Scheme 2). Therefore, mechanistic studies were carried out on the photoswitching of TTA UC with steady-state and nanosecond/picosecond time-resolved spectroscopy.

First, perylene and DTE-1 were mixed, and photoswitching of the fluorescence of perylene by DTE-1(c) was studied, because the absorption wavelength of DTE-1(c), 570 nm, is

longer than that of 2,6-diiodoBodipy, and thus resonance energy transfer (RET) or an inner filter effect is possible. However, no fluorescence quenching was observed (Figure S15). The same result was observed with DTE-2 (Figure S16). Therefore, we conclude that photoswitching of TTA UC does not occur via quenching of the singlet excited state of perylene; thus,  $k_4$  in Scheme 2 is negligible. RET in the mechanically mixed solution of perylene and DTE-1(c) is impossible (Figure S15).<sup>37</sup>

Quenching of the singlet excited state of 2,6-diiodoBodipy was studied with fluorescence spectroscopy. The fluorescence of 2,6-diiodoBodipy cannot be quenched by DTE-1(c) (Figures S13 and S14); this is also demonstrated in TTA UC (Figure 2a,e). This non-efficient FRET was also supported by studying the quenching of the singlet excited state of the un-iodinated Bodipy (Figures S11 and S12). The singlet-state lifetime of 2,6-diiodoBodipy (0.38 ns) is much shorter than that of unsubstituted Bodipy (3.86 ns), which means the singlet excited state of 2,6-diiodoBodipy is more difficult to quench; thus,  $k_1$  is negligible.<sup>32</sup>

The quenching constant  $k_2$  was measured with nanosecond time-resolved transient absorption spectroscopy by monitoring the decreasing triplet-state lifetime of  $^3[\text{I-Bodipy}]^*$  in the presence of DTE-1(c), as  $k_2 = (3.05 \pm 0.11) \times 10^5 \text{ M}^{-1}$ . Similarly, the  $k_{TTET}$  value was measured as  $(1.04 \pm 0.037) \times 10^6 \text{ M}^{-1}$ . Since  $k_{TTET}$  is ca. 3-fold of  $k_2$ , we propose that the quenching of  $^3[\text{perylene}]^*$  by DTE-1(c) is more significant than the quenching of  $^3[\text{I-Bodipy}]^*$  by DTE-1(c). In support of this postulation, the  $k_3$  value was measured for the quenching of the delayed fluorescence lifetime (TTA UC emission, Figure 4b),  $k_3 = (1.17 \pm 0.024) \times 10^6 \text{ M}^{-1}$ . Therefore, we conclude



**Figure 4.** (a) Stern–Volmer plots of the quenching processes: quenching the triplet lifetime of B-1 by DTE-1(c) ( $k_2$ ) or Py ( $k_{TTET}$ ), quenching the delayed fluorescence lifetime of perylene ( $k_3$ ), and quenching the fluorescence lifetimes of B-1 and perylene by DTE-1(c) ( $k_1$ ,  $k_4$ ). (b) Quenching the delayed fluorescence lifetime of perylene by DTE-1(c) ( $k_3$ ):  $[\text{B-1}] = 1.0 \times 10^{-5} \text{ M}$  in deaerated  $\text{CH}_3\text{CN}$ , 20 °C.

that it is by quenching of the  $^3[\text{perylene}]^*$  state that the TTA UC is photoswitched by DTE-1(c). It should be clarified that long-lived delayed fluorescence was normally observed (up to ca. 142.0  $\mu\text{s}$ ),<sup>38,39</sup> however, this long fluorescence lifetime was due to the energy pooling effect of the TTET process, not the inherent lifetime of the singlet state of perylene. All the bimolecular quenching constants ( $k_q$ ) were calculated (see SI for details), and the same conclusion was derived. For example, the  $k_q$  of  $k_3$  was calculated as  $(8.24 \pm 0.17) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is higher than the typical  $k_{TT}$  values (up to 10-fold).<sup>12</sup>

In summary, photoswitching of triplet–triplet annihilation upconversion (TTA UC) was achieved for the first time. The method uses dithienylethene (DTE) as the photochromic unit, 2,6-diiodoBodipy as the triplet photosensitizer, and perylene as

the triplet energy acceptor/emitter. In the presence of open-form DTE, TTA UC was not perturbed. Upon photoirradiation of the mixture at 254 nm, the closed form of DTE was produced, and the TTA UC was completely quenched. The TTA UC can be photoswitched ON upon subsequent visible light irradiation of the solution, and the photoswitch is reversible. With steady-state and nanosecond time-resolved spectroscopy, we confirmed that the closed form of DTE acts as a triplet energy acceptor, i.e., mainly as the quencher of the perylene triplet excited state among several possible quenching pathways. Therefore, the photoswitching of TTA UC is not via the singlet excited state of DTE. These results will offer significant additional, unprecedented dimensions for TTA UC with controllable spatial or temporal resolution.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Detailed experimental procedures and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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