A building-block design for enhanced visible-light switching of diarylethenes

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Current development of light-responsive materials and technologies imposes an urgent demand on visible-light photoswitching on account of its mild excitation with high penetration ability and low photo-toxicity. However, complicated molecular design and laborious synthesis are often required for visible-light photoswitch, especially for diarylethenes. Worse still, a dilemma is encountered as the visible-light excitation of the diarylethene is often achieved at the expense of photochromic performances. To tackle these setbacks, we introduce a building-block design strategy to achieve all-visible-light photochromism with the triplet-sensitization mechanism. The simply designed diarylethene system is constructed by employing a sensitizer building-block with narrow singlet-triplet energy gap ($\Delta E_{ST}$) to a diarylethene building-block. A significant improvement on the photochromic efficiency is obtained as well as an enhanced photo-fatigue resistance over those under UV irradiation. The balance between the visible-light excitation and decent photochromism is thus realized, promoting a guiding principle for the visible-light photochromism.
Recent developing of smart materials with a photo-controllable manner prefers visible light as the trigger over traditional UV light, as visible light provides a mild excitation for sustainable applications and precise operation\textsuperscript{1-3}. This requires the photo-responsive units, photoswitches, to work efficiently under visible-light irradiation. Nonetheless, one serious restriction of conventional photoswitches is that at least in one direction of the switching needs UV light, which often suffers from light-induced damaging, high scattering/low penetration and non-selective absorption/excitation through most media\textsuperscript{4-6}. Therefore, designing photoswitches and shifting their operation wavelengths into visible-light window has become an urgent task. As a well-known P-type (thermo irreversible) photochromore, diarylethenes (DAE) possess excellent photochromic performances and photoisomer thermo-stability, qualifying as a star molecule in photoswitch family\textsuperscript{7-11}. Diarylethenes have recently reached to the bioscience, such as sub-resolution bio-imaging\textsuperscript{12,13} and enzyme/inhibitor mimicking\textsuperscript{14-16}, in which visible-light excitation is highly demanded. Regarding the development of visible-light diarylethenes still lags behind, due to the lack of effective design strategies that would guide the fabrication of diarylethenes with both visible-light responsiveness and efficient photochromism. Previous design of visible-light diarylethene mainly includes two strategies: 1. Direct excitation through HOMO-LUMO gap engineering; 2. Indirect excitation or sensitization33. (2) The D-A structure provides a medium for visible-light driven diarylethenes, as a trade-off effect between the narrow singlet-triplet energy gap (~450 nm for DT, Supplementary Fig. 1, ε \textsuperscript{T1}=2.0 \times 10^{-5} \text{M}^{-1} \text{cm}^{-1} at 420 nm) that ensures an efficient, visible-light excitation. (3) Both demands of triplet energy level matching and the visible-light excitation for the TTET-induced, visible-light photochromism are easily satisfied, benefiting from the narrow ∆E\textsubscript{ST} feature of our sensitizer. Conventional sensitizers with strong visible-light absorbance usually possess much lower triplet energy levels that mismatch those of diarylethenes, resulting in the disenablement of TSP. Our strategy wards off this problem and provides a simple building-block design for the visible-light DAE photochromic system. Furthermore, our design requires no conjugation extension between the sensitizer and DAE (Fig. 1b). The electronic independent sensitizer and DAE building blocks retain their own properties and prevent the possible intramolecular electronic interactions in elongated π-conjugation\textsuperscript{22,23}, resulting in good cooperation rather than perturbation on the desired photochromic performances.

**Selection of matched DAE/sensitizer building blocks.** To select proper DAE/sensitizer building blocks with matched triplet energy levels for visible-light photochromism, the TSP of DAEs mixed with different narrow ∆E\textsubscript{ST} sensitizers was first checked. The D-A type sensitizer, DT (S\textsubscript{1}=2.54 eV, T\textsubscript{1}=2.53 eV; Supplementary Table 1) and PT (S\textsubscript{1}=2.53 eV, T\textsubscript{1}=2.47 eV)\textsuperscript{34} were mixed with a conventional DAE-1o (open isomer; S\textsubscript{1}=4.19 eV, T\textsubscript{1}=2.49 eV, Supplementary Table 1) at 10\textsuperscript{-4} M, respectively. As shown in Supplementary Fig. 2a, the TSP of DAE-1o/DT upon irradiation with visible light (λ = 420 nm) were detected, as a characteristic peak of the closed isomer, DAE-1c, appeared around 530 nm (identical with the closed isomer under 313 nm irradiation, Supplementary Fig. 3). Note that the DAE-1o alone is inert under 420 nm irradiation (Supplementary Fig. 3), demonstrating a possible participation of the triplet state during visible-light photochromism and the matched triplet energy levels between DAE-1o and DT. In contrast, DAE-1o/PT only exhibited slight photochromism (Supplementary Fig. 2b), indicating an unsatisfactory triplet energy level matching between PT and DAE-1o. Notably, DAE-1o/DT hardly underwent photochromism in a diluted solution (2 \times 10^{-5} M, Supplementary Fig. 3), which presented an evident concentration dependence of photochromism in mixed system.

The triplet-sensitized photochromism mechanism was further proved by transient absorption spectroscopy, monitoring the decay of the peak at 620 nm upon nanosecond-pulsed laser excitation (Supplementary Fig. 4). The transient absorption decays of the
sensitizer DT at 620 nm under both aerated and deaerated conditions were measured as well (Supplementary Fig. 5). A faster decay, with a lifetime of 65 ns, was detected in aerated toluene, as compared with 2973 ns in deaerated toluene, confirming that the transient absorption band at 620 nm could be attributed to the excited triplet state of DT. A concentration-dependent excited transient absorption band at 620 nm could be attributed to the excited triplet state of DT. A concentration-dependent excited transient absorption band at 620 nm could be attributed to the excited triplet state of DT. A concentration-dependent excited transient absorption band at 620 nm could be attributed to the excited triplet state of DT. A concentration-dependent excited transient absorption band at 620 nm could be attributed to the excited triplet state of DT. A concentration-dependent excited transient absorption band at 620 nm could be attributed to the excited triplet state of DT. 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Visible-light photochromic performances of DAE-DT. Based on the preliminary results, DAE-DT was designed by connecting properly selected DT sensitizer and DAE building blocks with a 1:1 ratio (Fig. 1). DAE-o-DT (open isomer of DAE-DT) exhibits a strong absorption band at around 380 nm (absorbance of DT, Fig. 2a), which extends to ca. 450 nm (CT band of DT) and thus ensures the visible-light excitation. The visible-light photochromism of DAE-1o/DT mixture was indicated, the energy level matching TTET process between DAE-1o and the sensitizer DT was converged to construct the DAE-DT dyad for visible-light photochromism study.

To evaluate the high efficiency of the visible-light photocycloreversion, quantum yields and conversion ratios (Table 1 and Supplementary Tables 2–4, Supplementary Fig. 8–10) were determined. The photocyclization quantum yields with 420 nm excitation were calculated as $\Phi_{o-c} = 0.37$ (in toluene) with open-to-close conversion ratio of 80%. To our delight, the photochromic efficiency of this TSP system under visible-light excitation was higher than the UV-induced ring closure efficiency ($\Phi_{c-o} = 0.26$ with open-to-close conversion ratio of 81%), and comparable with that of the bare DAE-1o core ($\Phi_{o-c} = 0.36$ with photocyclization reversion of 85%). The photocycloreversion quantum yield $\Phi_{c-o}$ was determined as 0.006 ($\lambda = 546$ nm), almost identical to the DAE-1o core ($\Phi_{c-o} = 0.007$). The resulted photocyclization/photocycloreversion quantum yields indicate a much enhanced visible-light photochromism based on our strategy, which is usually suppressed in previous designs of visible-light DAEs[17,21–23]. Besides, compared with the mixed system ($2 \times 10^{-3}$ M, n/n = 1:1, Supplementary Fig. 3, green dash
DAE-o-DT during repetitive switching cycles consisting of alternate 420 nm/550 nm irradiation (triplet excitation, black) and 313 nm/550 nm irradiation. Insets: photographs of color changes of DAE-o-DT in deaerated toluene before and after irradiation.

Mechanism studies of the triplet-sensitized photochromism. To validate the mechanism of the intramolecular TTET process that contributes to the visible-light photochromism, different photocyclization performances of DAE-o-DT were carried out under argon bubbling, oxygen bubbling and addition of anthracene as the triplet quencher (Fig. 3a), respectively. The photochromism of DAE-o-DT was significantly affected in oxygen bubbling and quencher containing samples, as the photocyclization quantum yields fell to $\Phi_{o,c} = 0.23$ and 0.18, respectively (Table 1). The results suggest that the triplet state plays a crucial role in the photocyclization of DAE-o-DT.

The transient absorption spectroscopy was again applied to get a deeper insight into the intramolecular TTET mechanism for DAE-o-DT, through monitoring the decay of the peak at 620 nm upon nanosecond-pulsed laser excitation (Supplementary Fig. 4). After argon-bubbling degassing cycles, the transient absorption decays of DAE-o-DT at 620 nm were examined (Fig. 3b). To our delight, the excited triplet state lifetime of the sensitizer moiety decreased dramatically to 293 ns for DAE-o-DT (2973 ns for DT alone), which demonstrated the quenching of the DT excited triplet state.

Table 1 Photoreaction quantum yields of diarylethenes at the depicted wavelengths ($\lambda$). \(^{a,b}\)

| Photoreaction | $\lambda$ (nm) | $\Phi$ |
|---------------|----------------|-------|
| DAE-1o $\rightarrow$ DAE-1c | 313 | 0.36 |
| DAE-o-DT $\rightarrow$ DAE-c-DT | 420 | 0.03 |
| DAE-o-DT $\rightarrow$ DAE-o-DT (argon bubbling) | 420 | 0.37 |
| DAE-o-DT $\rightarrow$ DAE-c-DT (oxygen bubbling) | 420 | 0.23 |
| DAE-o-DT $\rightarrow$ DAE-c-DT (anthracene) | 420 | 0.18 |
| DAE-3C-DT-o $\rightarrow$ DAE-3C-DT-c (argon bubbling) | 420 | 0.30 |
| DAE-1c $\rightarrow$ DAE-o-DT | 546 | 0.007 |
| DAE-c-DT $\rightarrow$ DAE-o-DT | 546 | 0.0066 |

\(^ {a}$DAE-1o = 2 × 10^{-5} M, [DAE-o-DT] = 2 × 10^{-5} M

\(^ {b}$In toluene at 300 K

\(^ {c}$DAE-1o = [DT] = 2 × 10^{-5} M

The photoluminescence quantum yields of DAE-o-DT were further investigated to validate the FRET process. DAE-o-DT is endowed with a photoluminescence quantum yield of $\Phi = 0.26$, while the quantum yield of resultant PSS upon irradiation with 420 nm is quenched to around $\Phi = 0.02$, confirming again that the intramolecular FRET in DAE-c-DT. The fluorescence-switching of DAE-DT could be conducted more than ten cycles with negligible degradation (Supplementary Fig. 11).
and DAE-o-DT (2.5 × 10⁻⁵ M) at 620 nm. c The luminescence lifetime spectra of DT (2.5 × 10⁻⁴ M) and DAE-o-DT (2.5 × 10⁻⁴ M) at 495 nm. d The emission decays of DT (2.5 × 10⁻⁴ M) and DAE-o-DT (2.5 × 10⁻⁴ M) at 77 K in toluene. e Frontier molecular orbitals of DAE-o-DT and DT by B3LYP functional and the 6-31 G(d) basis set, respectively.

The luminescence lifetime of DAE-o-DT as well as the DT sensitizer was also measured to further prove the intramolecular TTET mechanism. The narrow ΔEST feature of DT allows the reverse intersystem crossing (RISC) process from the triplet to the singlet state. This phenomenon has been widely applied in designing thermally activated delayed fluorescence (TADF) materials. The fluorescence of such molecule consists of two components: prompt fluorescence (~ns lifetime) and delayed fluorescence (~μs lifetime). The latter is attributed to the RISC process. Accordingly, we investigated the delayed fluorescence lifetime of DAE-o-DT and DT, respectively. For DT alone, the lifetimes of prompt and delayed fluorescence were 24 ns and 5.10 μs, respectively, consistent with the typical character of TADF materials. Interestingly, compared with DT, the lifetime of delayed fluorescence for DAE-o-DT was remarkably reduced to 0.14 μs, while that of prompt fluorescence did not vary too much (23 ns). This result demonstrated the existence of the intramolecular TTET process. Moreover, the decays of the photoluminescence lifetime at 77 K decreased dramatically from 198.3 μs for DT alone to 4.7 μs for DAE-o-DT, which further confirmed the existence of triplet energy transfer in this visible-light photochromic system (Fig. 3d).

Theoretical calculations were carried out at the B3LYP/6-31 G (d) level of theory to further study the visible-light TSP. As exhibited in Fig. 3e and Supplementary Tables 5 and 6, the HOMO and LUMO of the DAE-o-DT are mainly localized on the dihydroacridine unit and triazine unit of the DT moiety, respectively, which is similar to the DT sensitizer. This result reveals the direct excitation of the DT moiety of DAE-o-DT upon 420 nm irradiation. The above studies give a clear picture on the whole process of visible-light photochromism via intramolecular TTET mechanism (Fig. 1a). First, the sensitizer DT is excited by the visible light (λ = 420 nm) and the excited triplet state [DAE-o-DT*] is formed through ISC from the excited singlet state [DAE-o-DT]. Upon the sequential intramolecular TTET, the energy is transferred from [DAE-o-DT*] to [DAE-o-DT*], which results in the photocyclization of DAE-o-DT and yields the closed DAE-c-DT via a triplet-sensitized pathway. The visible light could not induce the photochromism via the singlet pathway, as the DAE molecule cannot reach the excited singlet state [DAE-o-DT*] through visible-light excitation.

Solvent effects on the triplet-sensitized photochromism. The D-A structure of the DT sensitizer prompted us to further investigate the solvatochromic effect on the visible-light TSP. First, emission performances of DAE-o-DT were examined in different solvents with increasing polarity (Fig. 4a). An obvious solvatochromic effect on the emission spectra was observed with a redshift of the fluorescence peak from 444 nm in cyclohexane to 598 nm in acetone, indicating a lowering of excited energy levels with the increasing solvent polarity. Accordingly, a declined visible-light TSP performance was determined (Fig. 4b and Supplementary Fig. 13), as the photocyclization quantum yield dropped from Φo-c = 0.40 in cyclohexane to Φo-c = 0.008 in acetone.
acetone (Supplementary Table 4). Though DAE-DT presents the best visible-light photochromism in cyclohexane, the relatively lower solubility may hamper its further applications. As a result, toluene was selected as the solvent in this work.

All-visible-light photoswitchable patterning. With this highly efficient, fatigue-resistant, visible-light photochromic DAE-DT in hand, we developed an all-visible-light patterning application for information storage medium. We prepared the filter paper by soaking it in a DAE-o-DT solution (1 mM) and drying afterward. By exposing the filter paper to the recording visible light ($\lambda = 420$ nm) locally through mask 1, specific images could be successfully patterned (Fig. 5). The image could be erased as the erasing visible light ($\lambda > 550$ nm) was imposed. Multiple images could be consecutively patterned and erased with respective masks under all-visible-light recording-erasing cycles, and no color fading was observed. Meanwhile, a vague photoswitchable patterning was obtained by soaking the filter paper with a mixed solution of DAE-1o and DT (1 mM, molar ratio = 1:1, Supplementary Fig. 14). The much attenuated photochromism of DAE-1o/DT in filter paper is probably due to the reduced mobility in solid state that significantly affects the intramolecular TTET process. The result indicates again the highly efficient intramolecular TTET of DAE-DT for all-visible-light photoswitchable patterning in solid state. These results present a promising application of DAE-DT for future light-manipulative data storage.

Discussion

We developed an all-visible-light diarylethene system by introducing a narrow $\Delta E_{ST}$ type sensitizer to the DAE core. Taking advantages of the unique features of the sensitizer (narrow $\Delta E_{ST}$, strong visible-light absorption, etc.) and the intramolecular TTET process, the newly designed DAE-DT was endowed with a remarkable visible-light photochromism of high efficiency and robust fatigue resistance. Therefore, the long-time dilemma in previous design strategies—the trade-off effect between the visible-light excitation and photochromic performances, have been resolved. This smart strategy may fulfill the requirements for further development and modulation of visible-light photoswitches in both molecular structure designs and corresponding applications. First, the narrow $\Delta E_{ST}$ feature of the twisted D-A sensitizer overcomes the issue of triplet energy mismatch in conventional visible-light excited sensitizer (due to the wide $\Delta E_{ST}$)\textsuperscript{34}. With the booming development of organic luminescence\textsuperscript{41–43}, numbers of newly-designed narrow $\Delta E_{ST}$ compounds are being presented every year, thus enriching our sensitizer database and offering a simple and versatile design of visible-light DAE systems. Second, the building-block strategy can facilitate the bespoke construction of DAE-sensitizer systems with demanded visible-light excitation wavelengths, by appropriately selecting sensitizer and diarylethene building blocks from the database. Third, the modular building of DAE-sensitizer system can also be directed by various means, e.g., supramolecular self-assembly\textsuperscript{44} and polymer chemistry\textsuperscript{45}, which may inspire further
Preparation of DAE dyads

Spectroscopy measurements. UV/Vis spectra were recorded on Varian Cary 500 (1 cm quartz cell). Fluorescence emissions were measured on Varian Cary Eclipse and the excited wavelength was 365 nm. Nanosecond transient absorption measurements were performed on LP-920 laser (Shenyang HB optical Technology) for photophysical characterization. Photocyclization conversion ratio measurement.

Photocyclization conversion ratio measurement. The ratio of the equilibrium concentrations of the open form \( C_0 \) and closed forms \( C_{2} \) at a given photostationary state (PSS) is expressed as follows:\(^{2,38}\)

\[
\frac{C_0}{C_0 + C_2} = \frac{\epsilon_{\alpha} \times \Phi}{\epsilon_{\alpha} \times \Phi + \epsilon_{\beta} \times A_{2}}
\]

where \( \epsilon_{\alpha} \) and \( \epsilon_{\beta} \) are the molar absorption coefficients of the open and closed forms, \( A_{\alpha} \) and \( A_{2} \) are the absorption of a sample of same concentration containing only the open or closed form, \( \Phi_{\alpha-\beta} \) and \( \Phi_{\alpha-2} \) are quantum yields of cyclestruction and cyclization, respectively. By comparing the PSS’s obtained under irradiation at two different wavelengths \( \lambda_1 \) and \( \lambda_2 \), a couple of equations of type (1) are obtained as follows (assuming that the ratio \( \Phi_{\alpha-\beta}/\Phi_{\alpha-2} \) does not change with the irradiation wavelength):

\[
\frac{C_{1}}{C_{2}} = \frac{A_{1}/A_{2}}{A_{\alpha}/A_{2}}
\]

where \( A_{1} \) and \( A_{2} \) are the photocyclization conversion ratios in PSS state at the given wavelength of \( \lambda_1 \) and \( \lambda_2 \), respectively. The absorbance \( A \) measured at any particular wavelength \( \lambda \) of a mixture of open and closed forms was introduced, while the overall concentration \( C_{0} + C_{2} \) is constant and the formula can be obtained as follows: where \( A_{1} \) and \( A_{2} \) are the photocyclization conversion ratios in PSS state at the given wavelength of \( \lambda_1 \) and \( \lambda_2 \), respectively. The absorbance \( A \) measured at any particular wavelength \( \lambda \) of a mixture of open and closed forms was introduced, while the overall concentration \( C_{0} + C_{2} \) is constant and the formula can be obtained as follows:

\[
A_{\lambda} = A_{\lambda_1} + \frac{A_{\lambda_2} - A_{\lambda_1}}{\alpha}
\]

Combining Eq. (3) with Eq. (4), we can obtain:

\[
1 - \frac{\alpha_{1}/\alpha_{2}}{1 + \alpha_{1}/\alpha_{2}} = 1 + \frac{\Delta_{1}/\alpha_{1}}{1 + \Delta_{1}/\alpha_{2}}
\]

where \( \Delta = (A_{0}-A)/A_{0} \) is the relative change of absorbance observed when a solution of open form is irradiated to the PSS. Moreover, the ratio \( \rho = \alpha_{1}/\alpha_{2} \) of the conversion yields at two different PSS’s, resulting from irradiation at two different wavelengths, is equal to the ratio of the \( \Delta \)’s measured at any given wavelength (the wavelength that maximizes the \( \Delta \)’s is usually chosen). Equating and developing Eq. (5) yields the final formula:

\[
\alpha_{2} = \frac{\Delta_{1} - \Delta_{2}}{1 + \Delta_{1} - \rho(1 + \Delta_{2})}
\]

where all the parameters \( \Delta \) and \( \rho \) are experimentally accessible. The numerical value determined by this equation may then be used to calculate the absorption spectrum of the pure closed form by means of Eq. (4).

Calculation of photocyclization reaction quantum yields. The photocyclization quantum yields of DAEs at 313 nm, 420 and 546 nm were measured with the potassium ferrioxalate (K3[Fe(C2O4)3]) as the actinometer. The photocyclization and photocyclization quantum yields were calculated based on the following equation:

\[
\Phi_{\lambda} = \frac{\Delta A/\Delta t}{(Nhv/1) \times \epsilon_{\lambda} \times F_{x}}
\]

where \( \Delta A/\Delta t \) is the change of absorbance upon irradiation at detection wavelength, \( \epsilon_{\lambda} \) is the molar extinction coefficient at detection wavelength \( (\epsilon_{530nm} = 17,906 \text{M}^{-1} \text{cm}^{-1} \text{for DAE-1c, 19,000 M}^{-1} \text{cm}^{-1} \text{for DAE-c-DT}) \) and \( F_{x} \) is the mean fraction of light absorbed, the value of which is 1−10−7. For photocyclization quantum yields, it should be the absolute value of \( \Phi_{\lambda} \).

Photocyclizable photonic application. 4.9 mg DAE-e-DT or the mixture of 2.28 mg DAE-1c and 2.72 mg DT was dissolved in 5 ml of toluene. The solution was purged with argon for 10 min to remove the oxygen. Then a piece commercial filter paper (d = 11 cm) was soaked into the solution for 5 min. Then keep the wet paper in a vacuum chamber for 30 min to remove completely residual solvents. The mask of Chinese lantern, Chinese knot and the badge of East China University of Science and Technology were all bespoke commercially.

Data availability

The data that support the findings of this study are available from the corresponding author upon request.

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