Electronic Supplementary Information (ESI)

Cu$^{2+}$-selectivity gated photochromism on Schiff-modified diarylethenes with star-shaped structure

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1. Synthetic route

Scheme S1 Synthetic route of photochromic compound DTEG.
2. **HPLC analysis for the cyclization process with irradiation at 365 nm**

![HPLC spectra](image)

**Fig. S1** The HPLC spectra of compound **DTEG** (1×10^{-4} M) in acetonitrile without (above) and with (below) irradiation of 365 nm light at 25 °C under following conditions: Agilent C18 column, methanol as mobile phase, the detection wavelength of 254 nm.

Note: a peak with the residue time (R.T.) of 31.639 min appeared in the spectrum without UV light of 365 nm irradiation (Fig. S1 above). Upon irradiation with 365 nm light within the frame of 5 min, compound **DTEG** reached the photostationary state in acetonitrile, resulting in the appearance of three new peaks (R.T. = 3.334 min, 4.915 min, and 10.935 min) in the spectrum (Fig. S1 below), respectively. These three new peaks are attributed to the cyclization of one dithienylethene unit, two dithienylethene units and all dithienylethene units of compound **DTEG**, respectively, due to the different polarity of the compound with diverse cyclization numbers of dithienylethene units.
3. Absorption spectra of DTEG with Cu$^{2+}$

![Absorption spectra](image1)

**Fig. S2** UV–vis absorption changes of compound DTEG (10 μM) upon the titration of Cu$^{2+}$ ions (0–90 μM with a 5 μM interval) in acetonitrile solution at 25 °C. Inset: the corresponding photographic images before and after addition of Cu$^{2+}$ ions.

4. Emission spectra of DTEG with Cu$^{2+}$

![Emission spectra](image2)

**Fig. S3** Fluorescence changes of compound DTEG (10 μM) upon addition of different concentrations of Cu$^{2+}$ ions (10 μM, 30 μM, 60 μM, 90 μM) in acetonitrile solution at 25 °C, $\lambda_{ex} = 357$ nm. Slits: 5 nm/5 nm. Inset: the corresponding photographic images before and after addition of 9.0 equiv. of Cu$^{2+}$ ions.
5. Absorption spectra of DTEG in the photostationary state with Cu$^{2+}$

![Absorption Spectra of DTEG with Cu$^{2+}$](image)

**Fig. S4** UV−vis absorption changes of compound DTEG (10 μM) in the photostationary state upon the titration of Cu$^{2+}$ ions (0−90 μM with a 5 μM interval) in acetonitrile solution at 25 °C. Inset: the corresponding photographic images before and after addition of 9.0 equiv. of Cu$^{2+}$ ions.

6. The photographs of DTEG with metal ions

![Photographs of DTEG with Metal Ions](image)

**Fig. S5** Naked-eye visible images of compound DTEG (10 μM) upon the addition of various metal ions (90 μM) in acetonitrile solution at 25 °C.
7. Absorption spectra of DTEG in the photostationary state with metal ions

![Absorption spectra](image)

**Fig. S6** UV–vis absorption spectra of compound DTEG in the photostationary state in the presence of various metal ions at 25 °C. Metal ions are at concentrations of 90 μM.

8. The photographs of DTEG in the photostationary state with metal ions

![Photographs](image)

**Fig. S7** Naked-eye visible images of compound DTEG (10 μM) in the photostationary state upon the addition of various metal ions (90 μM) in acetonitrile solution at 25 °C.
9. Job’s plot of DTEG and Cu$^{2+}$

**Fig. S8** Job’s plot of compound DTEG and Cu$^{2+}$ ions, $A$ and $A_0$ are the absorbance value at 357 nm of compound DTEG in the presence and absence of Cu$^{2+}$ ions, respectively; the total concentration of compound DTEG and Cu$^{2+}$ ions is 20 μM in acetonitrile solution at 25 °C.
**10. MS spectrum of DTEG with Cu²⁺**

**Fig. S9**  MS (MALDI-TOF) spectrum of compound **DTEG** (10 μM) with Cu²⁺ ions (90 μM) in acetonitrile solution at 25 °C.
11. Absorption spectra of DTEG with Cu^{2+} upon irradiation with UV light

**Fig. S10** UV–vis absorption spectral changes of compound DTEG (10 μM) with different amounts of Cu^{2+} ions upon irradiation with 365 nm light in acetonitrile solutions: (A) 1.0 equiv.; (B) 3.0 equiv.; (C) 6.0 equiv.; and (D) 9.0 equiv.
12. The photographs of DTEG with Cu$^{2+}$ upon irradiation with UV light

Fig. S11 Naked-eye visible images of compound DTEG (10 μM) with different amounts of Cu$^{2+}$ ions upon irradiation with 365 nm light in acetonitrile solutions: 1.0 equiv., 3.0 equiv., 6.0 equiv., 9.0 equiv., and 12.0 equiv.
13. **Analysis for the binding mode between DTEG and Cu²⁺**

Table S1. Mayer bond order between copper atoms and surrounding nitrogen and sulfur atoms.

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<tr>
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<th>Cu–N (carbocation)</th>
<th>Cu–N (Schiff base)</th>
<th>Cu–S (thiophene)</th>
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<td>2</td>
<td>0.237</td>
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<td>0.190</td>
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<tr>
<td>3</td>
<td>0.237</td>
<td>0.168</td>
<td>0.189</td>
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Table S2. Natural population analysis for atomic charges of copper atoms and surrounding nitrogen and sulfur atoms.

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<th>Cu ion</th>
<th>N (carbocation)</th>
<th>N (Schiff base)</th>
<th>S (thiophene)</th>
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<tr>
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14. *Time-dependent (TD) DFT Analysis*

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<th>Compound</th>
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<th>Excitation energy</th>
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<td>DTEG</td>
<td>$S_1$</td>
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<td>$H-3 \to L$ (18%)</td>
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<td>$H-7(\beta) \to L(\beta)$ (7%)</td>
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<td></td>
<td>$H-1(\beta) \to L(\beta)$ (7%)</td>
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</tbody>
</table>
15. Molecular orbital values in DTEG

Fig. S12 Molecular orbital values along the line between the two reactive carbon atoms in DTEG molecule. The positions of the two atoms correspond to 0 and 1, respectively. Black, red, and blue colors denote the three diarylethene groups. In LUMO, the black, red, and blue lines coincide and only the blue line is shown.

16. Frontier molecular orbitals (α-spin) of Cu-DTEG

Fig. S13 Frontier molecular orbitals (α-spin) of complex Cu-DTEG.
17. Frontier molecular orbitals (\(\beta\)-spin) of Cu-DTEG

![Frontier molecular orbitals (\(\beta\)-spin) of complex Cu-DTEG.](image)

**Fig. S14** Frontier molecular orbitals (\(\beta\)-spin) of complex Cu-DTEG.
18. **Molecular orbital values in Cu-DTEG**

![Graphs showing molecular orbital values](image)

**Fig. S15** Molecular orbital values along the line between the two reactive carbon atoms in complex Cu-DTEG. The positions of the two atoms correspond to 0 and 1, respectively. Black, blue, and red colors denote the three diarylethene groups.
19. $^1$H NMR spectrum of DTEG

Fig. S16 $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of compound DTEG.
20. $^{13}\text{C} \text{ NMR spectrum of DTEG}$

Fig. S17 $^{13}\text{C} \text{ NMR (CDCl}_3\text{, 100 MHz) spectrum of compound DTEG.}$
21. **HRMS spectrum of DTEG**

Fig. S18 HRMS (ESI+) spectrum of compound DTEG.
22. Calculation of the photocyclization conversion yield and quantum yields

The absorption of the closed form of compound DTEG was determined by the Fischer’s method (E. Fischer, J. Phys. Chem., 1967, 71, 3704). The ratio of the equilibrium concentrations of the open form \( (C_o) \) and closed forms \( (C_c) \) at a given photostationary state (PSS) is expressed as follows:

\[
\frac{C_o}{C_c} = \frac{\Phi_{c\rightarrow o} \times \varepsilon_c}{\Phi_{o\rightarrow c} \times \varepsilon_o} = \frac{\Phi_{c\rightarrow o} \times A_c}{\Phi_{o\rightarrow c} \times A_o}
\]  

(E. 1)

where \( \varepsilon_o \) and \( \varepsilon_c \) are the molar absorption coefficients of the open and closed forms, \( A_o \) and \( A_c \) are the absorption of a sample of same chromophore concentration containing only the open or closed form, \( \Phi_{c\rightarrow o} \) and \( \Phi_{o\rightarrow c} \) are quantum yields of cycloreversion and cyclization, respectively. By comparing the PSS’s obtained under irradiation at two different wavelengths \( \lambda' \) and \( \lambda'' \), a couple of equations of type (E. 1) are obtained. Assuming that the ratio \( \Phi_{c\rightarrow o} / \Phi_{o\rightarrow c} \) does not depend on the irradiation wavelength, we get:

\[
\frac{C'_o}{C'_c} \cdot \frac{C''_o}{C''_c} = \frac{A'_c}{A'_o} \cdot \frac{A''_c}{A''_o}
\]

(E. 2)

We introduce the open form to closed form conversion yield \( \alpha \), equation (E. 2) evolves to:

\[
\frac{1 - \alpha'}{1 - \alpha''} = \frac{A'_c}{A'_o} \cdot \frac{A''_c}{A''_o}
\]

(E. 3)
In order to introduce experimental data into equation (E. 3), we can write that the absorbance $A$ measured at any particular wavelength $\lambda$ of a mixture of open and closed forms, where the overall concentration $C_o + C_c$ is constant, is given by:

$$A = (1 - \alpha)A_o + \alpha A_c$$

or

$$A_c = A_o + \frac{A - A_o}{\alpha}$$  \hspace{1cm} (E. 4)

This can be combined to equation (E. 3) and yields:

$$\frac{1 - \alpha'}{\alpha'} \div \frac{1 - \alpha''}{\alpha''} = 1 + \frac{\Delta'}{\alpha'} \div 1 + \frac{\Delta''}{\alpha''}$$  \hspace{1cm} (E. 5)

where $\Delta = (A-A_o)/A_o$ denotes the relative change of absorbance observed when a solution of open form is irradiated to the PSS. Furthermore, the ratio $\rho = \alpha'/\alpha''$ 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 (E. 5) yields the final formula:

$$\alpha'' = \frac{\Delta' - \Delta''}{1 + \Delta' - \rho(1 + \Delta'')}$$  \hspace{1cm} (E. 6)

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 equation (E. 4).
The photocyclization quantum yield can be calculated according to a simple photochromic model involving the open form (OF) and closed form (CF) isomers by means of a numerical integration procedure (M. H. Deniel, D. Lavabre and J. C. Micheau, in Organic Photochromic and Thermochromic Compounds. J. C. Crano and R. J. Guglielmetti, Eds. Plenum Press, New York, 1999, vol. 2, p. 167) using the differential equation (E. 7) and phenomenological equation (E. 8).

\[
\frac{dC_c}{dt} = I_o \times \frac{1 - 10^{-Abs(\lambda_{irr})}}{V \times Abs(\lambda_{irr})} \times \left( \Phi_{o\rightarrow c} \times \varepsilon_{o\lambda_{irr}} \times l \times C_o - \Phi_{c\rightarrow o} \times \varepsilon_{c\lambda_{irr}} \times l \times C_c \right)
\]

(E. 7)

\[
Abs(\lambda_{obs}) = \varepsilon_{c\lambda_{obs}} \times l \times C_c + \varepsilon_{o\lambda_{obs}} \times l \times C_o
\]

(E. 8)

where \(C_o\) and \(C_c\) are the concentrations of open form and closed form, \(I_o\) is the incident irradiation intensity, \(V\) is the volume of the solution, \(\lambda_{irr}\) and \(\lambda_{obs}\) are the irradiation and observation wavelengths, \(\varepsilon_o\) and \(\varepsilon_c\) are molar absorption coefficients of open and closed forms at irradiating wavelength (313 nm), respectively (H. Dürr and H. Bouas-Laurent, Photochromism: Molecules and Systems. Elsevier, Amsterdam, 2003; J. C. Crano and R. J. Guglielmetti, Organic Photochromic and Thermochromic Compounds. Plenum Press, New York, 1999).

Equation (E. 7) is too complicated to calculate \(\Phi_{o\rightarrow c}\), and thus practically, we employ an approximation method (S. Fukumoto and T. Nakashima, *Angew. Chem. Int. Ed.*, 2011, 50, 1565). When the photocyclization produces less than 5% closed form, \(C_c\) would be defined as 0, which brings about an error about ±0.05 in quantum yields. And due to \(\varepsilon_{o\lambda_{irr}} = 0\) at 517 nm, equations (E. 7) and (E. 8) can be simplified as:
\[
\frac{dC_C}{dt} = \frac{I_o \Phi_{o\rightarrow c}(1 - 10^{-\varepsilon o\lambda_{irr} C_o l})}{V} \tag{E. 9}
\]

\[
Abs(\lambda_{obs}) = \varepsilon_{c\lambda_{obs}} \times l \times C_c \tag{E. 10}
\]

Combining equations (E. 9) and (E. 10), we get equation (E. 11):

\[
\Phi_{o\rightarrow c} = \frac{V}{I_o l \left(1 - 10^{-\varepsilon o\lambda_{irr} C_o l}\right)} \frac{d Abs(\lambda_{obs})}{dt} \tag{E. 11}
\]

\[
\frac{d Abs(\lambda_{obs})}{dt} \]

can be easily obtained from the slope of time-dependent absorption changes, and \(I_o\) can be calculated from reference compound BTF6 with known \(\Phi_{o\rightarrow c}\). In this way, we acquired \(\Phi_{o\rightarrow c}\), with an error about ±0.05.

As can be deduced from Fischer analysis, the photocyclization conversion yield of compound DTEG at 365 nm was 62.0%. In addition, we obtained that the cyclization quantum yield and cycloreversion quantum yield (in a similar way using BTF6 as reference) of compound DTEG in acetonitrile solution were 16.1% at 313 nm and 0.681% at 517 nm, respectively.