Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information (ESI)

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

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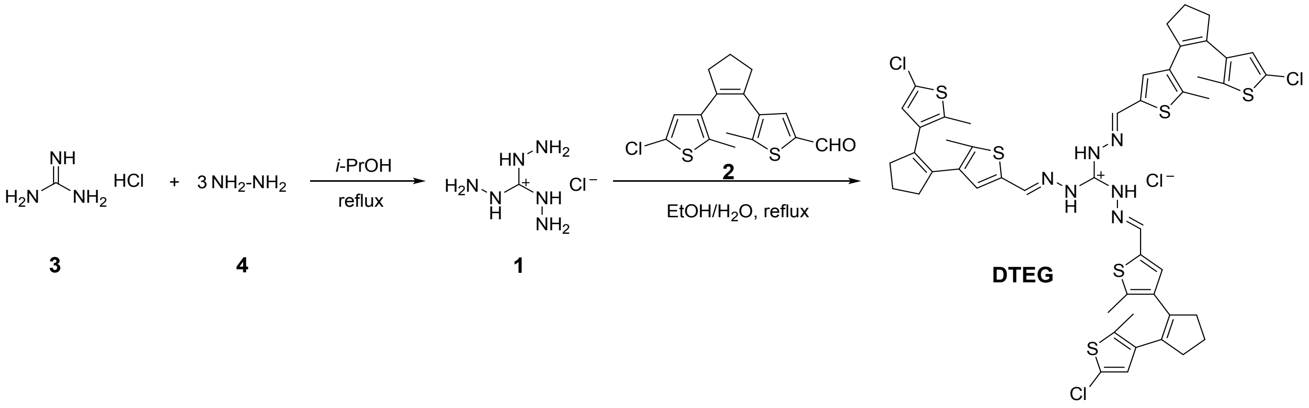
1. Synthetic route



Scheme S1 Synthetic route of photochromic compound **DTEG**.

2. *HPLC analysis for the cyclization process with irradiation at 365 nm*

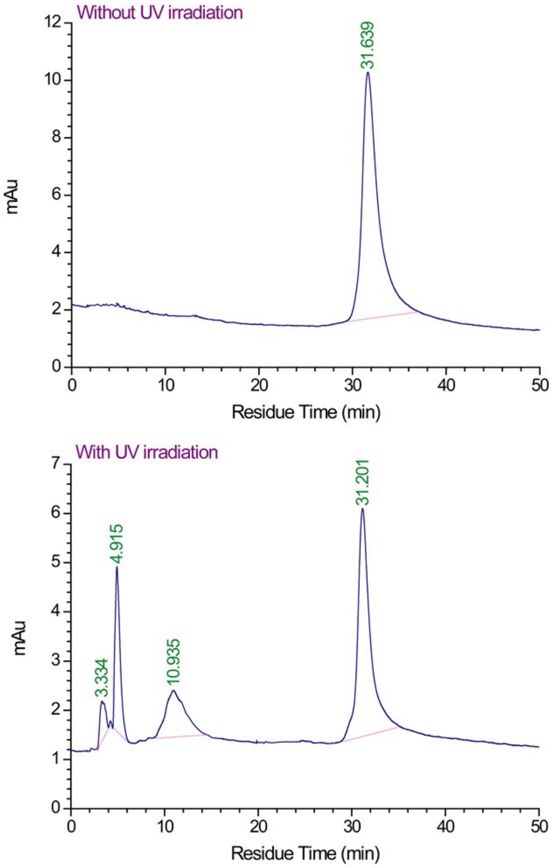


Fig. S1 The HPLC spectra of compound **DTEG** (1×10^{-4} M) in acetonitrile without (above) and with (below) irradiation of 365 nm light at 25 °C under following conditions: Agilent C18 column, methanol as mobile phase, the detection wavelength of 254 nm.

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 photostationay 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+}*

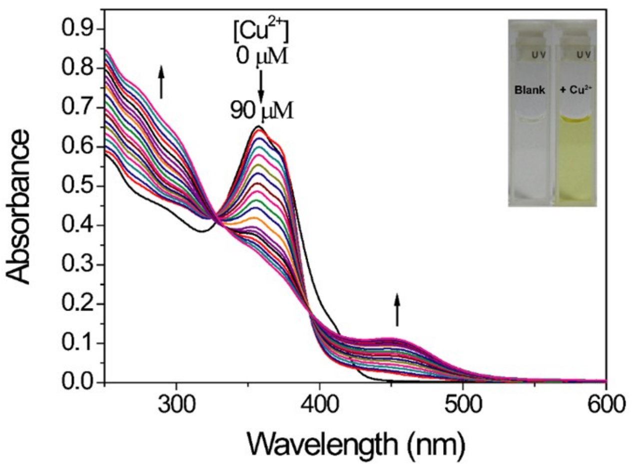


Fig. S2 UV−vis absorption changes of compound **DTEG** (10 μM) upon the titration of Cu^{2+} ions (0−90 μM with a 5 μM interval) in acetonitrile solution at 25 °C. Inset: the corresponding photographic images before and after addition of Cu^{2+} ions.

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

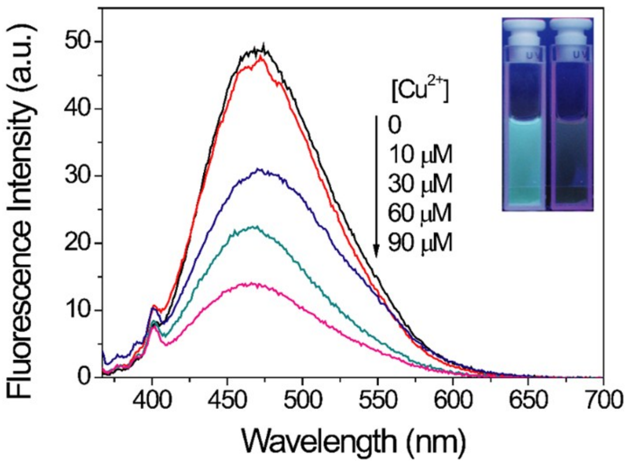


Fig. S3 Fluorescence changes of compound **DTEG** (10 μM) upon addition of different concentrations of Cu^{2+} ions (10 μM, 30 μM, 60 μM, 90 μM) in acetonitrile solution at 25 °C, λ_{ex} = 357 nm. Slits: 5 nm/ 5 nm. Inset: the corresponding photographic images before and after addition of 9.0 equiv.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

5. Absorption spectra of DTEG in the photostationary state with Cu^{2+}

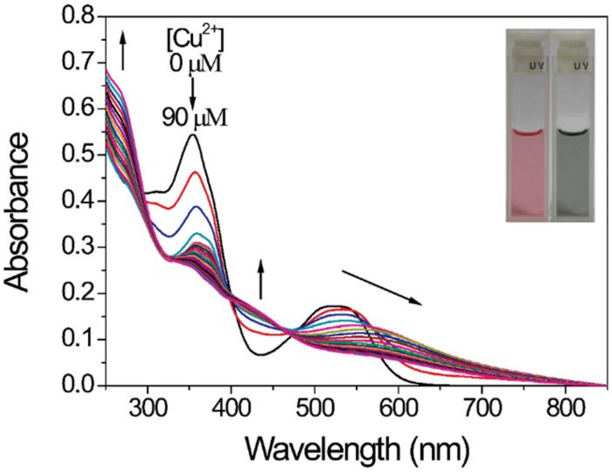


Fig. S4 UV−vis absorption changes of compound **DTEG** (10 μM) in the photostationary state upon the titration of Cu^{2+} ions (0−90 μM with a 5 μM interval) in acetonitrile solution at 25 °C. Inset: the corresponding photographic images before and after addition of 9.0 equiv. of Cu^{2+} ions.

6. The photographs of DTEG with metal ions

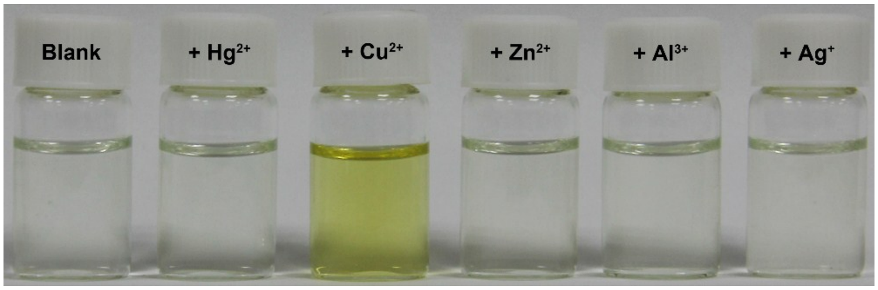


Fig. S5 Naked-eye visible images of compound **DTEG** (10 μM) upon the addition of various metal ions (90 μM) in acetonitrile solution at 25 °C.

7. *Absorption spectra of DTEG in the photostationary state with metal ions*

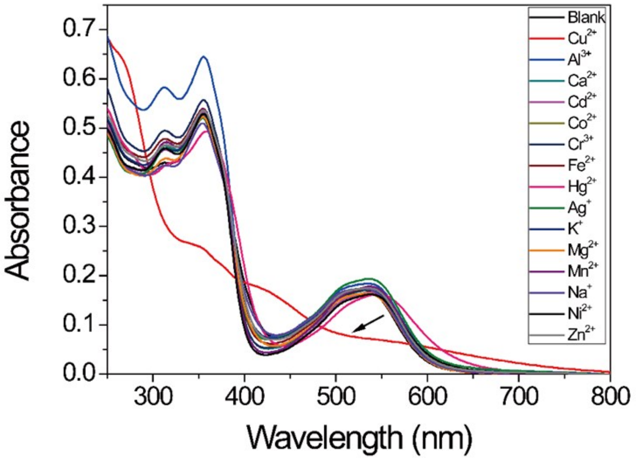


Fig. S6 UV−vis absorption spectra of compound **DTEG** in the photostationary state in the presence of various metal ions at 25 °C. Metal ions are at concentrations of 90 μM.

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

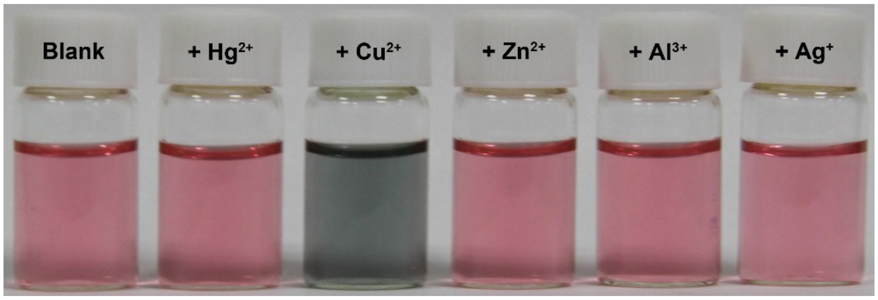


Fig. S7 Naked-eye visible images of compound **DTEG** (10 μM) in the photostationary state upon the addition of various metal ions (90 μM) in acetonitrile solution at 25 °C.

9. *Job's plot of DTEG and Cu^{2+}*

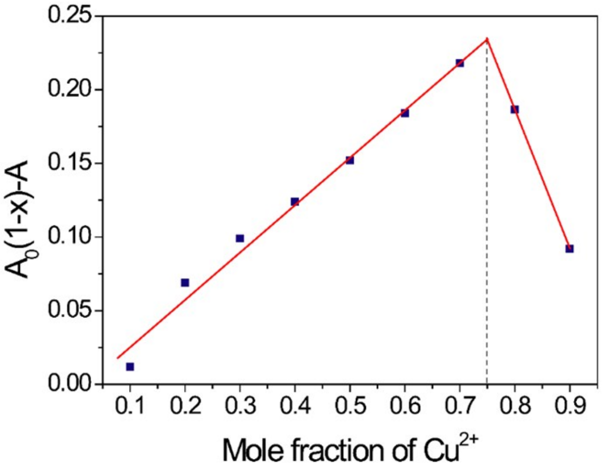


Fig. S8 Job's plot of compound **DTEG** and Cu^{2+} ions, A and A_0 are the absorbance value at 357 nm of compound **DTEG** in the presence and absence of Cu^{2+} ions, respectively; the total concentration of compound **DTEG** and Cu^{2+} ions is 20 μM in acetonitrile solution at 25 °C.

10. MS spectrum of DTEG with Cu^{2+}

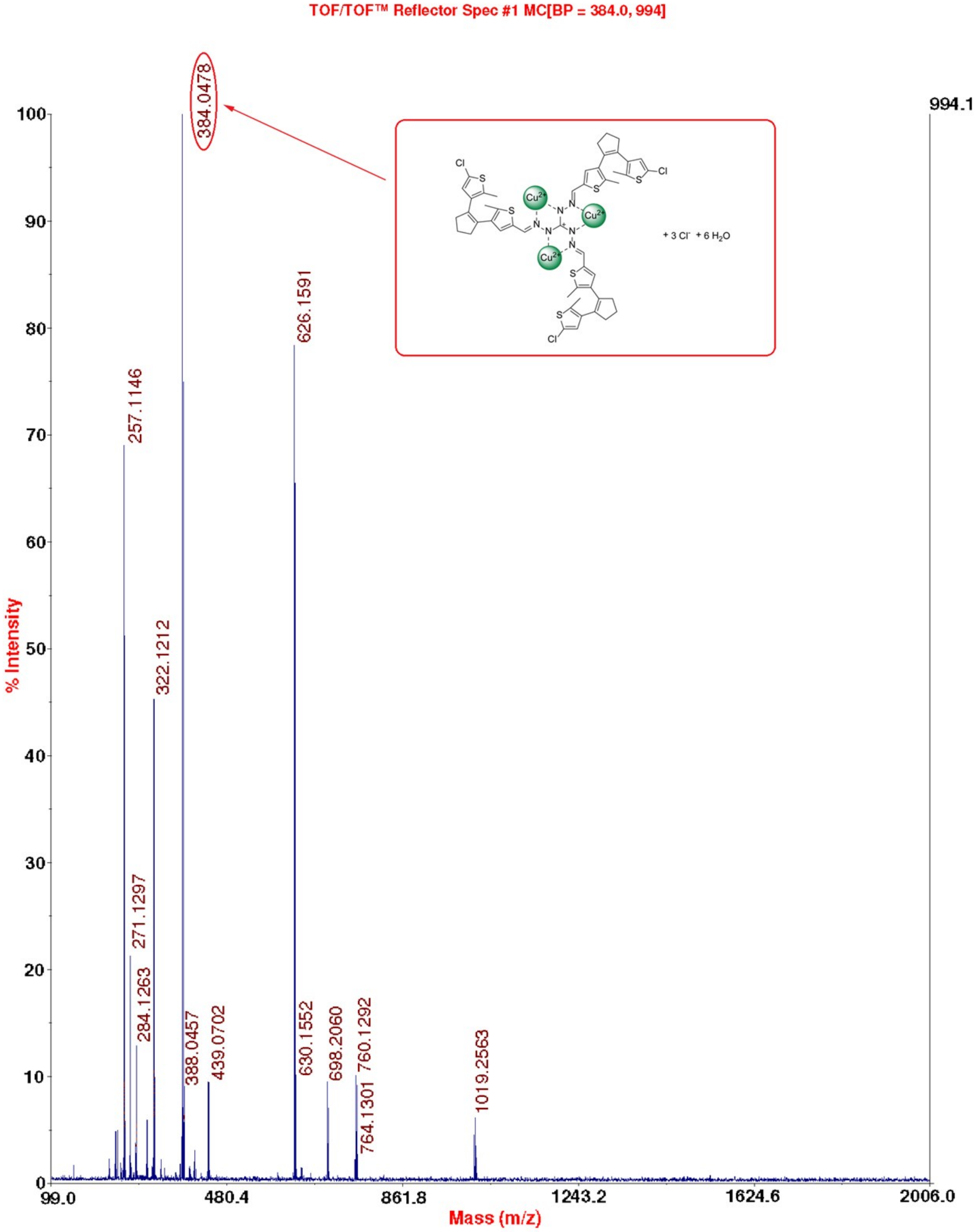


Fig. S9 MS (MALDI-TOF) spectrum of compound **DTEG** (10 μM) with Cu^{2+} ions (90 μM) in acetonitrile solution at 25 °C.

11. *Absorption spectra of DTEG with Cu^{2+} upon irradiation with UV light*

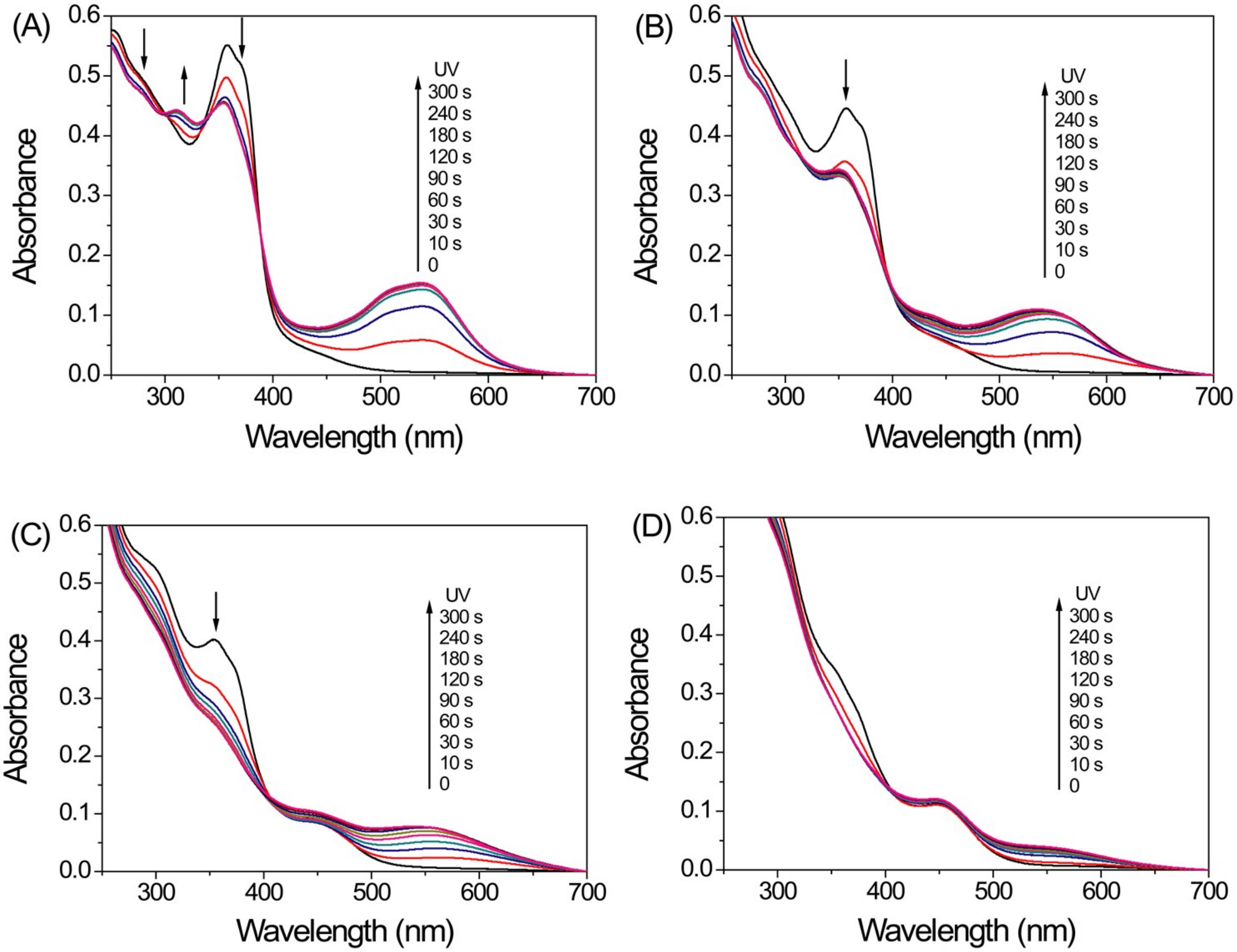


Fig. S10 UV−vis absorption spectral changes of compound **DTEG** (10 μM) with different amounts of Cu^{2+} ions upon irradiation with 365 nm light in acetonitrile solutions: (A) 1.0 equiv.; (B) 3.0 equiv.; (C) 6.0 equiv.; and (D) 9.0 equiv.

12. *The photographs of DTEG with Cu^{2+} upon irradiation with UV light*

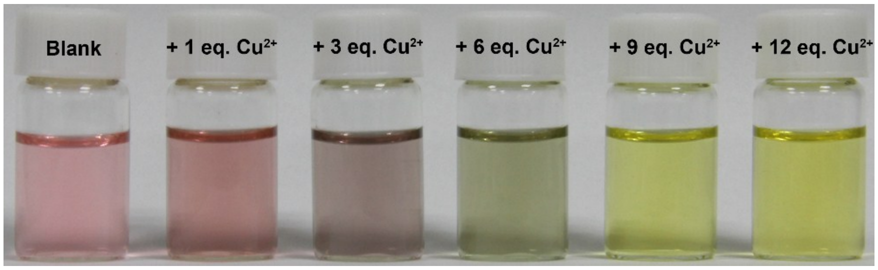


Fig. S11 Naked-eye visible images of compound **DTEG** (10 μM) with different amounts of Cu^{2+} ions upon irradiation with 365 nm light in acetonitrile solutions: 1.0 equiv., 3.0 equiv., 6.0 equiv., 9.0 equiv., and 12.0 equiv.

13. Analysis for the binding mode between DTEG and Cu^{2+}

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

	Cu–N (carbocation)	Cu–N (Schiff base)	Cu–S (thiophene)
1	0.224	0.173	0.144
2	0.237	0.171	0.190
3	0.237	0.168	0.189

Table S2. Natural population analysis for atomic charges of copper atoms and surrounding nitrogen and sulfur atoms.

	Cu ion	N (carbocation)	N (Schiff base)	S (thiophene)
1	+0.766	–0.413	–0.353	+0.494
2	+0.742	–0.423	–0.326	+0.475
3	+0.742	–0.417	–0.325	+0.472

14. Time-dependent (TD) DFT Analysis

Compound	Excited state	Excitation energy	Oscillator strength	MO compositions
DTEG	S_1	3.64 eV, 340 nm	1.1526	H-1 → L (32%) H-3 → L (18%) H → L (14%)
	S_2	3.64 eV, 340 nm	1.1444	H → L (32%) H-4 → L (18%) H-1 → L (15%)
	S_3	4.00 eV, 310 nm	0.0007	H-2 → L (34%) H-1 → L+1 (21%) H → L+2 (21%)
Cu–DTEG	S_1	1.03 eV, 1206 nm	0.1734	H(β) → L(β) (14%) H-6(β) → L(β) (12%) H(β) → L+1(β) (11%) H-6(β) → L+1(β) (9%)
	S_2	1.16 eV, 1069 nm	0.2605	H-7(β) → L(β) (24%) H-4(β) → L(β) (16%) H(β) → L+2(β) (7%) H-6(β) → L+1(β) (7%) H-7(β) → L+1(β) (7%)
	S_3	1.19 eV, 1045 nm	0.3068	H(β) → L+2(β) (27%) H-5(β) → L+2(β) (12%) H-6(β) → L+1(β) (9%) H-7(β) → L(β) (7%) H-1(β) → L(β) (7%)

15. Molecular orbital values in DTEG

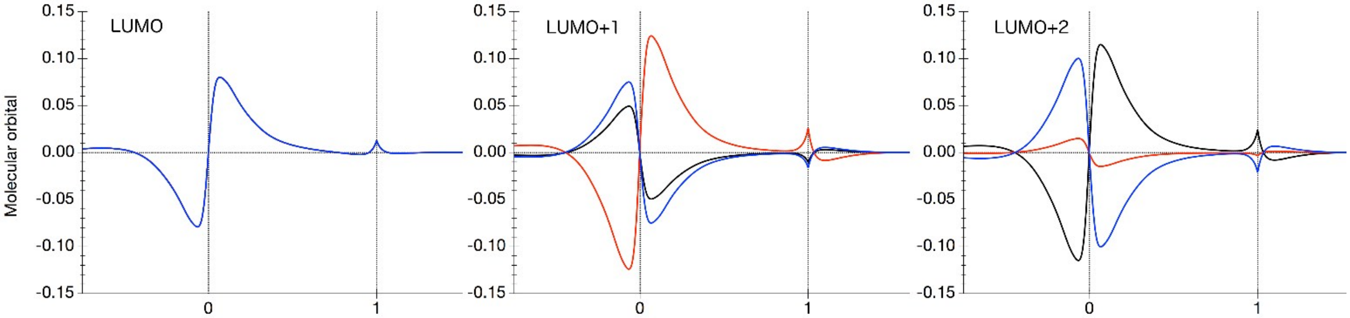


Fig. S12 Molecular orbital values along the line between the two reactive carbon atoms in **DTEG** molecule. The positions of the two atoms correspond to 0 and 1, respectively. Black, red, and blue colors denote the three diarylethene groups. In LUMO, the black, red, and blue lines coincide and only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

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

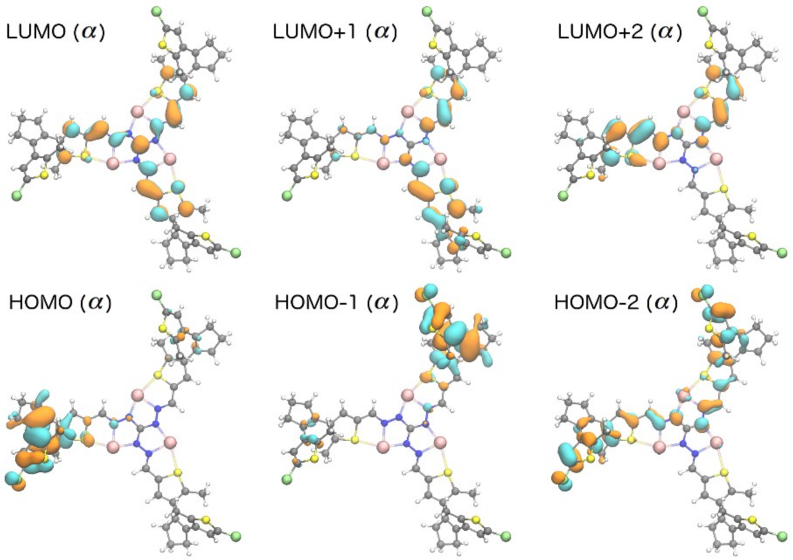


Fig. S13 Frontier molecular orbitals (α-spin) of complex **Cu-DTEG**.

17. Frontier molecular orbitals (β-spin) of Cu-DTEG

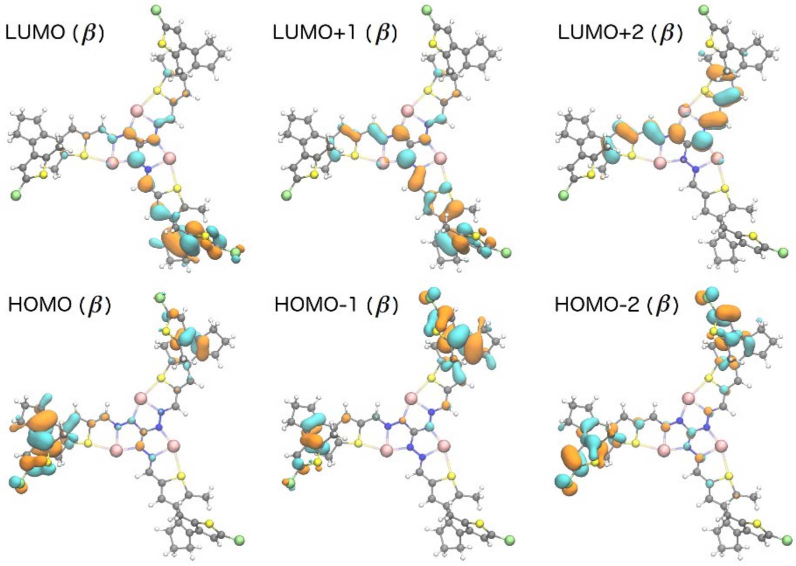


Fig. S14 Frontier molecular orbitals (β-spin) of complex **Cu-DTEG**.

18. Molecular orbital values in Cu-DTEG

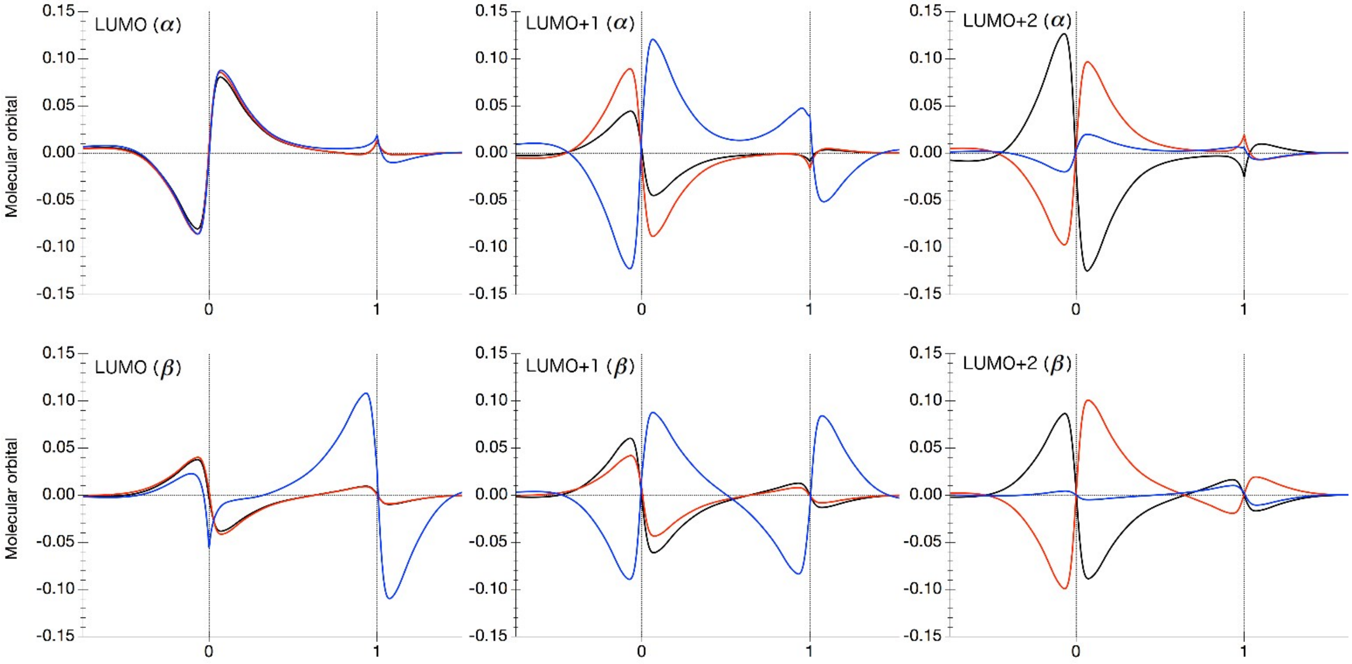


Fig. S15 Molecular orbital values along the line between the two reactive carbon atoms in complex **Cu-DTEG**. The positions of the two atoms correspond to 0 and 1, respectively. Black, blue, and red colors denote the three diarylethene groups.

19. ¹H NMR spectrum of DTEG

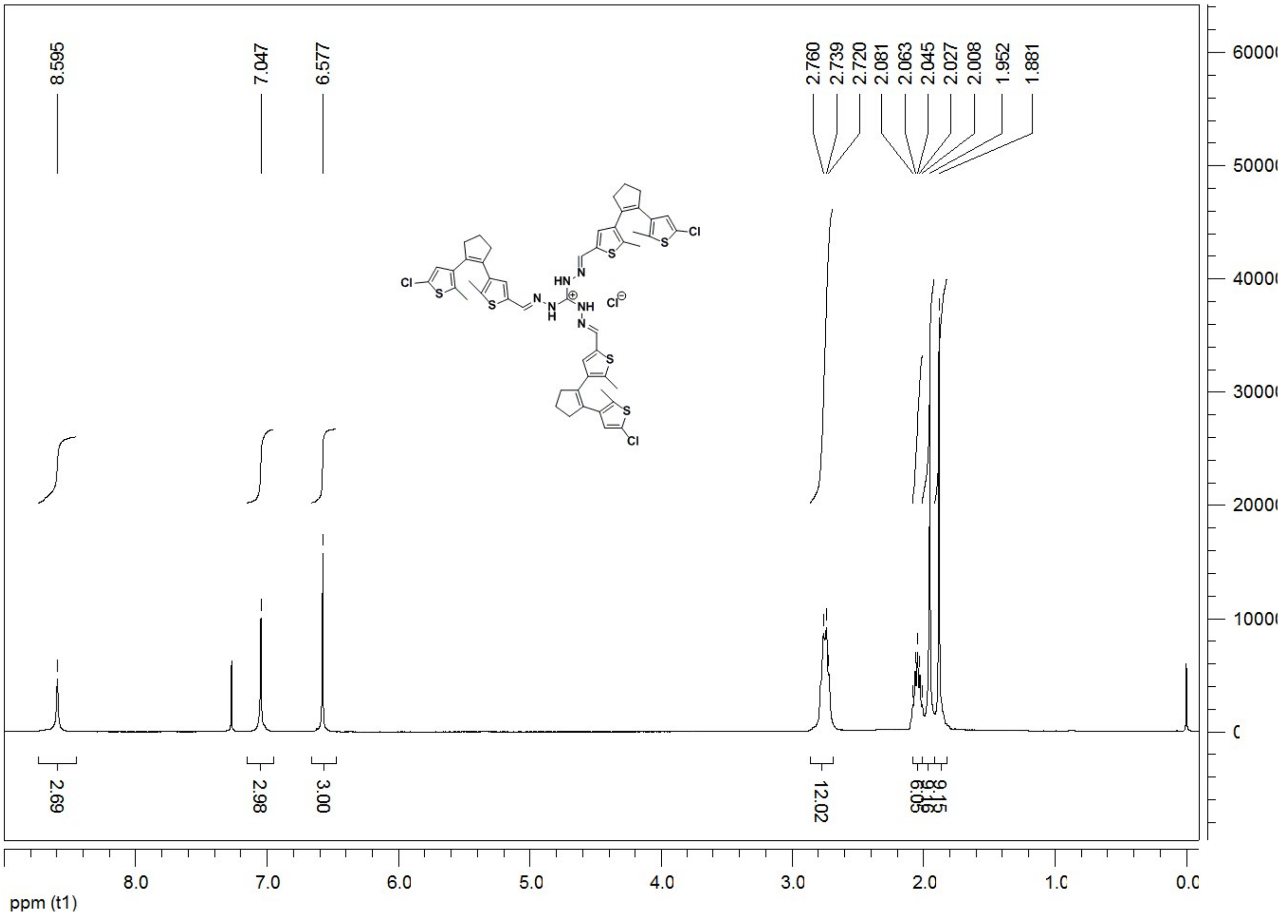


Fig. S16 ¹H NMR ($CDCl_3$, 400 MHz) spectrum of compound **DTEG**.

20. ^{13}C NMR spectrum of DTEG

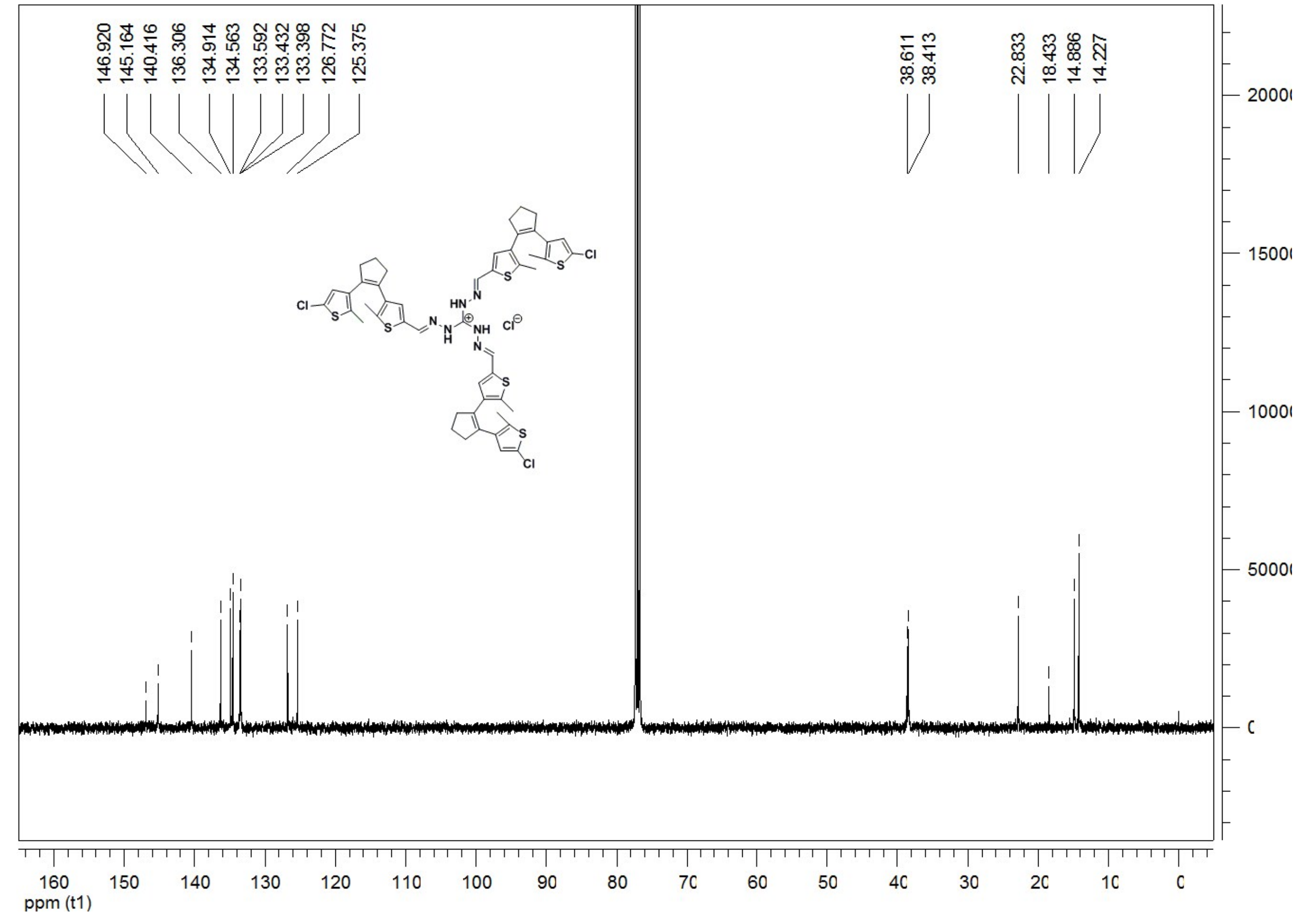
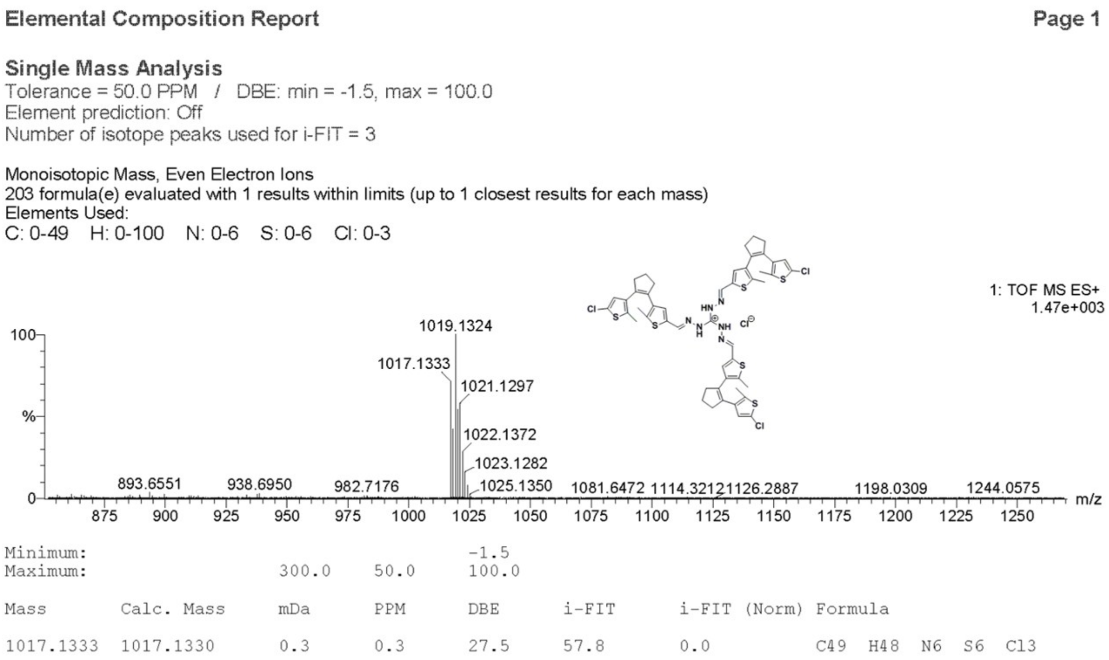


Fig. S17 ^{13}C NMR (CDCl$_3$, 100 MHz) spectrum of compound **DTEG**.

21. HRMS spectrum of DTEG



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
203 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-49 H: 0-100 N: 0-6 S: 0-6 Cl: 0-3

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Minimum:                                   -1.5
Maximum:                   300.0     50.0   100.0

Mass       Calc. Mass      mDa       PPM     DBE      i-FIT      i-FIT (Norm) Formula

1017.1333  1017.1330       0.3       0.3     27.5     57.8       0.0          C49  H48  N6  S6  Cl3
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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:

$$\frac{C_o}{C_c} = \frac{\Phi_{c\to o} \times \varepsilon_c}{\Phi_{o\to c} \times \varepsilon_o} = \frac{\Phi_{c\to o} \times A_c}{\Phi_{o\to c} \times A_o} \tag{E. 1}$$

where ε_o and ε_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, $\Phi_{c\to o}$ and $\Phi_{o\to c}$ are quantum yields of cycloreversion and cyclization, respectively. By comparing the PSS's obtained under irradiation at two different wavelengths λ' and λ'', a couple of equations of type (E. 1) are obtained. Assuming that the ratio $\Phi_{c\to o}$ / $\Phi_{o\to c}$ does not depend on the irradiation wavelength, we get:

$$\frac{C_o'}{C_c'} \Big/ \frac{C_o''}{C_c''} = \frac{A_c'}{A_o'} \Big/ \frac{A_c''}{A_o''} \tag{E. 2}$$

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

$$\frac{1-\alpha'}{\alpha'} \Big/ \frac{1-\alpha''}{\alpha''} = \frac{A_c'}{A_o'} \Big/ \frac{A_c''}{A_o''} \tag{E. 3}$$

In order to introduce experimental data into equation (E. 3), we can write that the absorbance A measured at any particular wavelength λ 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

$$A_c = A_o + \frac{A - A_o}{\alpha} \tag{E. 4}$$

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

$$\frac{1-\alpha^{'}}{\alpha^{'}} \Big/ \frac{1-\alpha^{''}}{\alpha^{''}} = 1 + \frac{\Delta^{'}}{\alpha^{'}} \Big/ 1 + \frac{\Delta^{''}}{\alpha^{''}} \tag{E. 5}$$

where $\Delta = (A\text{-}A_o)/A_o$ 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 Δ's measured at any given wavelength (the wavelength that maximizes the Δ's is usually chosen). Equating and developing (E. 5) yields the final formula:

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

where all the parameters Δ and ρ 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).

$$\frac{dC_C}{dt} = I_o \times \frac{1 - 10^{-Abs(\lambda_{irr})}}{V \times Abs(\lambda_{irr})} \times (\Phi_{o\to c} \times \varepsilon_{o\lambda_{irr}} \times l \times C_o - \Phi_{c\to o} \times \varepsilon_{c\lambda_{irr}} \times l \times C_c) \tag{E. 7}$$

$$Abs(\lambda_{obs}) = \varepsilon_{c\lambda_{obs}} \times l \times C_c + \varepsilon_{o\lambda_{obs}} \times l \times C_o \tag{E. 8}$$

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, λ_{irr} and λ_{obs} are the irradiation and observation wavelengths, ε_o and ε_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 for calculating $\Phi_{o\to c}$, 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:

$$\frac{dC_C}{dt} = \frac{I_o \Phi_{o \to c}\left(1 - 10^{-\varepsilon_{o\lambda_{irr}} C_o l}\right)}{V} \tag{E. 9}$$

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

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

$$\Phi_{o \to c} = \frac{V}{I_o l\left(1 - 10^{-\varepsilon_{o\lambda_{irr}} C_o l}\right)} \frac{dAbs(\lambda_{obs})}{dt} \tag{E. 11}$$

$\frac{dAbs(\lambda_{obs})}{dt}$ can be easily obtained from the slope of time-dependent absorption changes, and I_o can be calculated from reference compound **BTF6** with known $\Phi_{o \to c}$. In this way, we acquired $\Phi_{o \to c}$, 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.