Electronic Supplementary Information (ESI)

Multi-addressable photochromic terarylene containing benzo[*b*]thiophene-1,1-dioxide unit as ethene bridge: multifunctional molecular logic gates on unimolecular platform

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1. Characterization of BTO and BTO-Me





Figure S1. ¹H NMR (in CDCl₃. note: the peak at 5.30 ppm is from CH₂Cl₂), ¹H NMR (in DMSO- d_6 . note: the peak at 5.75 ppm is from CH₂Cl₂), ¹³C NMR (in CDCl₃) and HRMS spectrum of BTO.





Figure S2. ¹H NMR and ¹³C NMR (in CD₃CN) spectra and HRMS spectrum of BTO-Me.





Figure S3. Decay lines of absorption peaks of BTO at the PSS at 333 K. Absorbance monitoring at 333 K after reaching the PSS by UV irradiation at 365 nm in xylene $(2.0 \times 10^{-5} \text{ M})$, no obvious back reaction was observed at 391 and 575 nm after 20 h.

3. HPLC analysis data of BTO



Figure S4. HPLC traces of BTO eluted with CH_3OH at a flow rate of 0.6 mL·min⁻¹ detected at the isosbestic point: (1) Before UV irradiation; (2) Photostationary state (PSS) at 365 nm (C_{18} column, 250 × 4.6 mm).



4. Ions titration experiments of BTO in different order

Figure S5. Changes in absorption spectra of BTO in THF $(2.09 \times 10^{-5} \text{ M})$: (A) Adding 1.0 equiv. of Cu²⁺, and then 2.0 equiv. of Hg²⁺; (B) Adding 2.0 equiv. of Hg²⁺, then 5.0 and 10.0 equiv. of Cu²⁺.

5. Job plot of BTO-Hg $^{2+}$ and BTO-Cu $^{2+}$



Figure S6. Job plot of BTO-Hg²⁺ (the total concentration of BTO and Hg²⁺ is 50.0 uM).



Figure S7. Job plot of BTO- Cu^{2+} (the total concentration of BTO and Cu^{2+} is 50.0 uM).



6. Fluorescence spectra of BTO upon adding protons and ions

Figure S8. Fluorescence spectra changes of BTO upon adding Cu^{2+} , Hg^{2+} or protons in THF (2.09 × 10⁻⁵ M).



Figure S9. Fluorescence spectra changes of BTO upon adding different ions in THF $(2.09 \times 10^{-5} \text{ M}).$



Figure S10. Spectral changes of BTO-Me upon adding metal ions and protons in acetonitrile $(2.09 \times 10^{-5} \text{ M})$: (A) Absorbance changes; (B) fluorescence changes.



7. Calculation of the conversion yields and quantum yields

Figure S11. (A) Absorption spectra changes of BTO at different irradiation wavelengths in THF (2.09×10^{-5} M). The absorption spectrum of pure *c*-BTO was calculated using the reported procedure (E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704–3706); (B) Photochromism of BTO in THF (1.25×10^{-4} M).



Figure S12. Absorption spectra of the complexes at different irradiation wavelengths in THF (2.09×10^{-5} M). The absorption of the pure complex was calculated using the reported procedure (E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704–3706).

The absorption spectrum of the closed form was determined by the Fischer's method (E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704–3706 E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704–3706). The ratio of the equilibrium concentrations of the open form (C_0) and closed forms (C_c) at a given photostationary state (PSS) is expressed as follows:

$$\frac{C_o}{C_c} = \frac{\Phi_c \to o \times \mathcal{E}_c}{\Phi_o \to c \times \mathcal{E}_o} = \frac{\Phi_c \to o \times A_c}{\Phi_o \to c \times A_o}$$
(E. 1)

Where ε_0 and ε_c are the molar absorption coefficients of the open and closed forms, and A_0 and A_c are the absorption of a sample of same chromophore concentration containing only the open or closed form, 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 $\Phi_{c\to 0}/\Phi_{0\to c}$ does not depend on the irradiation wavelength, we get:

$$\frac{C_{o}^{'}}{C_{c}^{'}} \left/ \frac{C_{o}^{"}}{C_{c}^{"}} = \frac{A_{c}^{'}}{A_{o}^{'}} \right/ \frac{A_{c}^{"}}{A_{o}^{"}}$$
(E. 2)

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

$$\frac{1-\alpha'}{\alpha'} / \frac{1-\alpha''}{\alpha''} = \frac{A'_c}{A'_o} / \frac{A''_c}{A''_o}$$
(E. 3)

In order to introduce experimental data into equation (E. 3), we can write that the absorbance A measured at any particular wavelength λ of a mixture of open and closed forms, where the overall concentration $C_0 + C_c$ is constant, is given by:

$$A = (1 - \alpha)A_0 + \alpha A_c$$

or

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

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

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

Where $\Delta = (A - A_0)/A_0$ 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 of 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 absorption profiles obtained from photolysis continues were fitted with 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*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, vol. 2, p. 167) using the differential equation (E. 7) and phenomenological equation (E. 8).

$$\frac{dC_{\rm C}}{d\epsilon} = I_0 \times \frac{1 - 10^{-Abs(\lambda_{\rm irr})}}{Abs(\lambda_{\rm irr})} \times (\Phi_{0\to \rm C} \times \varepsilon_{0,\lambda_{\rm irr}} \times l \times C_0 - \Phi_{\rm C\to O} \times \varepsilon_{\rm C,\lambda_{\rm irr}} \times l \times C_{\rm C})$$
(E. 7)

$$Abs(\lambda_{obs}) = \varepsilon_{C,\lambda_{obs}} \times l \times C_C + \varepsilon_{O,\lambda_{obs}} \times l \times C_0$$
(E. 8)

where C_o and C_c are the concentrations of open form and closed form), I_0 is the incident irradiation intensity, 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 (365 nm), respectively (H. Dürr and H. Bouas-Laurent, Photochromism: Molecules and Systems, Elsevier, Amsterdam, 2003; J. C. Crano and R. Guglielmetti, Organic Photochromic and Thermochromic Compounds, Plenum Press, New York, 1999).

Fig. S11 shows the evolution of the absorbance values at 578 nm as a function of irradiation time at 365 nm (Open form (OF) \rightarrow Closed form (CF) reaction) and 575 nm (CF \rightarrow OF reaction). Under the irradiation at 365 nm light, the absorbance increases until the photo-stationary state is reached after 1000 s, and returns back completely to its initial level within 500 s upon visible irradiation at 575 nm. These absorption profiles were fitted with a simple photochromic model involving the OF and CF isomers by means of a numerical integration procedure using the differential E(7) and the phenomenological E(8), where $C_{\rm C}$ and $C_{\rm O}$ denote the concentrations of open form and closed form, I_0 is the incident irradiation intensity, $\lambda_{\rm irr}$ and $\lambda_{\rm obs}$ are the irradiation and observation wavelengths, respectively.

As can be deduced from Fischer analysis, the conversion yield of BTO at 365 nm was 77.6%. According to the Fischer analysis and photolysis continue, we obtain cyclization quantum yield ($\Phi_{o\rightarrow c}$) of BTO in THF are 28.5%. Similarly, we obtain the conversion yield and cyclization quantum yield of BTO-Hg²⁺ at 365 nm were 99.8% and 43.1% and the conversion yield and cyclization quantum yield of BTO-Cu²⁺ at 365 nm were 84.7% and 13.4%, respectively.

8. Spectra of BTO for constructing different molecular logic gates



8.1 Spectra of BTO for the half-adder and half-subtractor

Figure S13. Absorption spectra changes of BTO upon adding Hg^{2+} and UV irradiation (365 nm) in THF (2.09 × 10⁻⁵ M)



Figure S14. Absorption spectra changes of BTO upon adding H^+ and UV irradiation (365 nm) in THF (2.09×10^{-5} M).

Innuta		Outputs				
mpu	lS	Half-Adder Half-Su			ubtractor	
Le	Le	Out ₁	Out ₂	Out ₃	Out ₂	
In_1	III_2	AND	XOR	IHBIT	XOR	
(365 nm)	(п)	$(A_{638 \text{ nm}})$	$(A_{371 \text{ nm}})$	$(A_{345 \text{ nm}})$	$(A_{371 \text{ nm}})$	
0	0	0	0	0	0	
1	0	0	1	0	1	
0	1	0	1	1	1	
1	1	1	0	0	0	

	Fable	S1 .	Truth	tables	for	half	-adder	and	half	-subtr	actor
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8.2 Spectra of BTO for 2-to-4 decode



Figure S15. Absorption spectra changes of BTO upon adding Cu^{2+} and UV irradiation (365 nm) in THF (2.09 × 10⁻⁵ M).



Figure S16. Fluorescence spectra changes of BTO upon adding Cu^{2+} and UV irradiation (365 nm) in THF (2.09 × 10⁻⁵ M).

8.3 Spectra of BTO for 4-to-2 encode



Figure S17. Absorption spectra changes of BTO upon adding different Hg^{2+} , Cu^{2+} and UV irradiation (365nm) in THF (2.09 × 10⁻⁵ M).



Figure S18. Fluorescence spectra changes of BTO upon adding different Hg^{2+} , Cu^{2+} , protons and UV irradiation (365nm) in THF (2.09 × 10⁻⁵ M).

8.4 Spectra of BTO for 1:2 demutiplexer



Figure S19. Absorption spectra changes of BTO upon adding Hg^{2+} and further UV irradiation (365 nm) in THF (2.09 × 10⁻⁵ M).



Figure S20. Fluorescence spectra changes of BTO upon adding Hg^{2+} and further UV irradiation (365 nm) in THF (2.09 × 10⁻⁵ M).



Figure S21. Absorption spectra changes of BTO upon adding H^+ and UV irradiation (365 nm) in THF (2.09 × 10⁻⁵ M).



Figure S22. Fluorescence spectra changes of BTO upon adding H^+ and further UV irradiation (365 nm) in THF (2.09 × 10⁻⁵ M).

In	puts	outputs		
In ₁	In ₂	Out ₁	Out ₂	
(H ⁺)	(365 nm)	$F_{ m 467nm}$	$A_{638 \mathrm{~nm}}$	
0	0	0	0	
1	0	1	0	
0	1	0	0	
1	1	0	1	

 Table S2.
 Truth table for 1:2 demultiplexer

Characterization of *c*-BTO



Figure S23. ¹H NMR (in CDCl₃) spectrum of c-BTO.

9. Emission spectra of Closed from *c*-BTO, Open form BTO, and Photostationary state in methylene chloride at different state upon excitation at the isobestic point wavelength of 345 nm.



Figure S24. Emission spectra of BTO $(2.0 \times 10^{-5} \text{ M})$ in methylene chloride at different state upon excitation at the isobestic point wavelength of 345 nm: Closed from *c*-BTO, Open form BTO, and Photostationary state (PSS).