Electronic Supplementary Information (ESI)

# Water-compatible photochromism and molecular logic gates realized by a

# bis-glycosyl diarylethene

Xianzhi Chai,<sup>a1</sup> You-Xin Fu,<sup>a1</sup> Tony D. James,<sup>b</sup> Junji Zhang,<sup>a\*</sup> Xiao-Peng He<sup>a\*</sup> and He Tian<sup>a</sup>

<sup>a</sup> Key Laboratory for Advanced Materials & Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, PR China. Email: zhangjunji@ecust.edu.cn (J.Z.); xphe@ecust.edu.cn (X.-P.H.)
<sup>b</sup> Department of Chemistry, University of Bath, Bath, BA2 7AY, UK.
<sup>1</sup> Equal contribution.

# **Table of Contents**

- 1. Materials and general procedures
- 2. Synthesis
- 3. Additional Figures and Tables
- 4. Original spectral copies of new compounds

### 1. Materials and general procedures

All starting materials were obtained from commercial suppliers and were used as received. Solvents are of analytical purity and used without further treatment. Methyl 4aminobutanoate, EDCI and N,N-Diisopropylethylamine (DTEA) were purchased from Energy Chemical. Tetrakis(triphenylphosphine) palladium and *n*-butyl lithium were supplied by J&K Chemical. 1,2-bis(5-cholo-2-methyl-3-thienyl)cyclopentene (1) was synthesized and purified according to the established procedure.<sup>1,2</sup> Compound **2** was synthesized according to our previously established procedure.<sup>3</sup>

<sup>1</sup>H NMR spectra were recorded on a Bruker AM 400 spectrometer with tetramethyl silane (TMS) as internal reference. MS were recorded on EI or ESI mass spectroscopy. Absorption spectra were measured on a Varian Cary500 UV-Vis spectrophotometer. Fluorescence spectra were measured on a F97Pro Fluorescence spectrophotometer. Irradiation at 254 nm was carried out using a hand-hold UV lamp (the power density is *ca*. 2.0 W/m<sup>2</sup>), and visible irradiation using a flashlight (the power density is *ca*. 150 W/m<sup>2</sup>) with a broad band interference filters (Shenyang HB optical Technology) for  $\lambda$  > 500 nm.

For aborption and fluorescence spectral measurement, compound was dissolved in DMSO first and then diluted in a deionized water with 0.25‰ Triton X-100 (v/v). For acidbase switching experiments, TFA or TEA was dissolved in deionized water to obtain a 1 mM concentrated solution, which was then added into the above water solution.

The measurement of the ring-closing ( $\varphi_{254} = 0.176$ ) and ring-opening quantum yields ( $\varphi_{525} = 0.013$ ) were carried out according to a previous report.<sup>4</sup> In briefly, quantum yields of cyclization ( $\varphi_{o-c}$ ) and cycloreversion ( $\varphi_{c-o}$ ) were calculated upon irradiation at 313 and 517 nm, respectively, using **BTF6** as the reference by means of the formula below:

$$\varphi_{o-c} = \frac{V}{l\varepsilon_{c-d}l(1-10^{-l\varepsilon_{o-i}c})} \times \frac{dA}{dt}$$
$$\varphi_{c-o} = \frac{V}{l\varepsilon_{c-d}l(1-10^{-l\varepsilon_{c-i}c})} \times \frac{dA}{dt}$$

where  $\varphi_{\text{o-c}}$  is the photocyclization quantum yield of ring-open isomer at the irradiation wavelength,  $\varphi_{\text{c-o}}$  the photocycloreversion quantum yield of ring-closed isomer at the irradiation wavelength, *I* the optical path-length, *V* the volume of reaction solution, *I* the light intensity,  $\varepsilon_{\text{c-d}}$  the molar extinction coefficient of ring-closed isomer at the detection wavelength,  $\varepsilon_{\text{o-i}}$  the molar extinction coefficient of ring-open isomer at the irradiation wavelength,  $\varepsilon_{\text{c-i}}$  the molar extinction coefficient of ring-closed isomer at the irradiation wavelength,  $\varepsilon_{\text{c-i}}$  the molar extinction coefficient of ring-closed isomer at the irradiation wavelength and dA/dt thehe rate of absorbance change at the detection wavelength.

### 2. Synthesis



Scheme S1. Synthesis of compound 10.

## 2.1 Synthesis of Compound 3o



To a stirred solution of 1,2-bis(5-cholo-2-methyl-3-thienyl)cyclopentene (1) (1.00 g, 3.04 mmol) in THF (20 mL) at -78°C under Ar in the absence of light, was added dropwise 2.5 M *n*-BuLi in hexane (2.70 mL, 6.69 mmol), and the reaction mixture was stirred at -70°C for 30 min. Then the mixture was stirred at room temperature for another 30 min and recooled to -70°C. Then tributyl borate (1.38 g, 6.00 mmol) was quickly added. This reddish solution was stirred overnight at room temperature, and was then used in the Suzuki cross

coupling reaction without further purification.

A mixture of compound **2** (3.30 g, 6.00 mmol), the catalyst Pd (PPh<sub>3</sub>)<sub>4</sub> and THF (10 mL) was stirred for 15 min at room temperature. Then aqueous Na<sub>2</sub>CO<sub>3</sub> (8 mL, 2 M) was added. The resulting mixture was heated to a temperature of 60 °C, and the solution of boric acid ester above-mentioned was added dropwise by syringe. Subsequently, the mixture was heated to 70 °C, kept for 6 h and then cooled to room temperature. The resulting mixture was collected and solvent removed under reduced pressure to produce a brown solid. The solid was further purified by silica gel column to obtain **30** as a yellow solid (2.19 g, yield 60%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.57 (d, *J* = 7.3 Hz, 2H), 8.50 (d, *J* = 8.1 Hz, 2H), 8.40 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 8.2 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.05 (s, 2H), 4.23 (t, *J* = 7.0 Hz, 4H), 3.64 (s, 10H), 3.30 (br s, 8H), 2.85 (t, *J* = 7.4 Hz, 4H), 2.78 (br s, 8H), 2.44 (t, *J* = 7.6 Hz, 4H), 2.05-2.12 (m, 6H), 2.00 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  173.4, 164.5, 164.0, 156.1, 139.4, 136.7, 136.5, 134.7, 134.4, 133.6, 132.7, 131.2, 130.4, 129.9, 129.7, 126.1, 125.6, 125.3, 124.0, 123.1, 116.5, 114.9, 62.7, 53.1, 51.6, 39.4, 38.5, 31.7, 23.5, 23.0, 14.5. HRMS-ESI (*m*/*z*): [M+H]<sup>+</sup> Calcd. for C<sub>71</sub>H<sub>71</sub>N<sub>6</sub>O<sub>8</sub>S<sub>2</sub><sup>+</sup> 1199.4775, found 1199.4764.

#### 2.2 Synthesis of Compound 5



To a solution of **3o** (1.00 g, 0.833 mmol) in THF (10 mL) was added a solution of  $\text{LiOH}\cdot\text{H}_2\text{O}$  (0.70 g, 16.7 mmol) in  $\text{H}_2\text{O}$  (5 mL). Then the mixture was stirred at room temperature under argon for 24 h. Then the solution was concentrated under reduced pressure to remove THF. To the rest of the solution was added HCl aqueous solution dropwise to adjust the pH to neutral and precipitates formed. The precipitates were filtered,

re-dissolved in menthol and dried in reduce pressure to remove the remaining water. The crude product was used for the next step without further purification.

To the solution of the product in DMF (10 mL) above-mentioned was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 0.80 g, 4.17 mmol) and 1hydroxybenzotriazole (HOBt, 0.34 g, 2.50 mmol) at 0 °C. The mixture was stirred for 1 h under argon and then compound **4** (0.71 g, 1.67 mmol) and *N*,*N*-diisopropylethylamine (DIEA, 1 mL) were added. The mixture was stirred at room temperature for 24 h. The resulting mixture was poured into water and filtered to yield a yellowish powder, which was purified by silica gel column to obtain **5** as a yellow solid (0.83 g, 50%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.56 (d, *J* = 7.2 Hz, 2H), 8.49 (d, *J* = 8.1 Hz, 2H), 8.40 (d, *J* = 8.4 Hz, 2H), 7.90 (s, 2H), 7.67 (t, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 4H), 7.35 (d, *J* = 7.9 Hz, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 2H), 6.86 (t, *J* = 5.4 Hz, 2H), 5.81 (d, *J* = 9.4 Hz, 2H), 5.57-5.52 (m, 4H), 5.23 (dd, *J* = 10.3, 3.2 Hz, 2H), 4.61–4.49 (m, 4H), 4.23–4.10 (m, 10H), 3.66 (s, 4H), 3.30 (br s, 8H), 2.85 (t, *J* = 7.3 Hz, 4H), 2.79 (br s, 8H), 2.31 (t, *J* = 7.1 Hz, 4H), 2.20 (br s, 6H), 2.13–2.08 (m, 6H), 2.03 (br s, 6H), 2.00 (br s, 12H), 1.86 (br s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.8, 170.3, 170.1, 169.9, 169.0, 153.3, 145.6, 138.0, 136.9, 135.7, 135.1, 132.0, 129.0, 126.6, 125.8, 125.5, 122.6, 121.3, 117.9, 117.3, 115.0, 86.1, 70.8, 67.9, 66.9, 61.1, 53.8, 42.10, 36.6, 34.9, 33.8, 31.5, 29.7, 24.2, 20.6, 20.5, 20.2, 18.5, 17.4. HRMS-ESI (*m*/*z*): [M+H]<sup>+</sup> Calcd. for C<sub>103</sub>H<sub>111</sub>N<sub>14</sub>O<sub>24</sub>S<sub>2</sub><sup>+</sup> 1991.7337, found 1991.7339.

### 2.3 Synthesis of 10



To a stirring solution of compound **5** (0.50 g, 0.25 mmol) in MeOH (3 mL) was slowly added 1 M solution of MeONa in MeOH to adjust the pH to 9–10. The resulting mixture was left for 3 hours at room temperature. The reaction pH was then adjusted with  $H^+$  to pH 6 S-6

and the precipitate was filtered. The precipitate was washed with water sufficiently and dried in reduce pressure to produce a yellow product of **1o** (0.33 g, yield: 80%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.47–8.36 (m, 6H), 8.03 (s, 2H), 7.80 (t, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 6.8 Hz, 4H), 7.40–7.23 (m, 10H), 5.43 (d, *J* = 9.2 Hz, 2H), 5.34–5.30 (m, 2H), 5.23 (d, *J* = 4.3 Hz, 2H), 5.05 (s, 2H), 4.78 (s, 2H), 4.71-4.53 (m, 4H), 4.25 (t, *J* = 5.2 Hz, 4H), 4.06-3.97 (m, 6H), 3.05 (q, *J* = 7.1 Hz, 12H), 2.84 (s, 6H), 2.18 (t, *J* = 7.3 Hz, 8H), 2.03–1.86 (m, 12H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>)  $\delta$  174.5, 171.6, 163.6, 163.0, 153.3, 145.00, 140.2, 136.7, 134.3, 134.1, 131.5, 129.6, 129.0, 128.6, 126.2, 125.2, 124.8, 123.1, 122.6, 122.5, 121.4, 115.6, 88.0, 78.3, 73.7, 72.2, 69.3, 48.5, 45.4, 33.6, 31.2, 29.0, 24.4, 22.0. HRMS-ESI (*m*/*z*): [M+H]<sup>+</sup> Calcd. for C<sub>87</sub>H<sub>200</sub>N<sub>14</sub>O<sub>16</sub>S<sub>2</sub><sup>+</sup> 1655.6462, found 1655.6492.

# 3. Additional figures and tables



**Figure S1.** Absorption spectral changes of **3o** ( $1 \times 10^{-5}$  M) in CH<sub>3</sub>CN upon irradiation with UV (254 nm) and visible light (>500 nm).



**Figure S2.** (a) Absorption spectral changes of **1o**  $(1 \times 10^{-5} \text{ M})$  in water solution (with 0.25‰ Triton X-100) upon alternating additions of TFA (6.0 eq) and TEA (6.0 eq). (b) Absorption spectra of **1o** at four different states.



**Figure S3.** (a) pH-dependent fluorescence changes of **1o** ( $1 \times 10^{-5}$  M) as a function of pH (from 8.0 to 2.0) in water solution (with 0.25‰ Triton X-100). (b) Effect of pH on the fluorescence intensity changes of **1o** ( $1 \times 10^{-5}$  M)) at 520 nm.



**Figure S4.** Plot of pH vs log[( $I_{max}$ -I)/(I-I<sub>min</sub>)], where *I* is the fluorescence intensity of **10** at 520 nm upon excitation at 408 nm. The y-intercept<sup>a</sup> is the pK<sub>a</sub> value (4.41 ± 0.09) of **10**. According to the Henderson – Hasselbach equation, log[( $I_{max}$ -I)/(I-I<sub>min</sub>)] = pH – pK<sub>a</sub>. The pK<sub>a</sub> value for **10** was the y-intercept of a plot of pH vs log[( $I_{max}$ -I)/(I-I<sub>min</sub>)].



**Figure S5.** Absorption spectral changes (a) and fatigue resistance (b) of **1Ho**  $(1 \times 10^{-5} \text{ M})$  in water solution (with 0.25‰ Triton X-100) upon alternating UV (254 nm) and visible light (>500 nm) irradiations.



**Figure S6.** Stacked normalized fluorescence spectra status of **1o** ( $1 \times 10^{-5}$ mol/L) in water solution (with 0.25‰ Triton X-100) induced by UV/Vis and TFA/TEA stimuli. All emissions were produced upon excitation at 408 nm.

Compound	10	1c	1Ho	1Hc
φ	0.02	0.003	0.12	0.03

**Table S1.** Fluorescence quantum yields ( $\phi$ ) of the four forms of compound **10** 

Table S2. Truth table for INH gates

Input <sup>a</sup>	Quitauth		
In1 (UV)	In2 (TFA)	Output <sup>2</sup>	
0	0	0	
0	1	1	
1	0	0	
1	1	0	

 $^{\mathrm{a}}\text{The}$  UV irradiation time ( 254nm ) was 2 minutes and 6.0 eq of TFA was added.

<sup>b</sup>The normalized fluorescence intensity  $I_{520}$  was regarded as the output signal. When  $I_{520} \ge 0.5$ , the output signal was defined as **1** and the actual output values wwere  $2500 \le I_{520} < 5000$ . Otherwise, the output signal was defined as **0** and the actual output values were  $300 < I_{520} < 2500$ .

	Quiting with			
In1 (Vis)	In2 (UV)	In3 (TFA)	In4 (TEA)	Output
0	0	0	0	0
0	0	0	1	0
0	0	1	0	1
0	0	1	1	0
0	1	0	0	0
0	1	0	1	0
0	1	1	0	0
0	1	1	1	0
1	0	0	0	0
1	0	0	1	0
1	0	1	0	1
1	0	1	1	0
1	1	0	0	0
1	1	0	1	0
1	1	1	0	0
1	1	1	1	0

Table S3. Truth table for logic circuit

<sup>a</sup>The irradiation time of UV (254 nm) and visible light (>500 nm) was 2 minutes and 10 minutes, respectively. 6.0 eq. of both TFA and TEA were added.

<sup>b</sup>The normalized fluorescence intensity  $I_{520}$  was regarded as the output signal. When  $I_{520} \ge 0.5$ , the output signal was defined as **1** and the actual output values were  $2500 \le I_{520} < 5000$ . Otherwise, the output signal was defined as **0** and the actual output values were  $300 < I_{520} < 2500$ .

# 4. Original spectral copies of new compounds



<sup>13</sup>C NMR spectrum of compound **30** 



### HRMS spectrum of compound 30



<sup>1</sup>H NMR spectrum of compound **5** 



HRMS spectrum of compound 5



<sup>13</sup>C NMR spectrum of compound **10** 



HRMS spectrum of compound 10

### References

- 1. L. N. Lucas, J. J. D. De Jong, J. H. Van Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem.*, 2003, 155-166.
- 2. B. Qin, R. Yao, X. Zhao and H. Tian, Org. Biomol. Chem., 2003, 1, 2187-2191.
- Y. Fu, J. Zhang, H. Wang, J.-L. Chen, P. Zhao, G.-R. Chen and X.-P. He, *Dyes Pigm.*, 2016, 133, 372-379.
- 4. W. Li, C. Jiao, X. Li, Y. Xie, K. Nakatani, H. Tian and W. Zhu, *Angew. Chem. Int. Ed.*, 2014, **53**, 4603-4607.