Electronic Supplementary Information (ESI)

Photoswitching between black and colourless spectra exhibits resettable spatiotemporal logic

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Contents

1. Experimental details

All solvents were of analytical grade. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in $CDCl_3$ were measured on a Bruker AM-400 spectrometer with tetramethylsilane (TMS) as internal standard. MS were recorded on a Waters ESI mass spectroscopy. Absorption and fluorescence spectra were measured on a Varian Cary 100 spectrometer and a Horiba Scientific FluoroMax-4 spectrometer, respectively.

Synthesis

4-Bromo-5-methyl-2-phenylthiazole was synthesized according to reported methods (K. Uchida, T. Ishikawa, M. Takeshita, M. Irie, *Tetrahedron*, 1998, **54**, 6627-6633).

BBT or **4,5-dibromobenzo[1,2-*c*:3,4-*c*']bis[1,2,5]thiadiazole** was synthesized according to reported methods (W. H. Zhu, Y. H. Yang, R. Métivier, Q. Zhang, R. Guillot, Y. S. Xie, H. Tian, K. Nakatani, *Angew. Chem. Int. Ed.* **2011**, *50*, 10986-10990).

BTA and *c*-BTA. To a solution of 4-bromo-5-methyl-2-phenylthiazole (1.51 g, 5.97 mmol) in dry THF (30 mL) was added n-BuLi (2.63 mL, 6.57 mmol) dropwise at -78 °C under argon. After 1 h of stirring at -78 °C, $B(OCH_3)_3$ (0.8 mL, 7.23 mmol) was added. The reaction mixture was stirred at the same temperature for 2 h, then gradually warmed up to room temperature and used for the next Suzuki coupling reaction, the THF solvent was pumpde under reduced pressure at room temperature. The unpurified mixture was dissolved in dioxane, and reacted with 4,5-dibromobenzo[1,2-*c*:3,4-*c*']bis[1,2,5]thiadiazole (BBT) (0.352 g, 0.10 mmol) under Suzuki coupling reaction using $Pd(PPh_3)_4$ (0.1 g, 0.09 mmol) and K_2CO_3 aqueous solution (10 mL, 2 M) as catalysts in dioxane (35 mL) for 12 h. After cooling, water was added and the reaction mixture was extracted with ethyl acetate. The combined organic layer was washed with H_2O and brine, dried over anhydrous Na_2SO_4, and evaporated under reduce pressure. The crude product was purified by column chromatography (DCM) on silica gel and obtained as a light yellow solid **BTA** (193 mg, 35.7% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.84-7.82 (t, J = 4.4 Hz, 4H), 7.37 (s, 6H), 2.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 164.83, 156.56, 147.91, 146.16,

133.53, 130.99, 129.85, 128.86, 126.37, 12.43. MS (ESI, m/z): $[M + H]^+$ calcd for $C_{26}H_{17}N_6S_4$, 541.0398; found, 541.0393.

***c*-BTA** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.12-8.10 (m, 4H), 7.61-7.53 (m, 6H), 2.21 (s, 6H).

Preparation of photochromic film. The photochromic film was prepared under dark conditions as follows: 5.0 mg of **BTA** and 100 mg of PLA were dissolved in 6.0 mL of chloromethane. The solution was filtered by a filtering membrane (0.22 μm) before being spin-coated on quartz plates using a spin-coater. After air drying for 24 h, several films with different thickness (14-32 μm) were thus obtained.

2. Photochromic and fluorescence properties of BTA

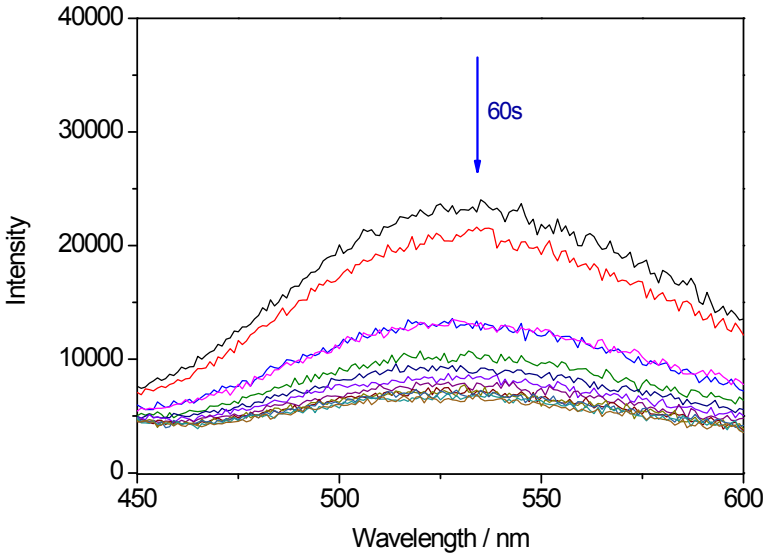


Figure S1. Changes in emission spectra of **BTA** upon 302-nm irradiation.

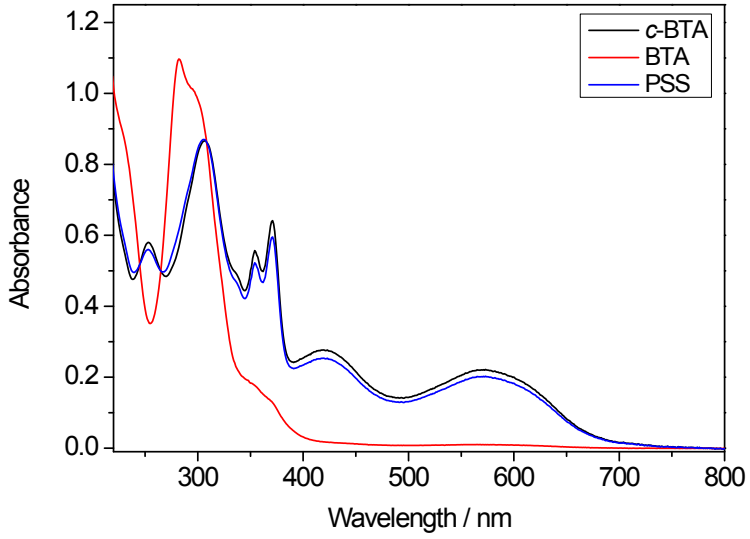


Figure S2. Pure closed form ***c*-BTA** (black line) was irradiated with visible light to pure open form **BTA** (red line), which was then irradiated with 302-nm UV light to return back to PSS (blue line), demonstrating ≥ 91% conversion.

3. Theoretical calculations

Computational details

We employed density functional theory (DFT) calculations to optimize the ground state geometries of compounds ***c*-BTA** and ***c*-BN** using the hybrid B3LYP functional [1] and the 6-31G** basis set [2]. Frequency analyses show that the optimized geometries are true minima on potential energy surface. Time-dependent (TD) DFT calculations were then carried out using the hybrid PBE0 functional [3] and the 6-311+G(d,p) basis set [4]. In DFT and TD-DFT calculations, solvent effects (chloroform for *c*-BTA and acetonitrile for *c*-BN) were taken into account by the polarizable continuum model (PCM) [5]. All calculations were carried out using the Gaussian09 program package [6].

References

[1] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[2] Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261.

[3] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

[4] Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654.

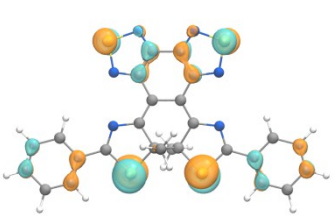
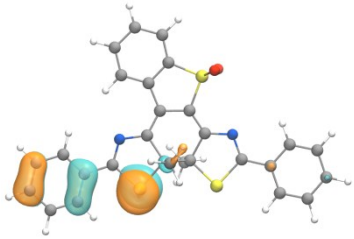
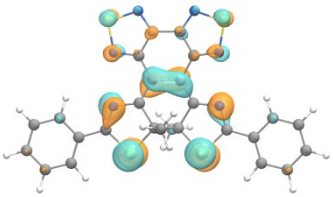
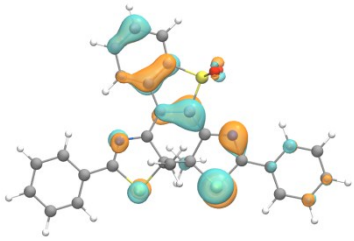
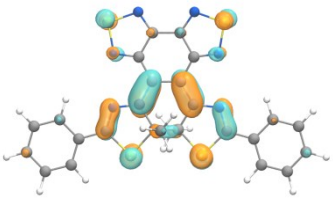
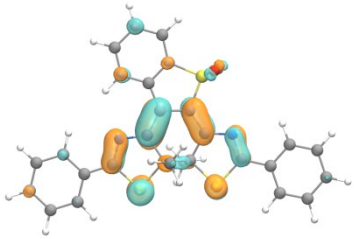
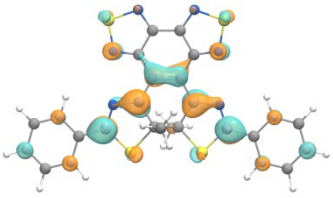
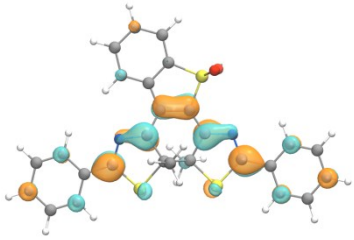
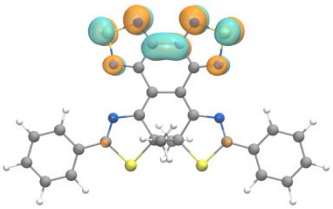
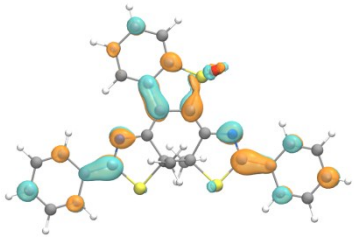
[5] Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999−3093.

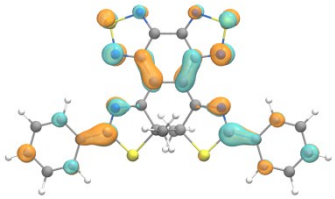
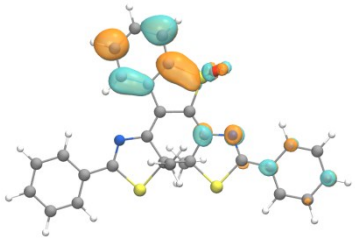
[6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision A.2; Gaussian, Inc.: Wallingford CT, 2009.

Table S1. TD-DFT results for low-lying excited states of compounds ***c*-BTA** and ***c*-BN**.

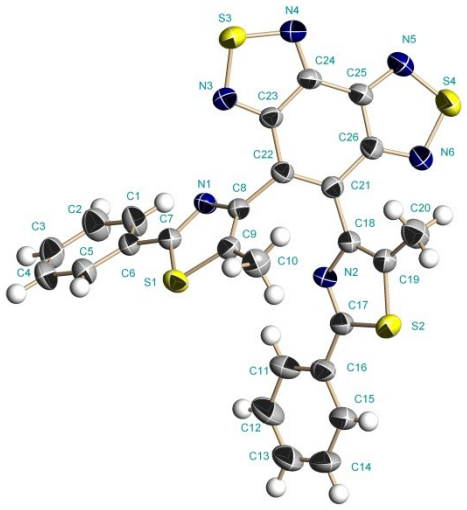
Compounds	Excited state	λ_{abs}	f	MO composition
***c*-BTA**	S_1	2.01 eV, 615 nm	0.275	H → L (99%)
	S_2	2.70 eV, 459 nm	0.181	H → L+1 (99%)
	S_3	2.83 eV, 437 nm	0.324	H → L+2 (97%)
	S_4	3.38 eV, 367 nm	0.287	H-1 → L (86%)
	S_5	3.69 eV, 336 nm	0.150	H-2 → L (93%)
***c*-BN**	S_1	2.23 eV, 556 nm	0.390	H → L (98%)
	S_2	3.08 eV, 402 nm	0.214	H → L+1 (93%)
	S_3	3.52 eV, 352 nm	0.318	H-1 → L (83%)
	S_4	3.77 eV, 329 nm	0.263	H-2 → L (83%)
	S_5	3.85 eV, 322 nm	0.176	H → L+2 (78%)

Table S2. Contour plot of frontier molecular orbitals of compounds ***c*-BTA** and ***c*-BN**.

	***c*-BTA**	***c*-BN**
HOMO-2		
HOMO-1		
HOMO		
LUMO		
LUMO+1		

LUMO+2		

4. Single crystal structure and relevant data for BTA



The single crystal structure of **BTA** was obtained by the diffusion method from a mixture of CH_2Cl_2 and octane at room temperature. The crystallographic data of **BTA** have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 1049488.

Table S3. Crystal and structural data of **BTA**

Compounds	**BTA**
Empirical formula	$C_{26}H_{16}N_6S_4$
Formula weight	540.69
Temp, K	293(2)
Crystal system	monoclinic
Space group	P21/n
a, Å	8.8711(9)
b, Å	25.349 (2)
c, Å	11.4426(4)
α, deg	90
β, deg	110.358(2)
γ, deg	90
Volume, Å^3	2412.4 (4)
Z	4

density(calc), mg/mm^3	1.489
crystal size,mm^3	0.10 × 0.07 × 0.01
index ranges	$-10 \le h \le 6$, $-30 \le k \le 16$, $-13 \le l \le 12$
reflections collected	4178
final *R* indices [I>=2σ (I)]	$R_1 = 0.0738$, $wR_2 = 0.1344$

Table S4. Bond lengths in **BTA**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.388(5)	C17	S2	1.736(3)
C2	C3	1.398(5)	C18	C19	1.372(4)
C3	C4	1.365(6)	C18	N2	1.385(4)
C4	C5	1.382(5)	C18	C21	1.487(4)
C5	C6	1.393(4)	C19	C20	1.485(5)
C6	C7	1.469(4)	C19	S2	1.719(3)
C7	N1	1.309(4)	C21	C22	1.366(4)
C7	S1	1.735(3)	C21	C26	1.455(4)
C8	C9	1.355(4)	C22	C23	1.464(4)
C8	N1	1.382(4)	C23	N3	1.337(4)
C8	C22	1.486(4)	C23	C24	1.420(4)
C9	C10	1.486(5)	C24	N4	1.336(4)
C9	S1	1.726(3)	C24	C25	1.432(4)
C11	C16	1.370(5)	C25	N5	1.336(4)
C11	C12	1.391(5)	C25	C26	1.422(4)
C12	C13	1.360(6)	C26	N6	1.341(4)
C13	C14	1.356(6)	N3	S3	1.622(3)
C14	C15	1.395(6)	N4	S3	1.624(3)
C15	C16	1.398(5)	N5	S4	1.626(3)
C16	C17	1.470(4)	N6	S4	1.618(3)
C17	N2	1.309(4)			

Table S5. Bond angles in **BTA**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C1	C2	121.5(3)	C18	C19	C20	129.6(3)
C1	C2	C3	119.3(4)	C18	C19	S2	108.5(2)
C4	C3	C2	119.8(4)	C20	C19	S2	121.8(2)
C3	C4	C5	120.4(3)	C22	C21	C26	118.9(3)
C4	C5	C6	121.1(4)	C22	C21	C18	123.1(3)
C1	C6	C5	117.9(3)	C26	C21	C18	117.9(3)
C1	C6	C7	120.2(3)	C21	C22	C23	118.5(3)
C5	C6	C7	121.9(3)	C21	C22	C8	123.2(3)
N1	C7	C6	124.1(3)	C23	C22	C8	118.2(2)
N1	C7	S1	113.8(2)	N3	C23	C24	112.9(2)
C6	C7	S1	122.1(2)	N3	C23	C22	124.2(3)
C9	C8	N1	116.7(3)	C24	C23	C22	122.7(3)
C9	C8	C22	127.0(3)	N4	C24	C23	114.9(3)
N1	C8	C22	116.2(3)	N4	C24	C25	127.1(3)
C8	C9	C10	129.6(3)	C23	C24	C25	118.0(3)
C8	C9	S1	108.7(2)	N5	C25	C26	114.3(3)
C10	C9	S1	121.7(3)	N5	C25	C24	127.6(3)
C16	C11	C12	120.1(4)	C26	C25	C24	118.2(3)
C13	C12	C11	120.5(4)	N6	C26	C25	113.1(3)
C14	C13	C12	120.1(4)	N6	C26	C21	123.9(3)
C13	C14	C15	121.0(4)	C25	C26	C21	122.7(3)
C14	C15	C16	118.9(4)	C7	N1	C8	110.6(3)
C11	C16	C15	119.4(3)	C17	N2	C18	110.5(3)
C11	C16	C17	120.4(3)	C23	N3	S3	106.2(2)
C15	C16	C17	120.2(3)	C24	N4	S3	105.1(2)
N2	C17	C16	124.2(3)	C25	N5	S4	105.6(2)
N2	C17	S2	114.0(2)	C26	N6	S4	106.3(2)
C16	C17	S2	121.8(2)	C9	S1	C7	90.20(15)
C19	C18	N2	116.5(3)	C19	S2	C17	90.51(15)
C19	C18	C21	123.0(3)	N3	S3	N4	100.88(13)
N2	C18	C21	120.2(3)	N6	S4	N5	100.66(14)

5. Photochromic performances of BTA in solid-state thin films

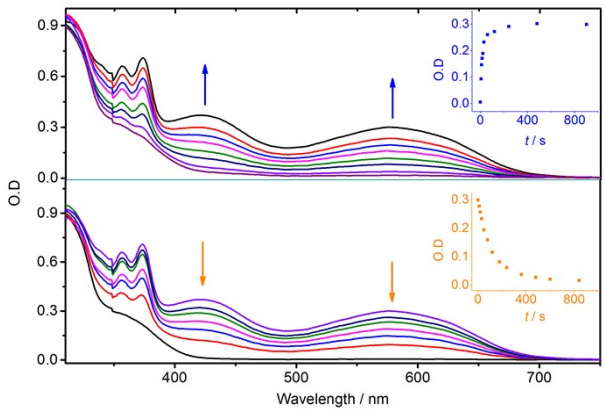


Figure S3. Top: Film photoswitching from **BTA** to PSS upon 365-nm irradiation (Film thickness: 30 μm, **BTA** / PLA = 5% w/w). Bottom: Photoswitching reverses ***c*-BTA** to **BTA** in the film upon > 510 nm light irradiation. Insert: absorbance changes at 579 nm as a function of irradiation time.

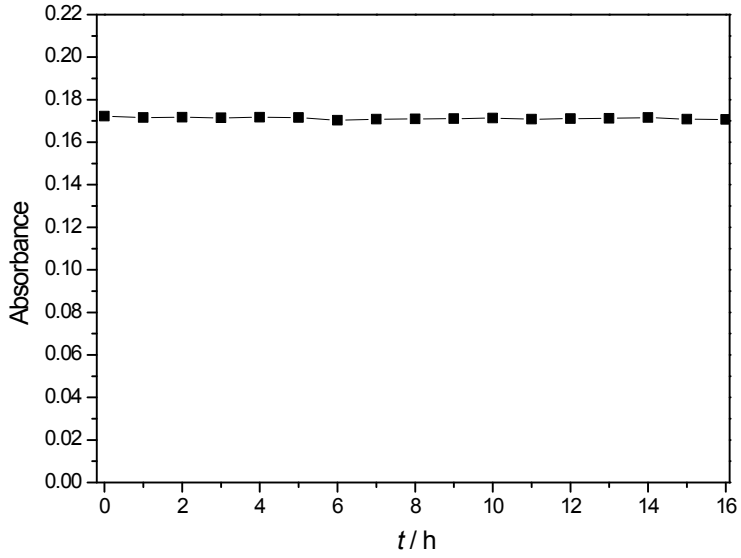


Figure S4. Absorbance of **BTA** film at 579 nm monitored at room temperature in CH_3CN after it reaches the PSS under UV action, no reversal reaction was observed after 16 h, indicating that ***c*-BTA**, like **BTA** in film, is thermally stable.

BTA film contained 5 % w/w of compound **BTA** in polylactic acid (PLA), and also showed excellent properties. Likewise in solution, the colorless ring-open **BTA** film can be photoconverted to black ring-closed

form ***c*-BTA** upon irradiation at 365 nm. The resultant ring-closed form has an absorption band at 423 and 579 nm; this appearance of the black-complement band is a characteristic indicator for a ring-open to ring-closed transformation in the film. Conversely, the visible-light irradiation (> 510 nm) on the photochemically generated ***c*-BTA** converts it back to its original colorless open form **BTA**.

As depicted in Fig. S5, the glazing film (BTA photoswitchable thin film) is fixed such that film has a 45° incident angle with respect to the modulating laser beams and a 45° incident angle with respect to the optical pulses. And then, four lasers (Fig. S6) encode digital information into the photoswitchable **BTA** ↔ ***c*-BTA** thin film. Through the optical fibres, the absorption changes will be monitored by a sensitive CCD camera (Fig. S7), and all the events are written and read in real time to and from the database.

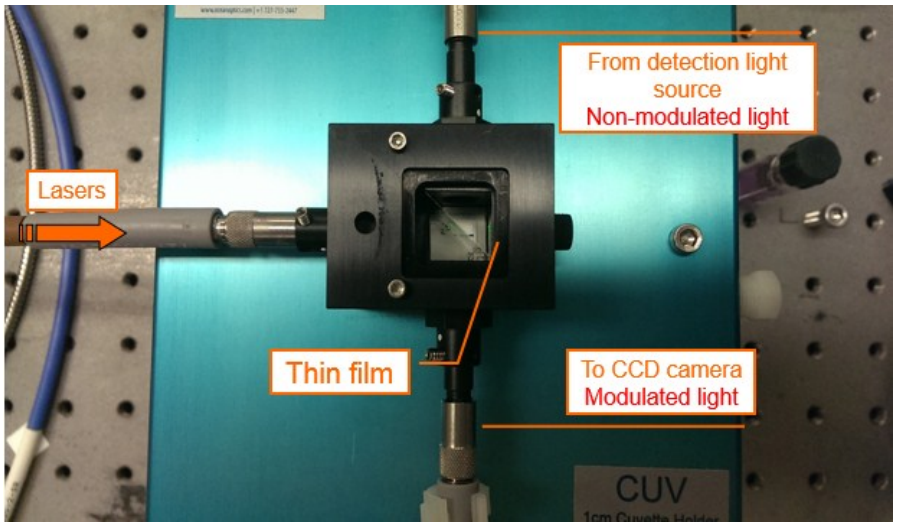


Figure S5. The practical illustration of photo-optical modulation system

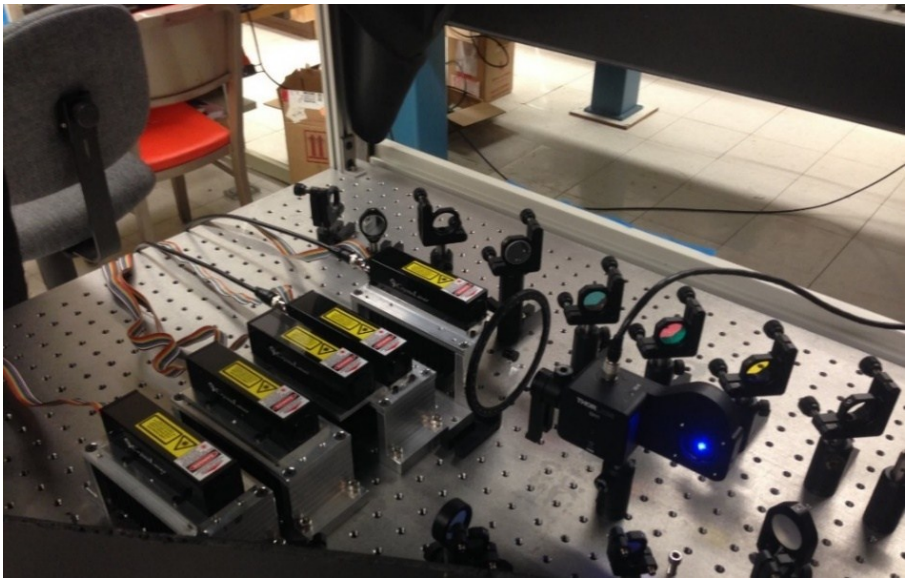


Figure S6. Laser guns (375, 473, 532, and 561 nm lasers all from *CrystaLaser*) for writing the information onto the photoswitchable thin films.

Figure S7. Ocean Optics **DH-2000** Deuterium-Halogen for providing the non-encoded inputs and the spectrometer for reading the detected light outputs.

6. BTA Characterizations

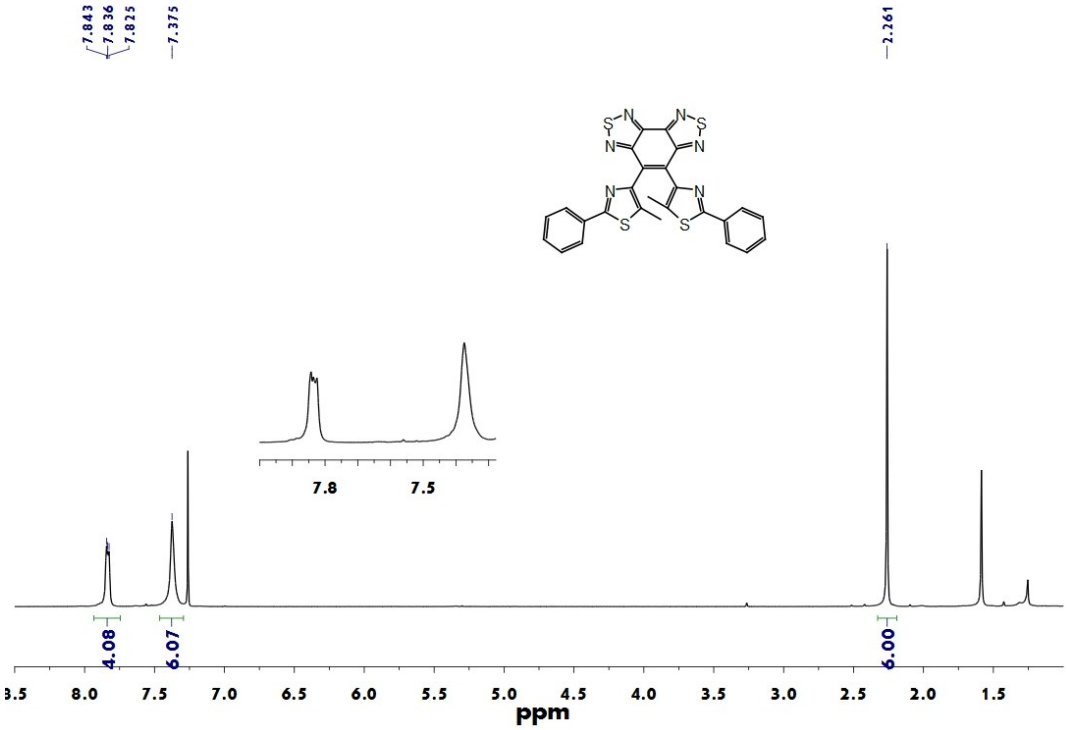


Figure S8. ^{1}H NMR spectrum of **BTA**.

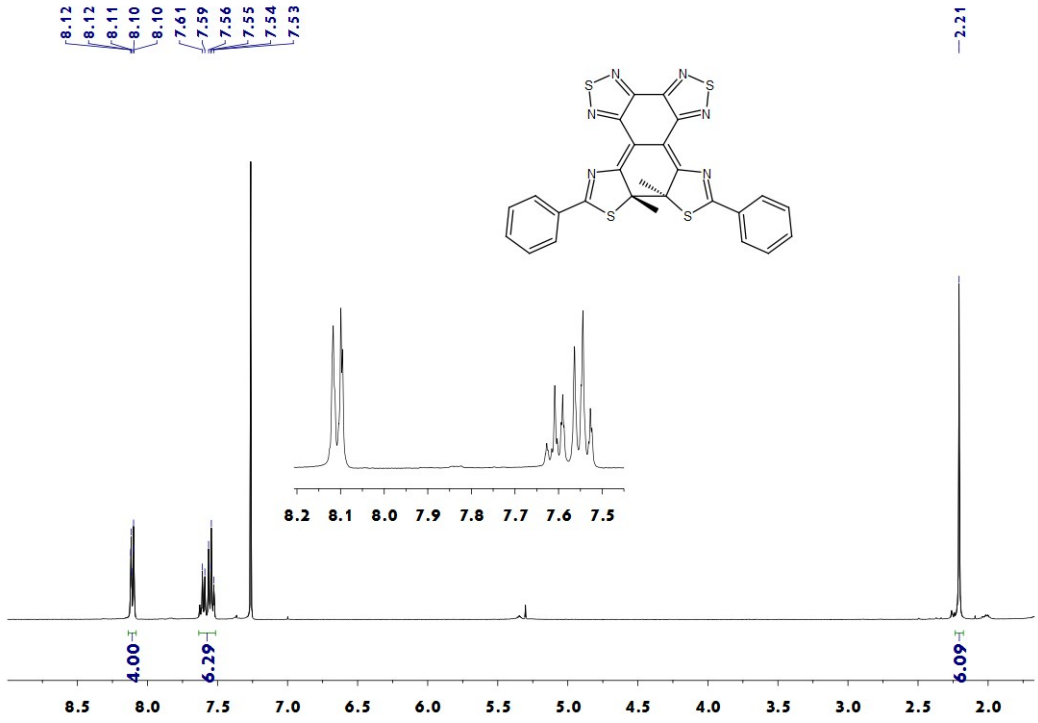


Figure S9. ^{1}H NMR spectrum of ***c*-BTA**.

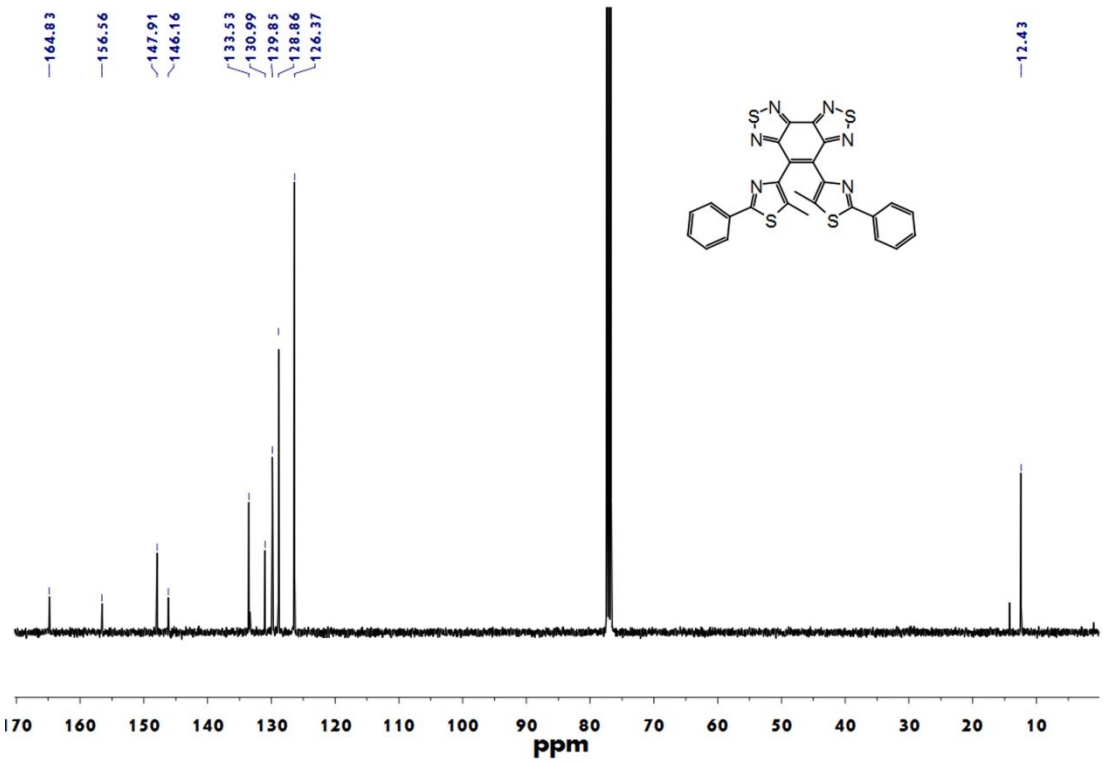


Figure S10 ^{13}C NMR spectrum of **BTA**.

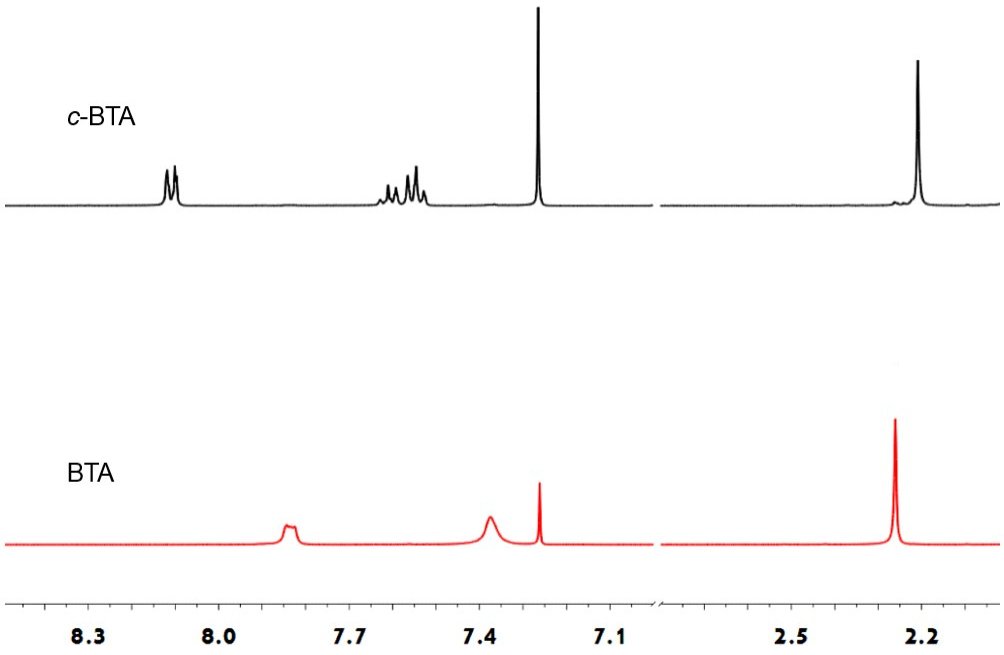


Figure S11. Comparing ^{1}H NMR spectra of ***c*-BTA** and **BTA**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-26 H: 0-20 N: 0-6 S: 0-4

ZHU-WH ECUST institute of Fine Chem 30-Sep-2011 20:34:56

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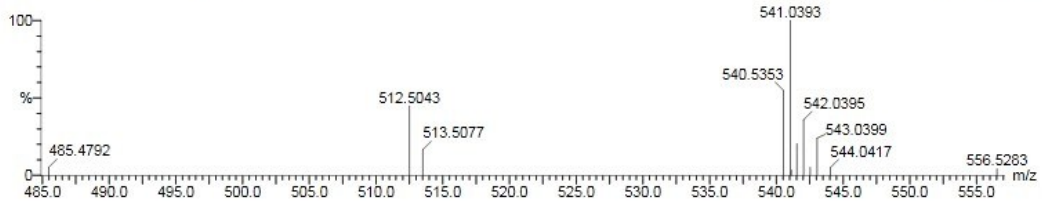

Minimum:				-1.5			
Maximum:		50.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
541.0393	541.0398	-0.5	-0.9	21.5	37.6	0.0	C26 H17 N6 S4

Figure S12. HRMS (ESI) spectrum of **BTA**.