

Electronic Supplementary Information (ESI)

A novel gated photochromic reactivity controlled by complexation/dissociation with BF₃

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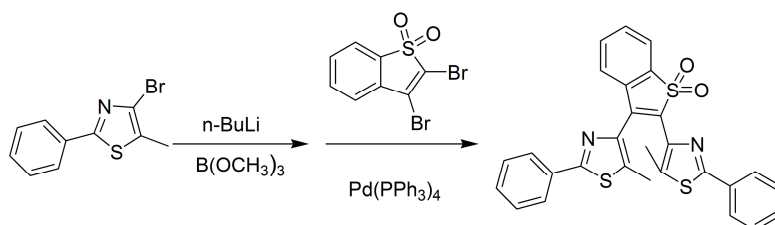
1. Experimental details

All solvents were of analytical grade. ^1H 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. UV-vis spectra were obtained using a Varian Cary 500 spectrophotometer (1 cm quartz cell) at 25 °C.

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). 2,3-Dibromo-benzo[*b*]thiophene-1,1-dioxide was synthesized according to reported methods (G. Barbarella, L. Favaretto, A. Zanelli, G. Gigli, M. Mazzeo, M. Anni, A. Bongini, *Adv. Funct. Mater.*, 2005, **15**, 664).

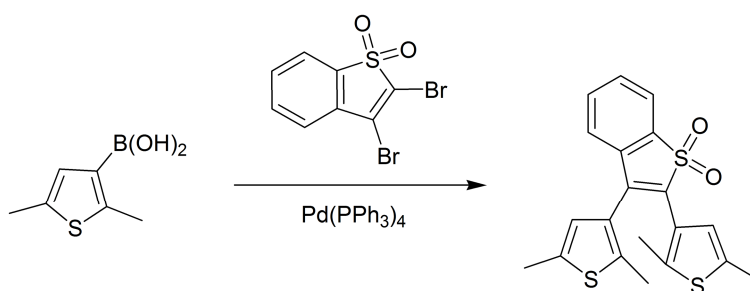
Dithiazoethene BN



Scheme S1 Synthetic route of BN

To a solution of 4-bromo-5-methyl-2-phenylthiazole (1.51 g, 5.97 mmol) in dry THF (30 mL) was added $n\text{-BuLi}$ (2.63 mL, 6.57 mmol) dropwise at -78 °C under argon. After 1 h of stirring at -78 °C, $\text{B}(\text{OCH}_3)_3$ (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 without purification. The unpurified mixture was reacted with 2,3-dibromo-benzo[*b*]thiophene-1,1-dioxide (0.26 g, 0.80 mmol) under Suzuki coupling reaction using $\text{Pd}(\text{PPh}_3)_4$ (0.1 g, 0.09 mmol) and K_2CO_3 aqueous solution

(10 mL, 2 M) as catalysts in THF (35 mL) for 12 h. After cooling, water was added and the reaction mixture was extracted with CH₂Cl₂. The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and evaporated under reduce pressure. The crude product was purified by column chromatography (PE : EA = 10 : 3 v/v) on silica gel and obtained as a light yellow solid **BN** (182 mg, 45% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.97-7.92 (m, 4H), 7.89-7.86 (m, 1H), 7.75-7.72 (m, 1H), 7.61-7.58 (m, 2H), 7.48-7.46 (m, 3H), 7.43-7.39 (m, 3H), 2.10 (s, 3H), 2.04 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 164.96, 164.93, 142.07, 138.56, 136.22, 135.65, 135, 133.44, 132.70, 132.41, 132.04, 131.15, 129.38, 129.29, 129.18, 128.08, 127.85, 125.58, 125.34, 124.75, 120.32, 11.56, 11.37. MS (ESI, m/z): [M + H]⁺ calcd for C₂₈H₂₁N₂O₂S₃, 513.0765; found, 513.0765.



Scheme S2 Synthetic route of **BT**

Dithienylethene **BT**

To a 100 mL two necked bottle charged with argon was added 2,3-dibromo-benzo[*b*]thiophene-1,1-dioxide (0.26 g, 0.8 mmol), 2 M K₂CO₃ 10 mL, 15 mL dioxane and Pd(PPh₃)₄ (0.1 g). The mixture was allowed to reflux for 15 min, then, 2,5-dimethylthiophen-3-ylboronic acid (0.5 g, 3.2 mmol) dissolved in 20 mL dioxane was introduced. The resulting mixture was allowed to reflux under the protection of argon at dark for 24 h. Then, the reactive mixture was poured into H₂O and extracted with ethyl acetate. The organic layer was separated and dried (Na₂SO₄). After concentration, the compound was purified by column chromatography on silica (PE : EA = 20 : 1 v/v) to give a pale yellow solid **BT** (140 mg, 45.3% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.83 (d, *J* = 6.8 Hz, 1H), 7.52-7.59 (m, 2H), 7.38 (d, *J* =

6.8 Hz, 1H), 7.03 (s, 1H), 6.61 (s, 1H), 2.45 (d, $J = 10$ Hz, 6H), 2.00 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 14.27, 14.37, 15.27, 15.29, 121.48, 122.83, 124.21, 124.77, 125.29, 127.21, 129.72, 133.29, 133.40, 133.78, 134.89, 136.27, 137.29, 137.57, 137.64, 139.84. MS (ESI, m/z): $[\text{M} + \text{K}]^+$ calcd for: $\text{C}_{20}\text{H}_{18}\text{O}_2\text{S}_3\text{K}$, 425.0106, found, 425.0122.

2. UV-Vis spectra of BN upon adding protons and ions

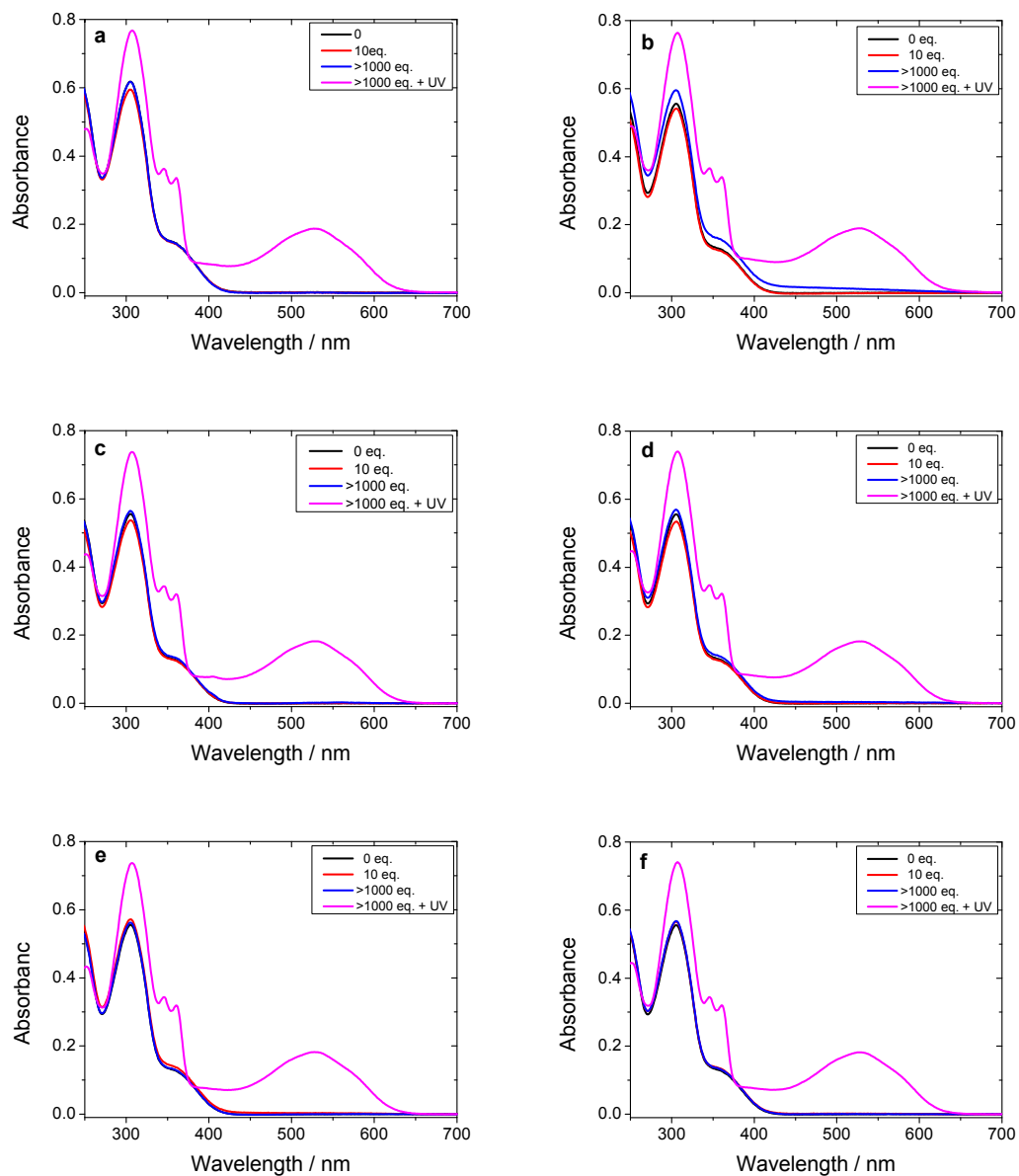


Fig. S1 Spectral changes of UV-Vis absorption (a- H^+ , b- Zn^{2+} , c- Mn^{2+} , d- Mg^{2+} , e- Ca^{2+} , f- Ba^{2+}) of BN (2.0×10^{-5} M) in CH_3CN upon titration on 0, 10, exceeded 1000 eq, and then upon irradiation with 365 nm light for 50 s.

3. Absorption changes of BT

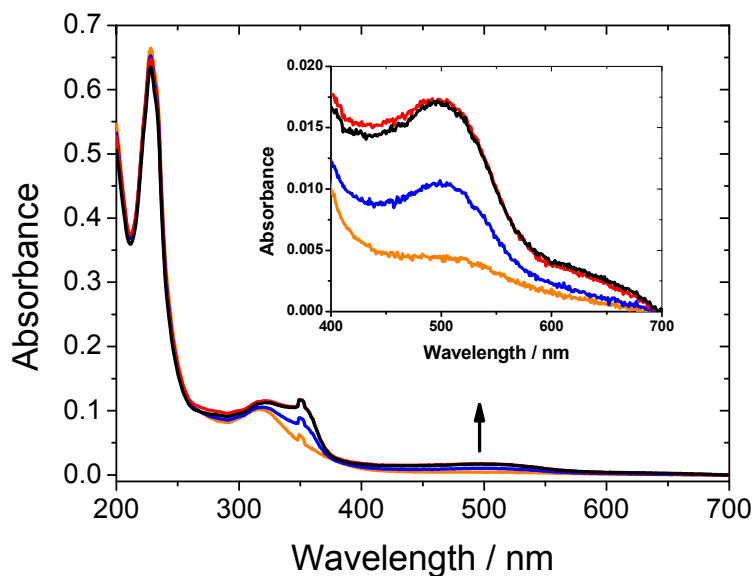


Fig. S2 Changes in absorption spectra of **BT** in CH₃CN upon irradiation with 365 nm light. (2.0×10^{-5} M) for 0 s (orange line), 10 s (blue line), 30 s (red line) and 50 s (black line). Insert: the enlarged view of absorbance in the range from 400 to 700 nm. Note: due to the low photocyclization conversion yield (8.1%) in the system of **BT**, the absorption band resulted from the photocyclized closed form is much lower than that of **BN**.

4. Calculation of the quantum yields

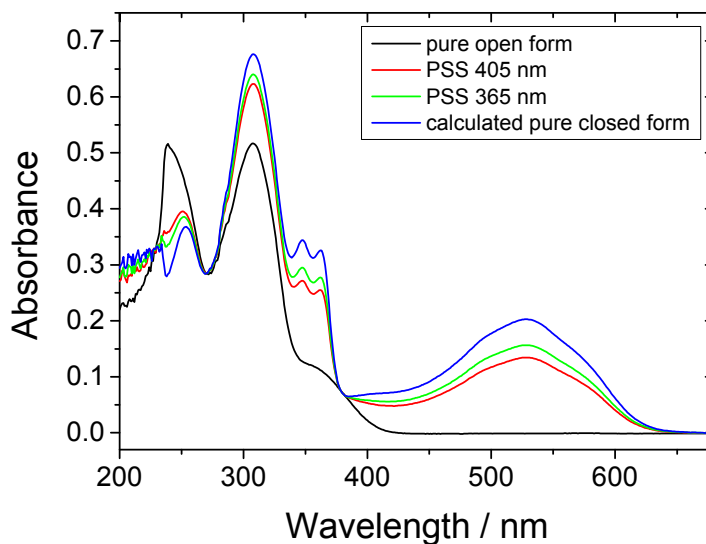


Fig. S3 Absorption spectra of **BN** at different irradiation wavelengths in THF (1.92×10^{-5} M). The absorption spectra of pure *c*-**BN** was calculated using the procedure described according to the reported reference (E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704).

The absorption spectrum of the closed form was determined by the Fischer's method. 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:

$$\frac{C_o}{C_c} = \frac{\Phi_{c \rightarrow o} \times \epsilon_c}{\Phi_{o \rightarrow c} \times \epsilon_o} = \frac{\Phi_{c \rightarrow o} \times A_c}{\Phi_{o \rightarrow c} \times A_o} \quad (\text{Equation 1})$$

Where ϵ_o and ϵ_c are the molar absorption coefficients of the open and closed forms, and A_o 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 (Equation 1) are obtained. Assuming that the ratio $\Phi_{c \rightarrow o} / \Phi_{o \rightarrow c}$ does not depend on the irradiation wavelength, we get:

$$\frac{C_o'}{C_c'} \bigg/ \frac{C_o''}{C_c''} = \frac{A_c'}{A_o'} \bigg/ \frac{A_c''}{A_o''} \quad (\text{Equation 2})$$

If we introduce the open form to closed form conversion yield α , equation (Equation 1) evolves to:

$$\frac{1-\alpha'}{1-\alpha''} \bigg/ \frac{\alpha'}{\alpha''} = \frac{A_c'}{A_o'} \bigg/ \frac{A_c''}{A_o''} \quad (\text{Equation 3})$$

In order to introduce experimental data into equation (Equation 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

$$A_c = A_o + \frac{A - A_o}{\alpha} \quad (\text{Equation 4})$$

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

$$\frac{1-\alpha'}{1-\alpha''} \bigg/ \frac{\alpha'}{\alpha''} = 1 + \frac{\Delta'}{\alpha'} \bigg/ 1 + \frac{\Delta''}{\alpha''} \quad (\text{Equation 5})$$

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 Δ 's measured at any given wavelength (the wavelength that maximizes the Δ 's is usually chosen). Equating and developing (Equation 5) yields the final formula:

$$\alpha'' = \frac{\Delta' - \Delta''}{1 + \Delta' - \rho(1 + \Delta'')} \quad (\text{Equation 6})$$

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 (Equation 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 using the differential equation (Equation 7) and phenomenological equation (Equation 8)

$$\frac{dC_c}{dt} = I_0 \times (\lambda_{irr}) \times \frac{1 - 10^{-Abs(\lambda_{irr})}}{Abs(\lambda_{irr})} \times (\Phi_{O \rightarrow C} \epsilon_0 \times (\lambda_{irr}) \times l \times C_o - \Phi_{C \rightarrow O} \times \epsilon_c \times (\lambda_{irr}) \times l \times C_c) \quad (\text{E.7})$$

$$Abs(\lambda_{obs}) = \epsilon_c \times (\lambda_{obs}) \times l \times C_c + \epsilon_o \times (\lambda_{obs}) \times l \times C_o \quad (\text{E.8})$$

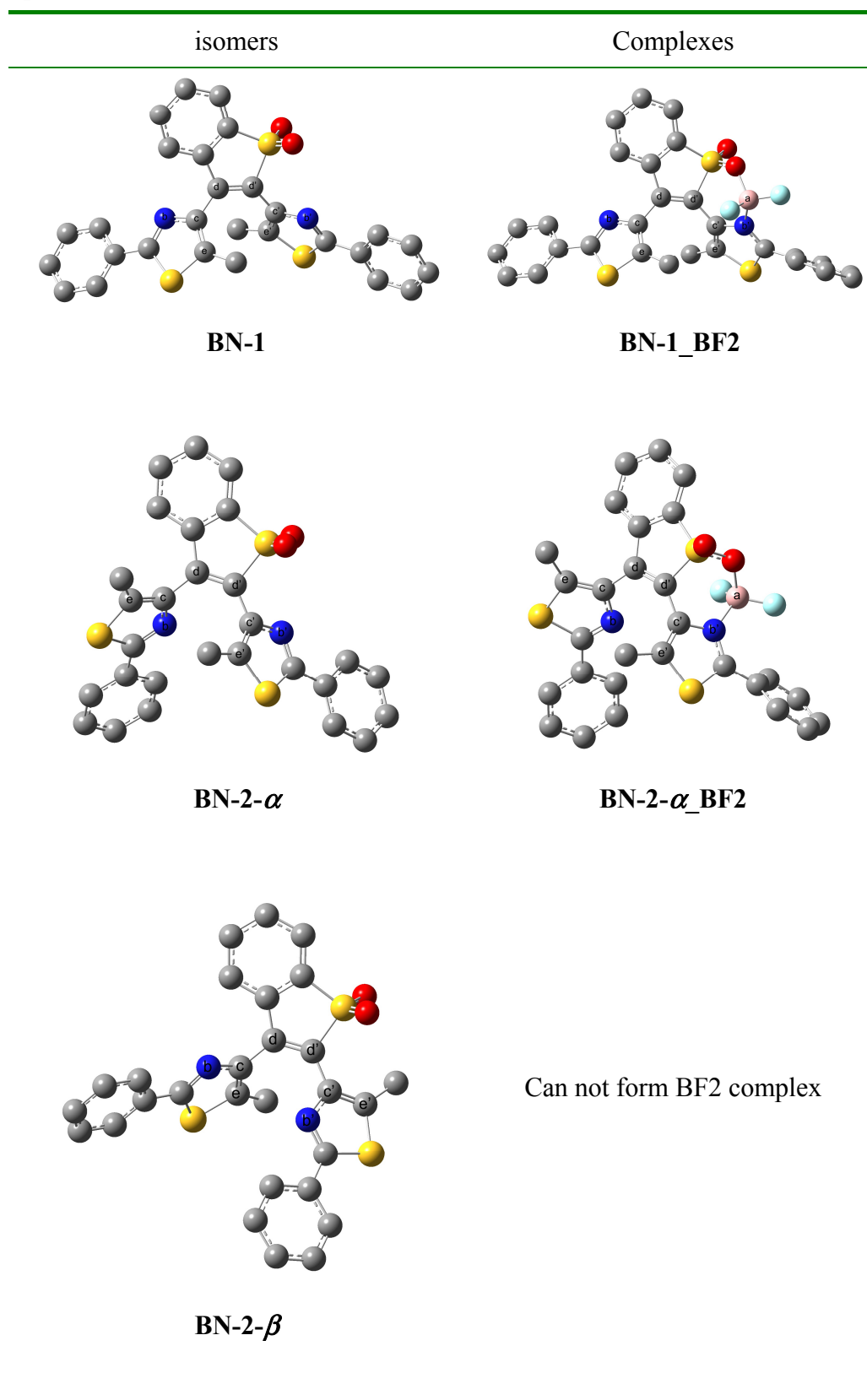
where C_o and C_c are the concentrations of open form and closed form, I_0 is the incident irradiation intensity, λ_{irr} and λ_{obs} are the irradiation and observation wavelengths, ϵ_o and ϵ_c are molar absorption coefficients of open and closed forms at irradiating wavelength (365 nm), respectively (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).

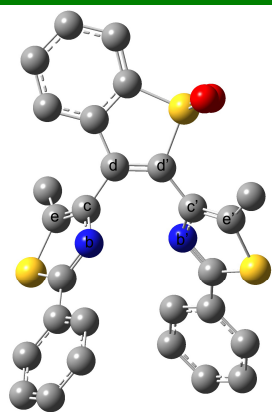
As can be deduced from Fischer analysis, the conversion yield of **BN** upon irradiation with 365 nm light was 77.3%. According to the Fischer analysis and photolysis continue, we obtain $\Phi_{o-c} = 41.2\%$ and $\Phi_{c-o} = 2.4\%$. Similarly, we obtain the conversion yield of **BT** upon irradiation with 365 nm light was 8.1%, $\Phi_{o-c} = 21.4\%$ and $\Phi_{c-o} = 11.6\%$.

5. Theoretical calculations

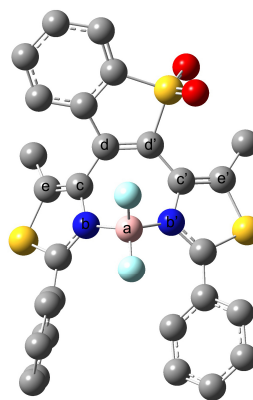
In order to unravel the underlying mechanism of the gated photochromism of **BN** in response to BF_3 , quantum mechanical calculations were performed within the framework of Gaussian09 program on the isomers of **BN** and the corresponding complexes formed with BF_3 (Tables S1 and S2). Due to the unsymmetrical nature of the bridging unit of **BN**, there are four other isomers located, including the parallel isomers **BN-2- α** and **BN-2- β** and the anti-parallel isomers **BN-3- α** and **BN-3- β** . Geometrical optimizations of these isomers and the corresponding complexes were carried out in gas phase at the PBE0/6-31+G(d,p) level. Single point energy calculations were performed with a larger basis set 6-311++G(2d,2p) on the optimized geometries of these complexes (Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009).

Table S1 Optimized geometries for different isomers and the corresponding complexes with BF₃ (Hydrogens are omitted for clarity).

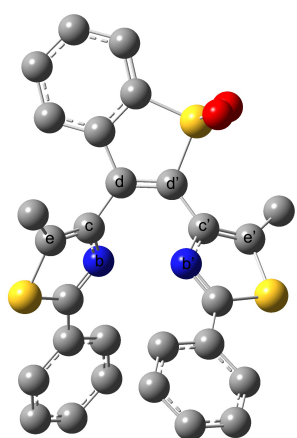




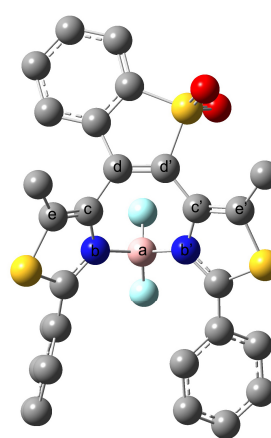
BN-3- α



BN-3- α _BF₂



BN-3- β



BN-3- β _BF₂

Table S2 Structural parameters for different isomers and the corresponding complexes and relative energies for the complexes in reference to the most stable complex formed

Conformations	Relative energy (kcal/mol)	d _{e-e'} (Å)	a-b-c-d (°)	a-b'-c'-d' (°)	d'-d-c-e (°)	d-d'-c'-e' (°)
BN-1	--	3.62	--	--	49.6	48.0
BN-1_BF2	6.02	3.75	--	5.5	47.4	57.8
BN-2-α	--	4.16	--	--	127.9	-49.8
BN-2-α_BF2	7.77	4.60	--	-0.4	134.5	-63.5
BN-2-β	--	4.37	--	--	-49.2	151.9
BN-3-α	--	5.36	--	--	-122.4	-139.6
BN-3-α_BF2	0.0	5.31	-12.2	-8.7	-123.5	148.4
BN-3-β	--	5.36	--	--	122.4	139.6
BN-3-β_BF2	0.0	5.31	12.2	8.7	123.5	-148.4

6. Characterization of BN and BT

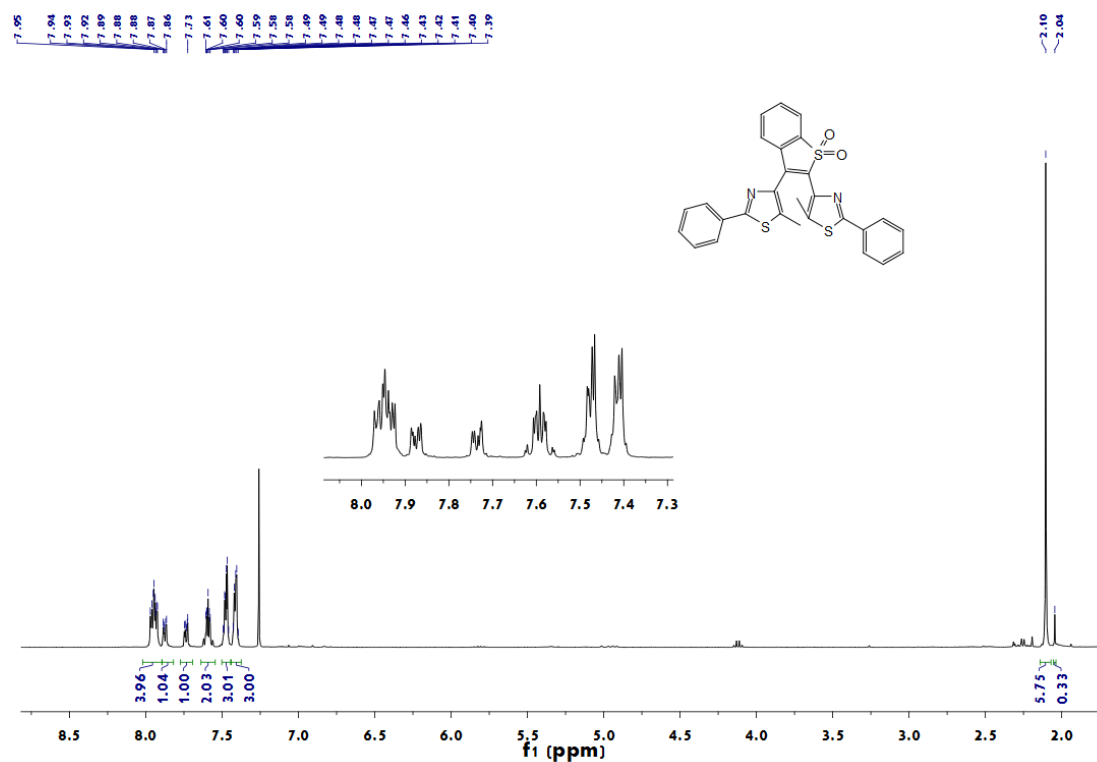


Fig. S4 ¹H NMR spectrum of BN.

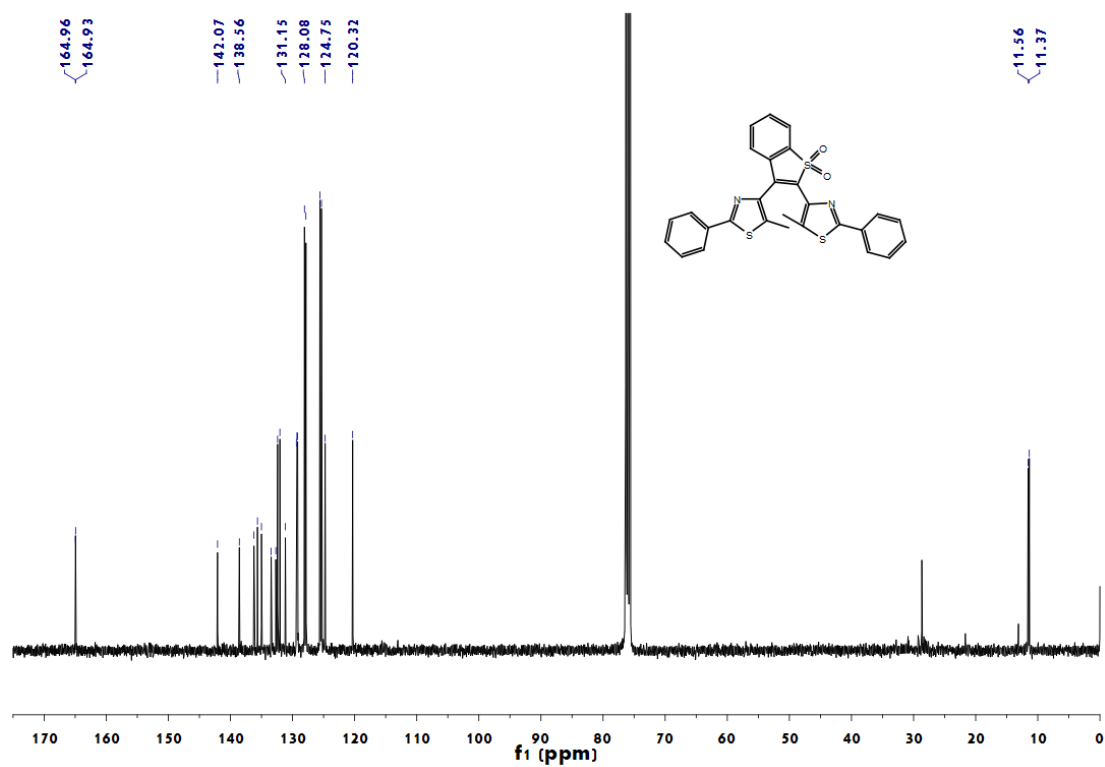


Fig. S5 ¹³C NMR spectrum of BN.

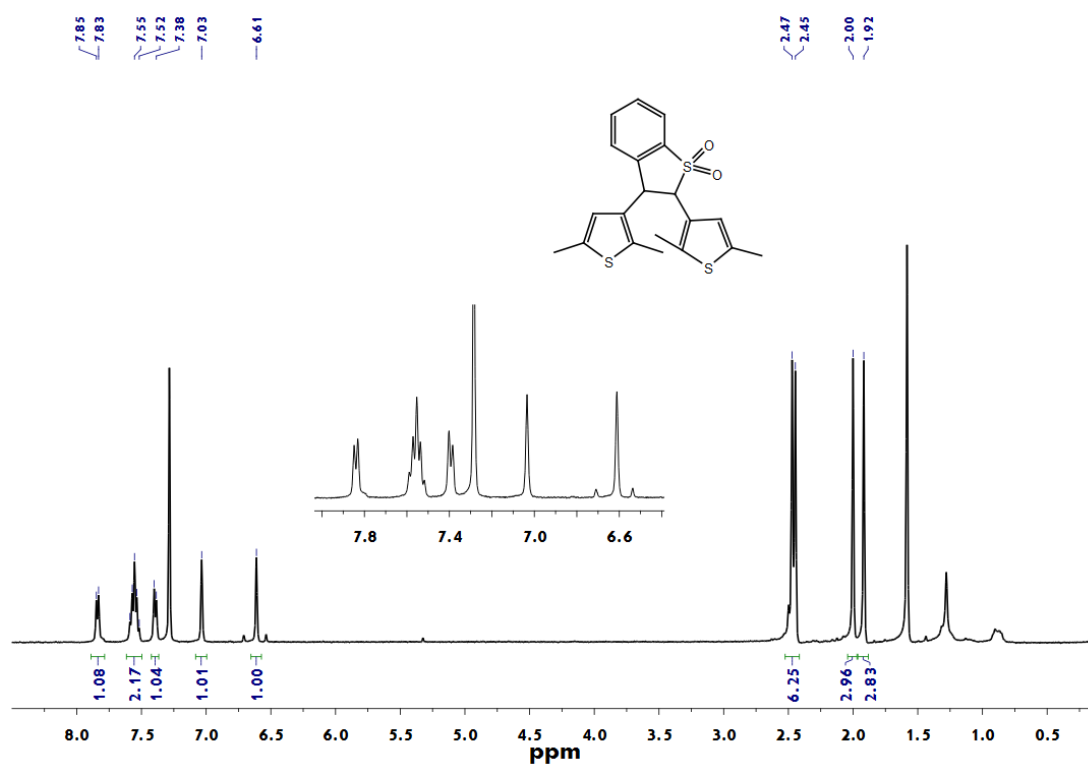


Fig. S6 ¹H NMR spectrum of BT.

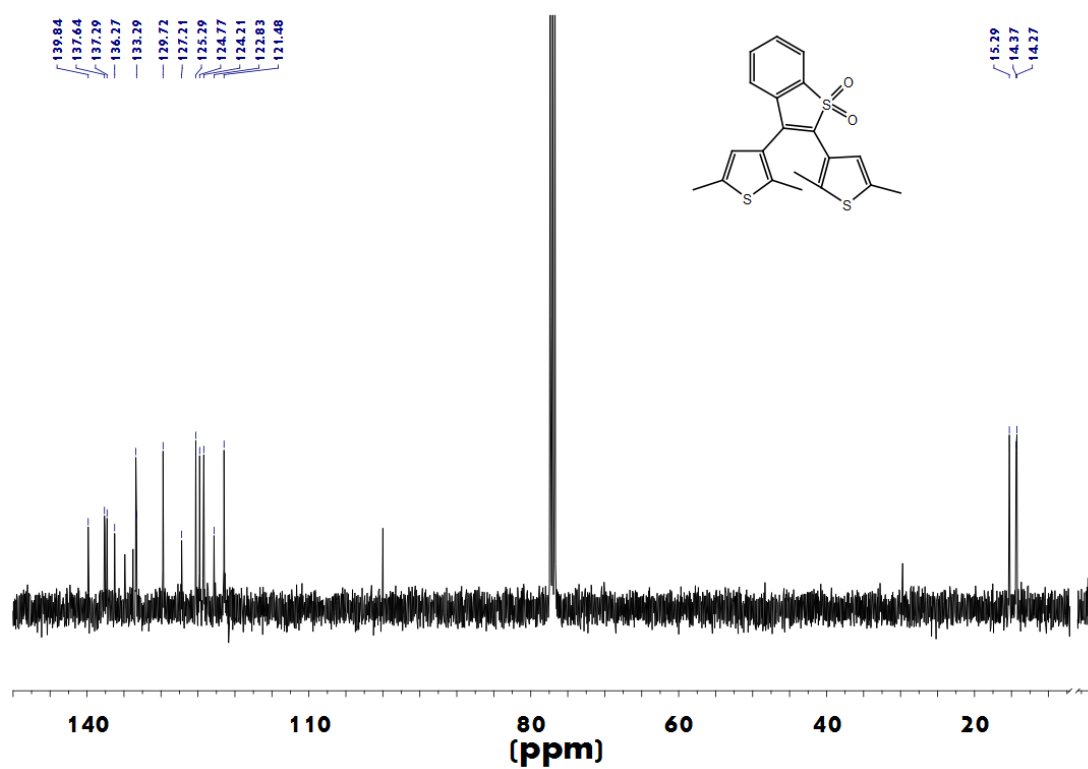


Fig. S7 ¹³C NMR spectrum of BT.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions

981 formula(e) evaluated with 8 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

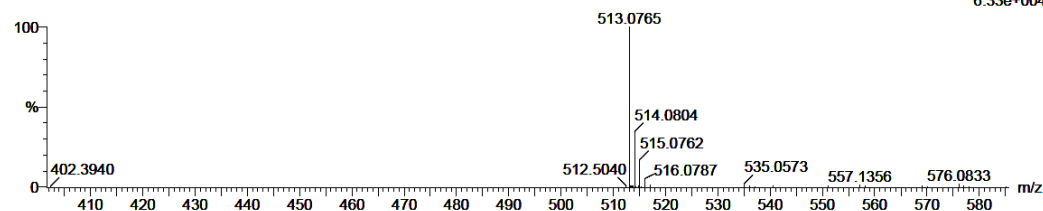
C: 0-50 H: 1-50 N: 1-8 O: 1-10 S: 1-3

ZHU-WH

LCT Premier

Key Lab for Advanced Materials — ECUST
1: TOF MS ES+
6.33e+004

ZWH-WY-003 20 (0.792) Cm (17:20)



Minimum:				-1.5					
Maximum:		3.0	50.0	50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
513.0765	513.0765	0.0	0.0	19.5	119.7	0.0	C28 H21 N2 O2 S3		

Fig. S8 HRMS (ESI) spectrum of BN.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions

367 formula(e) evaluated with 4 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

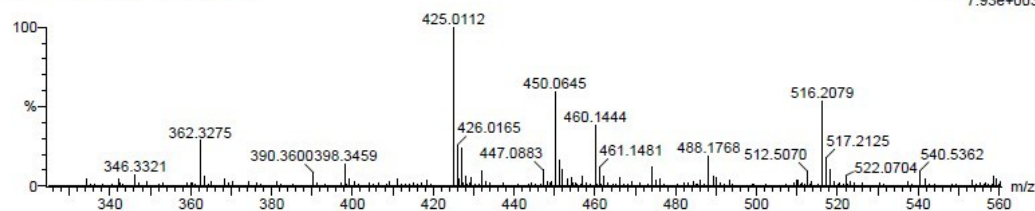
C: 20-32 H: 0-1000 O: 0-40 S: 0-3 K: 0-1

ZHU-WH

LCT Premier

Key Lab for Advanced Materials — ECUST
1: TOF MS ES+
7.93e+003

ZWH-CSJ-03 27 (0.841) Cm (18:31)



Minimum:				-1.5					
Maximum:		2.0	5.0	50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
425.0112	425.0106	0.6	1.4	11.5	409.0	0.0	C20 H18 O2 S3 K		

Fig. S9 HRMS (ESI) spectrum of BN.