Electronic Supplementary Information (ESI)

Reversible photoswitching specifically responds to mercury(II) ions: the gated photochromism of bis(dithiazole)ethene

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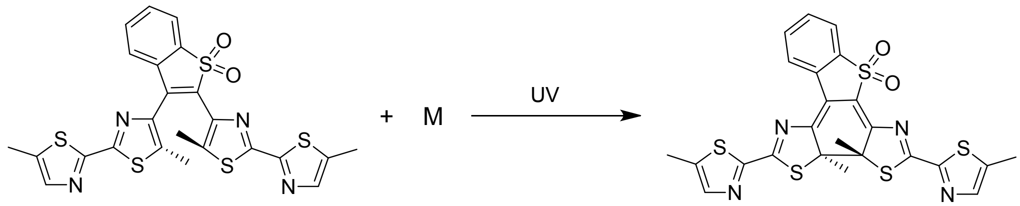
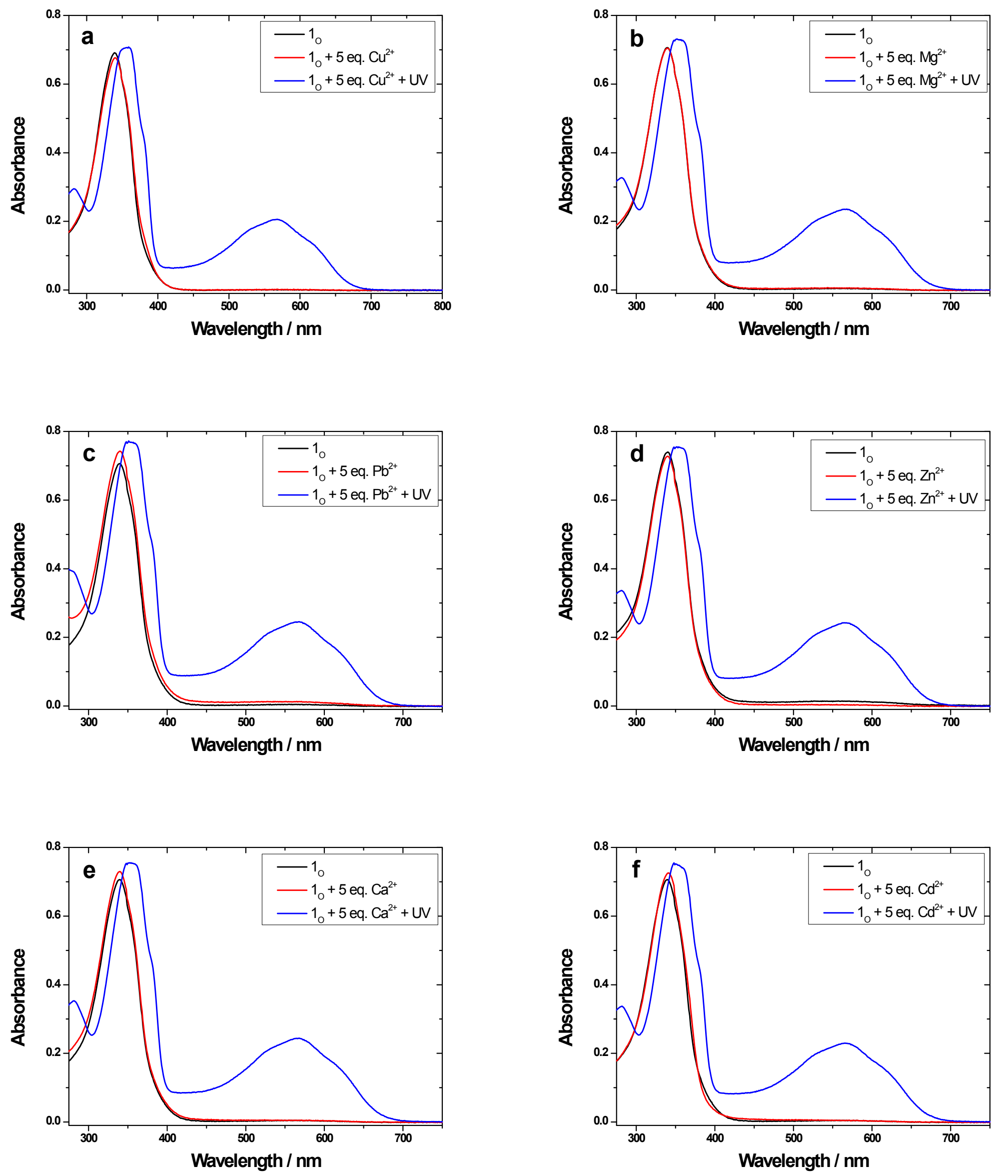
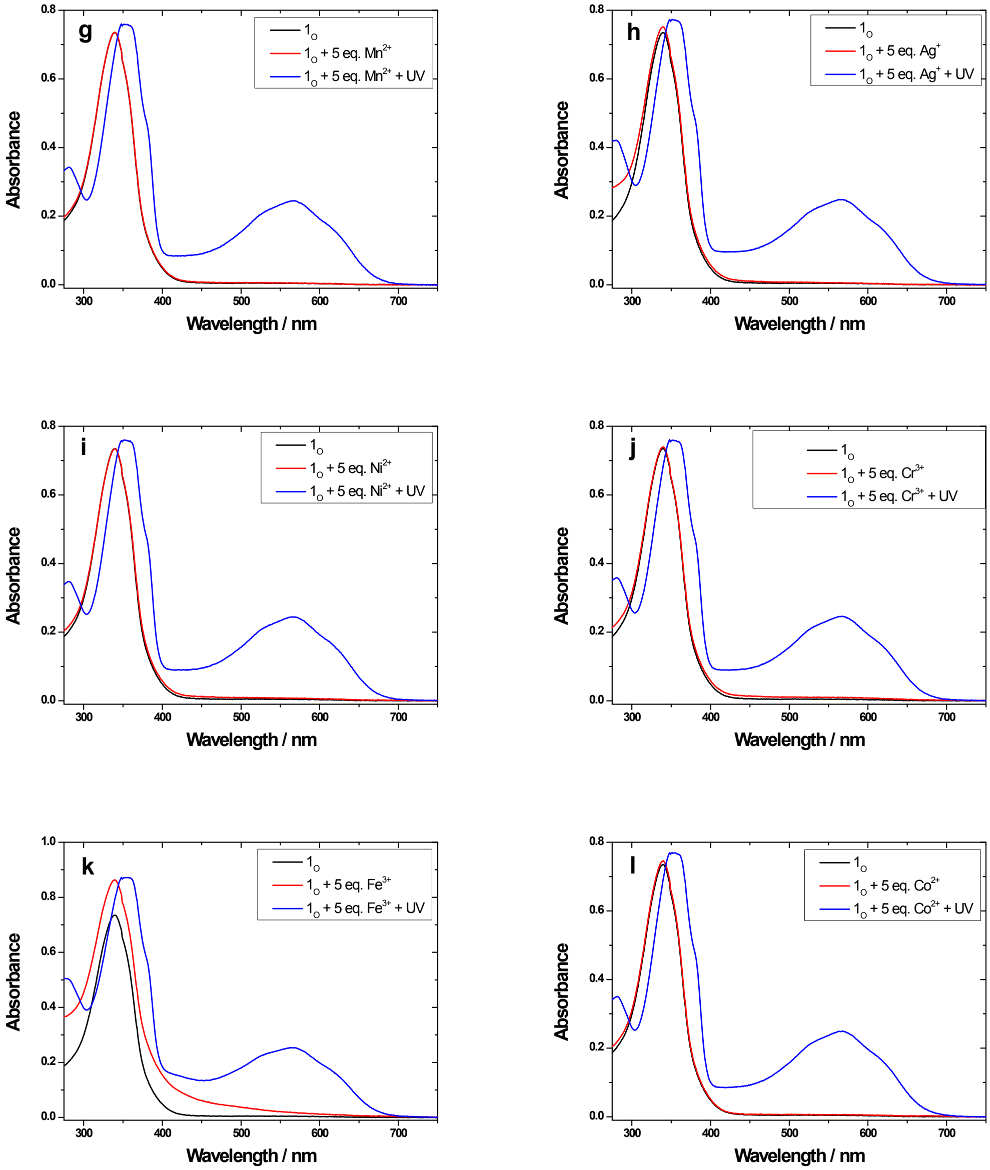
1. UV-Vis spectra of 1 upon adding protons and metal ions






g
1_o
1_o + 5 eq. Mn^{2+}
1_o + 5 eq. Mn^{2+} + UV
h
1_o
1_o + 5 eq. Ag^{+}
1_o + 5 eq. Ag^{+} + UV
i
1_o
1_o + 5 eq. Ni^{2+}
1_o + 5 eq. Ni^{2+} + UV
j
1_o
1_o + 5 eq. Cr^{3+}
1_o + 5 eq. Cr^{3+} + UV
k
1_o
1_o + 5 eq. Fe^{3+}
1_o + 5 eq. Fe^{3+} + UV
l
1_o
1_o + 5 eq. Co^{2+}
1_o + 5 eq. Co^{2+} + UV
Absorbance
Wavelength / nm

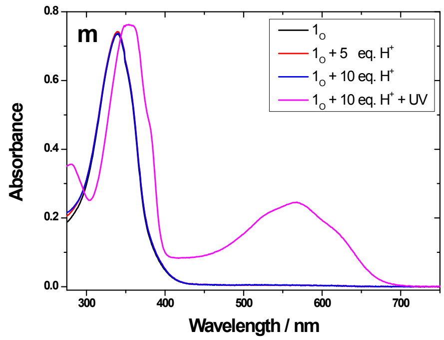
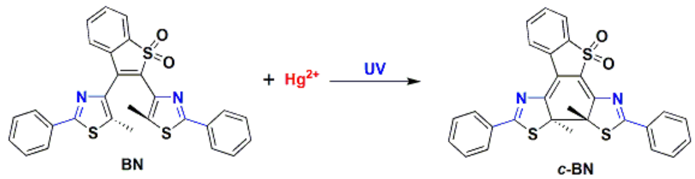


Fig. S1 UV-Vis absorption changes in the presence of various ions (a-Cu^{2+}, b-Mg^{2+}, c-Pb^{2+}, d-Zn^{2+}, e-Ca^{2+}, f-Cd^{2+}, g-Mn^{2+}, h-Ag^{+}, i-Ni^{2+}, j-Cr^{3+}, k-Fe^{3+}, l-Co^{2+}, m-H^{+} as perchlorates were used) of $\mathbf{1_O}$ (2.0×10^{-5} M) in CH_3CN, and then upon irradiation with 365-nm light for 50 s.

2. UV-Vis spectra of 2 upon adding Hg^{2+}



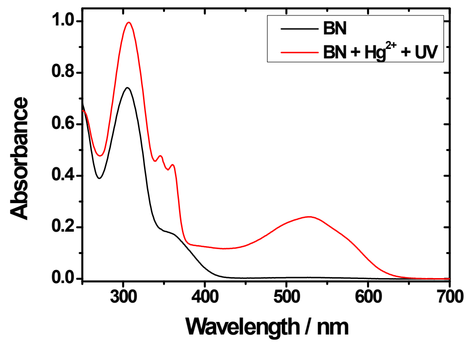


Fig. S2 In the presence of 5 eq. $Hg(ClO_4)_2$, absorption spectra of **2** (**BN)** in CH_3CN (black line), and after 365-nm light irradiation (red line).

3. Titrating curve of 1 and Hg^{2+}

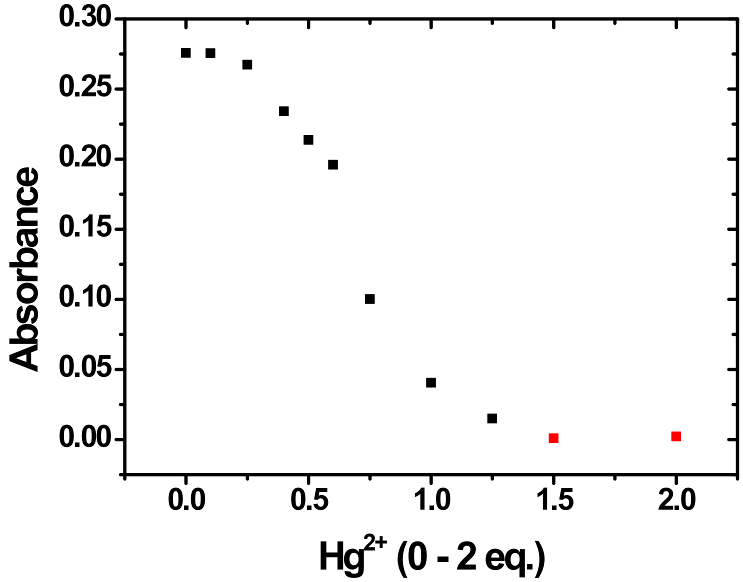


Fig. S3 Absorption changes at 568 nm due to interconversion of $\mathbf{1_O}$ to $\mathbf{1_C}$ (2.0×10^{-5} M) upon titration of $Hg(ClO_4)_2$, followed by 365-nm irradiation for 50 s, respectively.

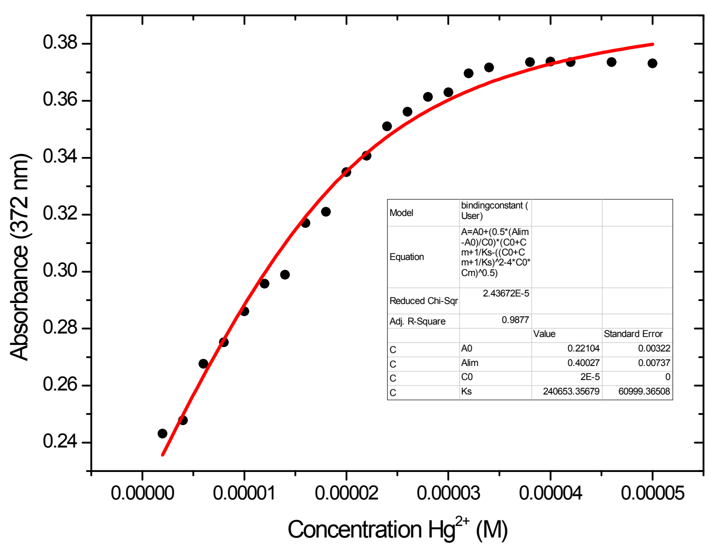


Fig. S4 Absorption changes at 372 nm of $\mathbf{1_O}$ (2.0×10^{-5} M) upon titration of $Hg(ClO_4)_2$.

4 Gating of molecular Photoswitching

In a typical experiment, the molecular photoswitch $\mathbf{1_O}$ concentration was c = 1.0 × 10^{-5} M, in 1 mL volume. The corresponding equivalence of $HgClO_4$ in CH_3CN was added to the above photoswitching system, which was tested using the following conditions. The UV irradiation was carried out using a 375-nm laser operating at 6.4 μW/mm³. Typically UV-laser on time averaged from 200 seconds to 270 seconds. Because visible lasers have relatively low energy per photon, three visible lasers were used simultaneously to impart the ring-opening reaction for 250-350 seconds. The wavelengths are 561 nm, 532 nm, and 473 nm; together they produce 175 μW/mm³. These switching lasers were applied orthogonally to the incoming and out-going light used to measure absorbance values. The light source for the absorbance measurements came from an Ocean Optics DH-200-BAL module via an UV-NIR transparent optical fiber. A similar optical fiber was used to deliver the output light to a CCD detector (Ocean Optics QE65 Pro) for simultaneous measurements of absorbance at all wavelength. The absorbance data were collected using the Ocean Optics SpectraSuite software.

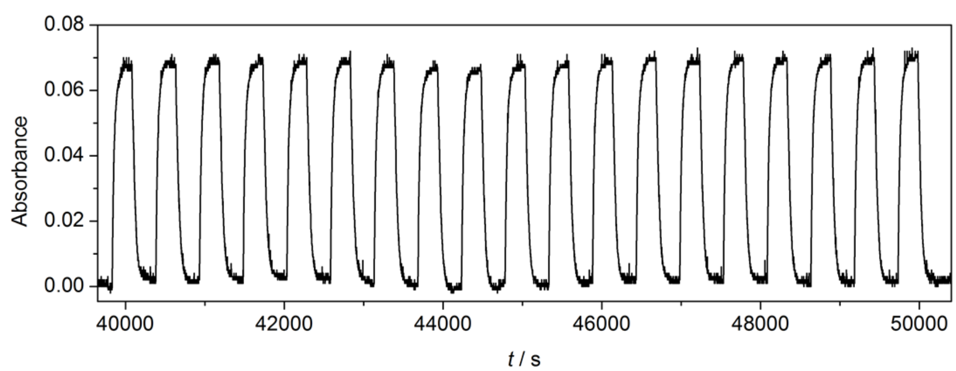
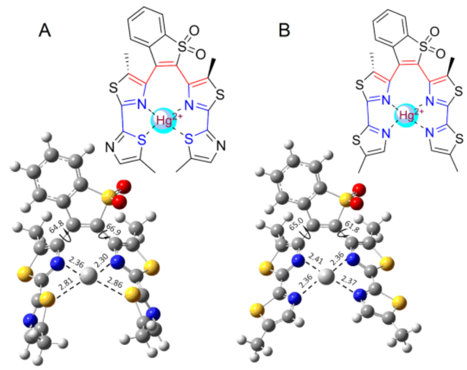


Fig. S5 Alternating a 375-nm UV laser and three visible lasers (473, 532, and 561-nm) causes the interconversion between $\mathbf{1_O}$ and $\mathbf{1_C}$. Partial equivalent of Hg(II) ions (1_O + 0.5 eq. Hg^{2+}) were added to gate the magnitude of the photoswitching. In this case, the photoswitching was reduced to 70%, but fatigue resistance remains excellent.

5. Theoretical calculations



1_L▪Hg-1 **1_L▪Hg -2**

Table S1. Structural parameters for the complexes and relative energies

Compound	Relative energy (kcal mol^{-1})	$d_{f\text{-}f'}$ (Å)	$d_{a\text{-}b}$ (Å)	$d_{a\text{-}b'}$ (Å)	$d_{a\text{-}c}$ (Å)	$d_{a\text{-}c'}$ (Å)	|e'-e-d-b| (º)	|e-e'-d'-b'| (º)
1_L▪Hg-1	42.3	5.16	2.36	2.30	2.81	2.86	64.8	66.9
1_L▪Hg -2	0	5.30	2.41	2.36	2.36	2.37	65.0	61.8

Quantum chemical calculations were performed within the framework of Gassian09 program.[S1] Geometrical optimizations were carried out in gas phase at the PBE0/6-31G(d) level, except for Hg, LANL2DZ basis set was used. **1_L▪Hg-2** was predicted to be the most stable complex formed with Hg^{2+}, that is, **1_L▪Hg-1** was 42.3 kcal mol^{-1} less stable than **1_L▪Hg-2**.

[S1] 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 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009