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
**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 1$_0$ (2.0 $\times$ 10$^{-5}$ M) in CH$_3$CN, and then upon irradiation with 365-nm light for 50 s.
2. UV-Vis spectra of 2 upon adding Hg$^{2+}$

![Diagram](image)

**Fig. S2** In the presence of 5 eq. Hg(ClO$_4$)$_2$, absorption spectra of 2 (BN) in CH$_3$CN (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 $1_0$ to $1_c$ (2.0 $\times$ 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 $1_0$ (2.0 $\times$ 10$^{-5}$ M) upon titration of Hg(ClO$_4$)$_2$. 
4 Gating of molecular Photoswitching

In a typical experiment, the molecular photoswitch $1_o$ concentration was $c = 1.0 \times 10^{-5}$ M, in 1 mL volume. The corresponding equivalence of HgClO$_4$ in CH$_3$CN 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 $\mu$W/mm$^3$. 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 $\mu$W/mm$^3$. 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 $1_o$ and $1_c$. 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

Table S1. Structural parameters for the complexes and relative energies

| Compound  | Relative energy (kcal mol⁻¹) | d_a-b (Å) | d_a-b' (Å) | d_a-c (Å) | d_a-c' (Å) | |e'-e-d-b| (°) | |e-e'-d'-b'| (°) |
|-----------|------------------------------|-----------|-------------|-----------|------------|---------------|-------------|
| 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 Gaussian09 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 Hg²⁺, that is, 1_L▪Hg-1 was 42.3 kcal mol⁻¹ less stable than 1_L▪Hg-2.