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COMMUNICATION

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

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
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DOI: 10.1039/x0xx00000x

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Photoswitching of bis(dithiazole) can be regulated by Hg(II) ions and EDTA in an “lock-and-unlock” manner. The molecular photoswitch provides an enzyme-like binding pocket that selectively binds specifically to mercury ions, thus modulating the degree of photoswitching in its presence.

Photoswitching has distinct advantages because it responds fast, triggers reversible chemical reactions, and enables super-high resolution nanoscopy.¹ In specific photoresponses, the photochromic switching² has been used to induce neural signal,³ enzyme inhibition,⁴ DNA incorporation,⁵ conductance switch,⁶ photomechanical response,⁷ as well as information encoding⁸ and multi-addressable states.⁹ Although basic properties such as thermal stability, fatigue resistance and fast response offer essential properties of molecular devices,¹⁰ gated photoswitching offers additional protection as well as regulation and controls in data manipulation, chemical and biological sensing, non-destructive read-out, and drug delivery.^{11,12} Despite these desired applications, selectively gated photoswitching has rarely been studied.¹³ Using the nitrogen atoms in dual dithiazole subunits,¹⁴ herein, we explore the unique metal binding size and geometry to design mercury-ion specifically gated photoswitching using previously synthesized bis(dithiazole)ethene (**1_O**, Fig. 1). Upon addition of equal amount of EDTA, the gated photoswitching will resume operations. Thus the photoswitching gated (“Locked/Unlocked”) specifically and only by Hg(II) is both highly selective and efficiently reversible, suitable for ionic probes.

Although the ring-open form **1_O** looks like a conjugate system with alternating double and single bonds, the electrons in the two dithiazole-units remain highly localized. As a result, the colorless **1_O** absorbs intensively at high-energy wavelengths around 340 nm. Upon 365-nm irradiation, colorless **1_O** absorbs the excitation photon and undergoes a photochemical conversion to yield purple **1_C** (Figs. 1A and 2A).^{8a} The resultant ring-closed form **1_C** has completely delocalized π -electrons and thus has an

absorption band at 568 nm, in the low-energy side of the spectrum, indicative of the typical photochromic characteristic.

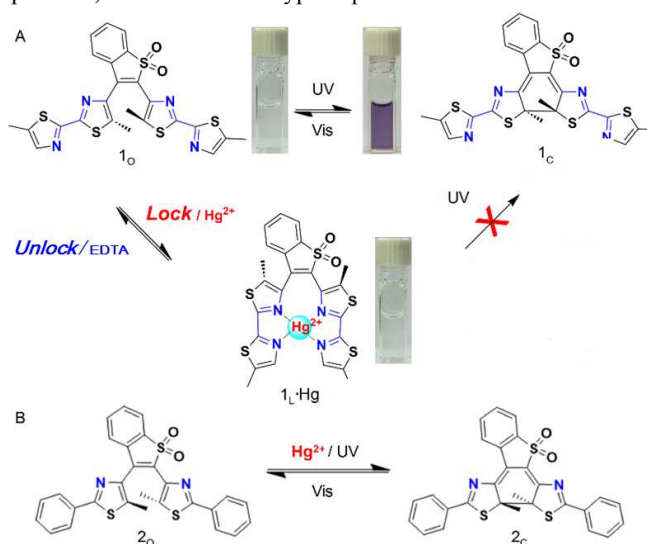


Fig. 1 (A) UV and visible light photochemically converts **1_O** and **1_C** reversibly and quantitatively. However, addition of Hg(II) induces the formation of **1_C•Hg** complex and thus locks the photochemical conversion from the open form **1_O** to the closed form **1_C**. EDTA unlocks such a blockade by removing the Hg²⁺ ions from the binding pocket and simultaneously releasing the **1_C** state. Therefore, photoswitching resumes. (B) In contrast, when the dithiazole was replaced with phenyl thiazole, the resultant bithiazolethene **2** cannot be locked by Hg²⁺ ions under the same irradiation of UV and visible light stimulations.

The photostationary state (PSS) starting from pure **1_O**, which was reached within 20 s upon irradiation at 365 nm (1 mW; $c = 2.0 \times 10^{-5}$ M), is pure **1_C**—the closed form. Conversely, visible light irradiation (> 510 nm) on the photochemically generated pure **1_C** converts it back to the colorless open form pure **1_O** (Fig. 1A). Accordingly, the newly synthesized **1_O** photochemically switches to

$\mathbf{1}_C$ and back quantitatively, which lays the foundation for quantitative and reversible photoswitching.

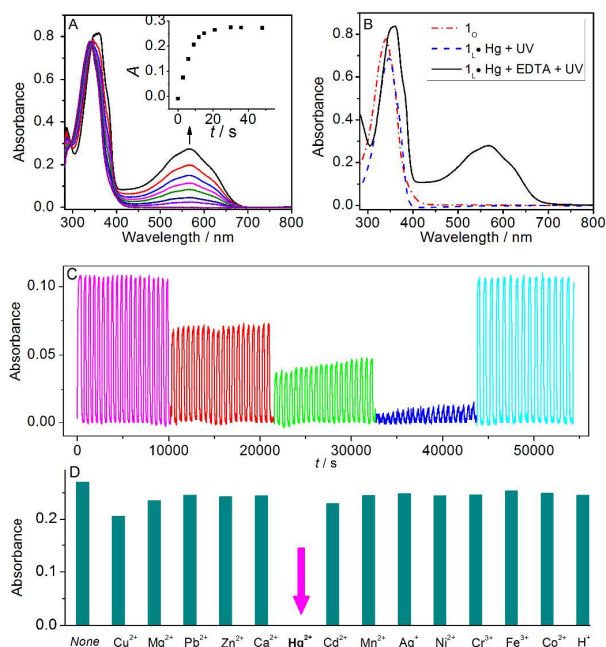


Fig. 2 (A) Without Hg(II) ions, the open form $\mathbf{1}_O$ can be easily photoswitched to the closed form $\mathbf{1}_C$ upon 365-nm irradiation (2.0×10^{-5} M, CH_3CN). (B) With 1.5 eq. Hg^{2+} ions at equilibrium, the open form $\mathbf{1}_O$ (red dot dash line) cannot be photochemically converted to the closed form $\mathbf{1}_C$ by 365-nm UV irradiation (blue dash line). Thus the Hg^{2+} ions effectively lock the photoswitching via forming a $\mathbf{1}_O \cdot \text{Hg}$ complex, but EDTA binds Hg^{2+} ions more strongly to unlock the photoswitching interconversions (solid black line). (C) Highly regular and dynamic photoswitching between $\mathbf{1}_O$ and $\mathbf{1}_C$ (1.0×10^{-5} M, CH_3CN , 568 nm) induced by alternating a 375-nm UV laser and three visible lasers (473, 532, and 561-nm) was gated by no mercury (pink line), 0.5 eq. Hg^{2+} (red line), 1.0 eq. Hg^{2+} (green line), and 2 eq. Hg^{2+} (blue line). Finally, 2 eq. EDTA was added to release the gated photoswitching (cyan line). The reproducible zero-absorbance and maximum amplitude manifest excellent fatigue resistance and remarkable reversibility at various gated levels. (D) When $\mathbf{1}_O$ was switched to $\mathbf{1}_C$, the absorption changes at 568 nm were used to gauge the degree of photoswitching and hence selectivity. At 2.0×10^{-5} M $\mathbf{1}_O$ and various metal ions also at 2.0×10^{-5} M concentration, 30-s UV irradiation (365 nm, 1mW) was applied. Only Hg(II) can lock the photoswitch; all other metal ions allow the photochemical conversion from $\mathbf{1}_O$ to $\mathbf{1}_C$ to continue as if the metal ions were absent.

In addition to the quantitative photoswitching between two scaffolds: bisthiazole ethene and cyclohexadiene, the two dithiazole units can cooperatively function as a photoswitchable chelating ligand to capture the complementary metal ion. Upon addition of 1.5-equivalent $\text{Hg}(\text{ClO}_4)_2$ to $\mathbf{1}_O$ at equilibrium, photoexcitation at 365-nm cannot drive the bisthiazole ethene into cyclohexadiene configuration as evidenced by no obvious change in absorption spectra and no signature band of the closed state at 568 nm (Fig. 1A and 2B). In other words, the molecular photocyclization ($\mathbf{1}_O$) was completely locked by Hg(II). To open the lock, EDTA quantitative titration recovers the photoswitching behavior completely intact. Such a *Lock-Unlock* pair is quite unique in gating reversible and quantitative photoswitching.

Amazingly, the system of $\mathbf{1}_O/\mathbf{1}_C$ exhibits high fatigue resistance in the gated photoreactivity. This point is exemplified in Fig. 2C when the $\mathbf{1}_C$ and $\mathbf{1}_O$ back-and-forth shuttling was repeated many times via alternating irradiation with one UV laser (375 nm) or three visible lasers (473, 532 and 561 nm) (Fig. 2C). The absorbance is oscillating between minimum zero and maximum value repeatedly, corresponding to absorption values of the pure $\mathbf{1}_O$ and $\mathbf{1}_C$ forms, respectively, up to 20 cycles. Upon addition of 0.5 eq. Hg^{2+} to the $\mathbf{1}_C/\mathbf{1}_O$ shuttling system, about 30% of the molecular photoswitches were locked. The absorbance maximizes at the PSS of $\mathbf{1}_O + 0.5$ eq. Hg^{2+} , corresponding about 70% of pure $\mathbf{1}_C$ because of the gated photoreactivity (Fig. 2C). Likewise, addition 1.0 or 2.0 eq. Hg^{2+} causes the photoswitching magnitude to drop to 40% or 10%, respectively. Note that in these kinetic experiments in Figure 2C, the Hg(II) and $\mathbf{1}_O$ system was not allowed to reach equilibrium to save time. Thus, the residual photoswitching, observed with 2.0 equivalent of Hg(II) is apparently due to the non-complexed $\mathbf{1}_O$ ligands (vide infra). The apparent effect is that 2.0 equivalent Hg(II) locked the photoswitching in this dynamic and non-equilibrium process, whereas 1.5 equivalent Hg(II) are sufficient at equilibrium conditions.

Actually, absorption titration curve reveals the one-to-one complex of $\mathbf{1}_O \cdot \text{Hg}$ with a moderate association constant ($K_a \geq 2.41 \times 10^5 \text{ M}^{-1}$) (Fig. S4 in ESI[†]).¹⁵ Here the partial photoreaction occurring in the presence of Hg^{2+} can be attributed to the portion of the non-complexed photochromic molecules. In addition, photoexcitation pumps energy into the complex, mostly the ligand, thus favoring the dissociation of the complex. Thus there is a slight tendency to freeing up more $\mathbf{1}_O$ molecules under photoswitching perturbation (Fig. 2C). Conversely, the photoswitching was recovered completely when 2.0 eq. EDTA was added to the system. The impressive fatigue resistance, excellent regularity, and reproducible maximum and minimum give the impression as if the system has never gone through the gated-locking processes. Together, these results indicate that the $\mathbf{1}_C/\mathbf{1}_O$ photoswitching system shows excellent gated properties. Here Hg(II) switches off photoswitching, whereas EDTA switches photoswitching back on.

Interestingly, the locking action by the mercury ion is highly specific regarding to the metal ions. Many other metal ions such as Cu(II), Mg(II), Pb(II), Zn(II), Ca(II), Cd(II), Mn(II), Ag(I), Ni(II), Cr(III), Fe(III) and Co(II) as well as H^+ have been titrated to the photoswitching system of $\mathbf{1}_C/\mathbf{1}_O$, none possesses the gating properties of Hg(II) ions (Figs. 2D and S1 in ESI[†]). No locking properties were found in these metal ions upon UV irradiation. Moreover, the cooperative dithiazole units play a predominant role in the locking action because the reference compound **2** containing two monothiazole units has no such locking properties (Fig. 1B and S2 in ESI[†]), which also rules out the interaction between the ethene bridge (benzo[*b*]thiophene-1,1-dioxide) and Hg(II) since photoswitches **1** and **2** share the same ethene bridge. Here, the selective coordination between Hg(II) and two dithiazoles restrains the rotation required for photocyclization to cyclohexadiene, thus realizing the highly specific Hg(II)-gated “*Lock*” effect (Fig. 1A).

Previously, the crystal structure of $\mathbf{1}_O$ were solved by X-ray diffraction, and therefore confirming both chemical composition and molecular structure of the ligand $\mathbf{1}_O$.^{8a} Here, the formation of

1_L•Hg complex was further validated by high-resolution data (Figs. 3A and 3B), in which a parent ion peak at *m/z* 854.9207 (measured exact mass) corresponding to a 1:1 complex with a formula ion [C₂₄H₁₈ClHgN₄O₆S₅]⁺. The calculated exact mass for [1_L + Hg²⁺ + 5 ClO₄⁻]⁺ is 854.9210 according to MassLynx V4.1 software, only off < 1 ppm. The relative *m/z* intensities are 19, 38, 66, 62, 100, 46, 59, 20, 17, 5, 3, and 1% for peaks at 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, and 862 for both experimental measurements and theoretical calculations. The excellent agreement between measured and calculated exact mass coupled with a perfect matching of the isotope pattern identifies the formation of 1:1 complex of 1_L•Hg.

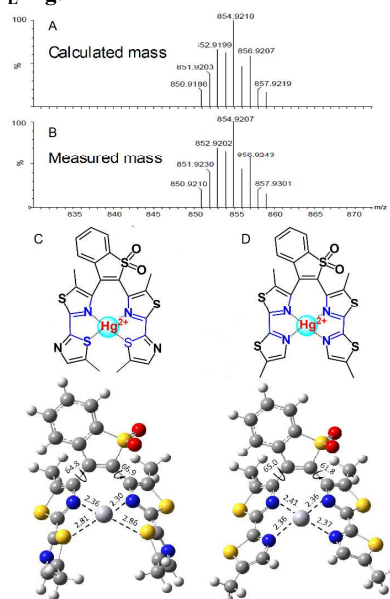


Fig. 3 Calculated exact mass (A) matches exceptionally well to the measured exact mass (B) in the high-resolution mass spectra (HRMS, ESI), validating the formation of 1_L•Hg complex. Two possible geometry-optimized candidates, 1_L•Hg-1 and 1_L•Hg-2, for this complex are shown in (C) and (D), with the four-nitrogen-coordinated mercury having 42.3 kcal mol⁻¹ lower energy than the mixed sulfur and nitrogen coordination.

What is the determinant of such an outstanding selectivity in gating photoswitching? Because the rigid dithiazoles rotate on the scaffold of ethene can only provide a square planar coordination pocket based on the X-ray structure of the ligand 1_O, metal ions must adopt near square planar geometry to fit into the binding site (Table 1).¹⁶ Metal ions Ca(II) and Cr(III) rarely form complexes with coordination number of four, thus they do not bind to the photoswitch 1_O. Most of the other ions such as Mg(II), Fe(III), Mn(II), Ni(II), Co(II), Cd(II), Zn(II), and Cu(II) have much smaller ionic radii (49–78 pm) to fit into the pocket of Hg(II), which is 96 pm, and thus no binding to the photoswitch 1_O. Only Ag(I) and Pb(II) have ionic radii of 100 pm and 98 pm, respectively, comparable to that of Hg(II). However, the radius-to-charge ratios for Ag(I) and Hg(II) are dramatically different, therefore Hg(II) forming a complex with photoswitch 1_O and Ag(I) does not. Finally, Pb(II) and Hg(II) have similar radii and radius-to-charge ratio, but they bind differently to the photoswitch. Why? Pb(II) ion has a lone pair of electrons in the 6p orbital occupying one of the

ligand position and it does not prefer to form the ψ-square pyramidal structure by accepting square planar coordination from 1_O. Instead, it prefers the ψ-trigonal bipyramidal coordination to minimize 90° lone-pair-bond repulsions. Consequently, Pb(II) ions often adopt unusual coordination numbers such as 7, 8, 9, 10, 11, and 12. Hg(II) ions, however, have a 5d¹⁰ configuration, thus no complication in crystal field stabilization energy, and readily accommodate regular coordination numbers of 2, 4, and 6. These analyses rationalize the unique mutual specificity between Hg(II) ions and photoswitch 1_O, which enables highly selective gating of molecular photoswitching.

Table 1. Ionic radii (*r*) and radius to charge ratios (*r/z*) in the environment of coordination number of 4 are correlated to the efficacy of the gating on the 1_O-1_C reversible photoconversion as measured by photoswitching percentage: A% = (A(1_C) - A(1_O))^{M^{1/2/3+}} / (A(1_C) - A(1_O))^{H⁺}.

M ⁿ⁺	Ca ²⁺	Mg ²⁺	Fe ³⁺	Cr ³⁺	Mn ²⁺	Ni ²⁺	Co ²⁺	Ag ⁺	Cd ²⁺	Pb ²⁺	Hg ²⁺	Zn ²⁺	Cu ²⁺
<i>r</i> /pm	-	57	49	-	66	52	58	101	78	98	96	60	56
<i>r/z</i>	-	28.5	24.5	-	33	26	29	101	39	49	48	30	28
A%	99.4	95.8	103.3	100.2	99.7	99.4	101.3	101.3	93.4	99.8	0	98.8	83.8

However, does the photoswitch use sulfur, nitrogen, or a combination of both to coordinate to Hg(II)? First, the two sulfur atoms near the ethene faced each other cannot participate the coordination because such a configuration will collapse the binding pocket. That leads to only two possible complexes depicted in Fig. 3C and 3D, and their structural parameters and relative energies are tabulated in Table S1†. Geometrical optimizations were carried out in gas phase at the PBE0/6-31G(d) level except for Hg, for which LANL2DZ basis set was used. The four-nitrogen-complex 1_L•Hg-2 was predicted to be the most stable, 42.3 kcal mol⁻¹ lower than 1_L•Hg-1, which uses the sulfur atoms of the terminal thiazoles to coordinate to the Hg(II) ion. In the 1_L•Hg-1 structure, the two methyl groups on the thiazole rings produce considerable repulsion, thus causing the Hg-S bond to elongate to 281–286 pm, considerable longer than typical Hg-S bond length of 236–240 pm.¹⁷ In contrast, the Hg-N bond lengths in 1_L•Hg-2 are 236–241 pm, in good agreement with crystallographic bond length of 229 pm.¹⁸ Therefore, we attribute the selectively gated photoswitching to the formation of the rigid Hg(II)-N square planar coordination.

In summary, we have constructed a unique mercury-ion gated molecular photoswitch, whose photochemical reactions depend on the presence of the very metal ion Hg(II). Many other metal ions were found to have no such ability to gate the photoswitching processes. The high selectivity to mercury ions is attributed to the perfect fit to the enzyme-like binding pocket created by the rotation of the bis(dithiazole)ethene (1_O). Additionally, the dithiazole units restrict to square planar coordination, which provides further selectivity to the screening of other metal ions. Because the 1_L•Hg complex does not bind strongly, a better chelator EDTA can replace the photoswitch, thus resuming the photoswitching functions. Together, the Hg(II) and EDTA exhibit “Lock/Unlock” functions to the photoswitching processes, turning the photochemical reactions off and on. The excellent reversibility and fatigue resistance make this selective gating of photoswitching remarkably reproducible.

This work was supported by National Science Foundation (CHE-1212429), National 973 Program (2013CB733700), NSFC/China, NSFC for Distinguished Young Scholars (Grant No. 21325625), the Oriental Scholarship, National Major Scientific Technological Special Project (2012YQ15008709), Fundamental Research Funds for the Central Universities (WK1013002), SRFDP 20120074110002, and CSC for Graduate Student Overseas Study Program (Grant No. 21325625).

Notes and references

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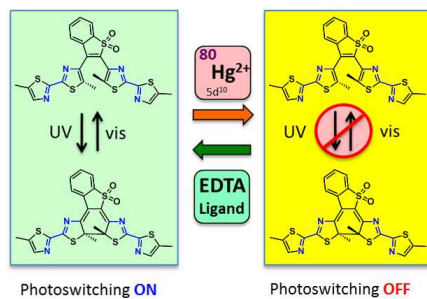
† Electronic Supplementary Information (ESI) available: Changes of 1 and reference 2 upon adding ions and theoretical calculation details. See DOI: 10.1039/c000000x/

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2 **Graphics for Contents**
3**Reversible photoswitching specifically responds to mercury(II) ions: the gated photochromism of bis(dithiazole)ethene**

Yue Wu, Weihong Zhu, Wei Wan, Yongshu Xie, He Tian and Alexander D. Q. Li**

Photochromic diarylethenes exhibit Hg(II)-induced gated photoreactivity, an unprecedented combination of “Lock/Unlock” function suitable as Hg(II) probes.

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