A Multiaddressable Photochromic Bisthienylethene with Sequence-Dependent Responses: Construction of an INHIBIT Logic Gate and a Keypad Lock

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Ⓢ *Supporting Information*

ABSTRACT: A photochromic bisthienylethene derivative (**BIT**) containing two imidazole units has been synthesized and fully characterized. When triggered by chemical ions (Ag^+), protons, and light, **BIT** can behave as an absorbance switch, leading to a multiaddressable system. **BIT** exhibits sequence-dependent responses via efficient interaction of the specific imidazole unit with protons and Ag^+. Furthermore, an INHIBIT logic gate and a keypad lock with three inputs are constructed with the unimolecular platform by employing an absorption mode at different wavelengths as outputs on the basis of an appropriate combination of chemical and photonic stimuli.

KEYWORDS: bisthienylethenes, photochromism, imidazole, sequence, INHIBIT, keypad lock
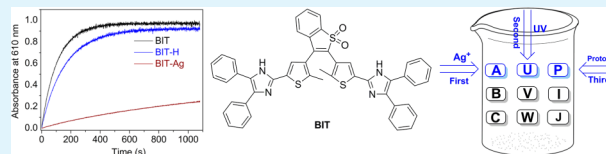
■ INTRODUCTION

Information processing for molecular computing devices has inspired scientists to design and construct a variety of systems that mimic the semiconductor logic functions.[1−18] Particularly, the keypad lock based on chemical and biomolecular systems has been raised with wide interest since it opens new opportunities to protect information as data security devices on the molecular scale.[19−23] What distinguishes the keypad lock from other combinational logic gates is the fact that its output signals are critically dependent upon the proper combination and sequence of input signals.[24−33] Proteins, enzymes, and nucleic acids offer the biomolecular platform for complicated logic gates like a keypad lock due to their natural specificity and compatibility.[20,23,25] The biomolecular logic systems based on DNA and enzymes/proteins can be easily scaled up for assembling large networking systems, which can be used for mimicking various electronic devices. However, the logic gates based on chemical molecular systems can also endow two distinct characteristics: (i) convenience in molecular tailoring and modulation for the output signals such as fluorescence or absorbance; (ii) easiness in realizing reversible multiaddressable states based on a unimolecular platform,[34,35] preferably allowing different input signals like protons, ions, redox, light, and even surface-enhanced Raman-scattered light.[15,24,36−38] Up to date, much sequence-dependent logic using fluorescence or absorbance as outputs has been developed.[21,25,28−32,39−42] In order to further boost the password in practical applications, there is still a great challenge in designing more complicated keypad locks using three or more inputs at the unimolecular platform.

Bisthienylethenes, as a promising photochromic system, can undergo a reversible transformation by photonic stimuli,

accompanying marked changes in optical and electronic properties, which can be potentially utilized for mimicking the operation of electronic logic gates on the molecular level.[35,36,43−48] In all cases, multiaddressable photochromic bisthienylethenes are more desirable in creating functional circuits in a straightforward fashion as an alternative to the time-consuming and difficult physical connection between different molecular systems.[49−52] Herein, we present a novel photochromic system **BIT** (Scheme 1) based on benzo[*b*]-thiophene-1,1-dioxide as an ethene bridge,[36,53,54] containing two phenyl-substituted imidazole units. By taking advantage of the specific basicity and coordination capability of the imidazole unit, **BIT** shows distinct multiple photochromic properties in the presence of protons and Ag^+. The absorption spectra of **BIT** display reversible changes under different pH values. In particular, the photocyclization properiy of **BIT** is restricted by the efficient coordination of **BIT** with Ag^+, which is demonstrated by NMR and UV/vis spectra. Thus, an INHIBIT logic gate can be constructed by the specific inputs of UV irradiation and Ag^+. Moreover, with the comibination of three inputs including protons, Ag^+, and light modulations, a molecular keypad lock is successfully constructed with the sequence-dependent characteristic of **BIT** in the absorption mode. As a proof of concept, this multiaddressable photochromic bisthienylethene with the sequence-dependent response provides a new platform for data processing on a molecular level, which could potentially authorize a user to verify authentication of a product or initiate a higher process.

Scheme 1. Proposed Binding Modes of BIT with Protons and Ag⁺ as Well as Photochromic Responses to Light Stimuli
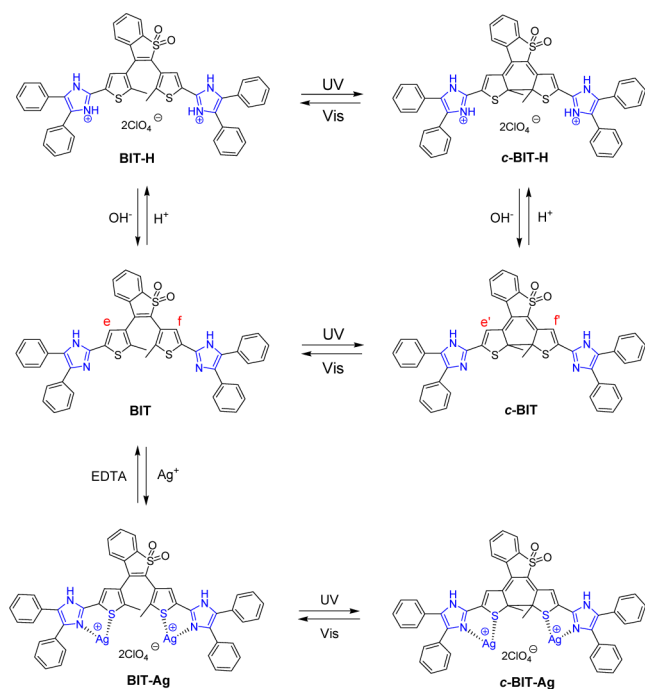
These molecular logic designs including a keypad lock can facilitate chemical (especially intracellular) sensing, small object recognition, and intelligent diagnostics, which can be constructed on the unimolecular platform by employing absorption and emission properties at different wavelengths as outputs, with the appropriate combination of chemical and photonic stimuli. Also, our system demonstrates large scope and diversity in terms of activation mechanism, response time, and property control in the design of logic gates, especially for the sequence-dependent keypad lock.

RESULTS AND DISCUSSION

Photochromic Properties and Fluorescence Modulation. The target molecule **BIT** was prepared by the conventional reaction of **BTA** with benzil in acetic acid. Its chemical structure was fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS (see the Experimental Section and the Supporting Information for details). The photophysical properties of **BIT** were investigated in a THF solution. Initially, **BIT** exhibited an intense absorption band centered at *ca.* 334 nm, which was ascribed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of the benzo[*b*]thiophene-1,1-dioxide core mixed with the diphenylimidazole unit.[55] Upon light irradiation at 365 nm, two intense broad absorption bands centered at 411 and 620 nm were observed in the absorption spectra of **BIT** (Figure 1A), along with a color change from colorless to cyan. It was indicative of the appearance of the closed form (*c*-**BIT**, Scheme 1) via the characteristic photocyclization reaction. In the photochromic system of **BIT**, the π-orbital symmetries for 1,3,5-hexatriene are only photocyclized with a conrotatory direction to cyclohexadiene upon UV-light irradiation.[43] The absorption bands in the visible region became gradually bleached to the regenerated open form as a result of the photochromic back reaction upon irradiation at visible light (>510 nm). Moreover, **BIT** showed moderate fluorescence with two bands at 387 and 585 nm upon excitation at the isosbestic point of 288 nm in THF (Figure
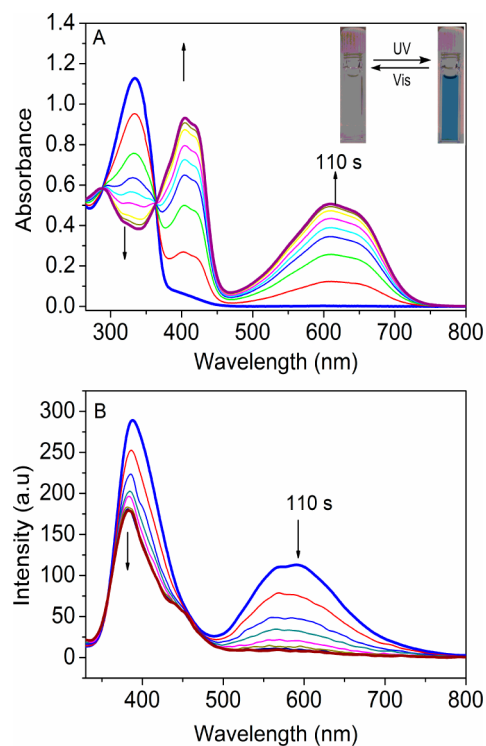

Figure 1. Optical properties of **BIT** (2.07×10^{-5} M) in THF upon irradiation with 365 nm light: (A) Absorption changes. Inset: photoimage from colorless to cyan. (B) Fluorescence changes ($\lambda_{ex} = 288$ nm).

1B). The emission could be a result of the donor−acceptor interaction between the electron-donating diphenylimidazole and thiopene units and the electron-withdrawing benzo[*b*]-thiophene-1,1-dioxide core.[56] However, upon photocyclization, its fluorescence intensity at 585 nm was quenched by 95% at the photostationary state (PSS) with respect to that of the initial open form. The quenched fluorescence may be a result of energy transfer between the open form and the closed form of **BIT** since the emission band at *ca.* 600 nm is overlapped with the absorbance of the PSS of **BIT** very well.

Multiaddressable Responses of Light, Protons, and Ag⁺. As a good Lewis base, imidazole is generally utilized as a proton acceptor or an efficient metal ligand.[57−62] Actually, when incorporating imidazole units into the photochromic system, **BIT** exhibits a specific response to protons and an efficient binding ability to Ag⁺. As shown in Figure 2A, upon the addition of 2.0 equiv of HClO₄ to the THF solution of **BIT**, the absorption band at *ca.* 334 nm decreased slightly, corresponding to the protonated form of **BIT** (**BIT-H**, Scheme 1). Upon further irradiation with 365 nm light, **BIT-H** became photocyclized as *c*-**BIT-H** and reached the PSS with two narrow absorption bands at 403 and 627 nm, respectively. With respect to *c*-**BIT**, the observed red-shift could be attributed to the protonation of imidazole units in *c*-**BIT-H**. Furthermore, the protonation−deprotonation process is reversibly controlled in both open and closed forms upon light irradiation and neutralization with base, which can be repeated several times without any obvious degradation (Figure S1 in the Supporting Information).

The metal ion coordination of **BIT** was also carried out in THF solution. As expected, among the test metal ions, including Na⁺, K⁺, Ag⁺, Ba²⁺, Ca²⁺, Mn²⁺, Zn²⁺, Co²⁺, Cd²⁺,
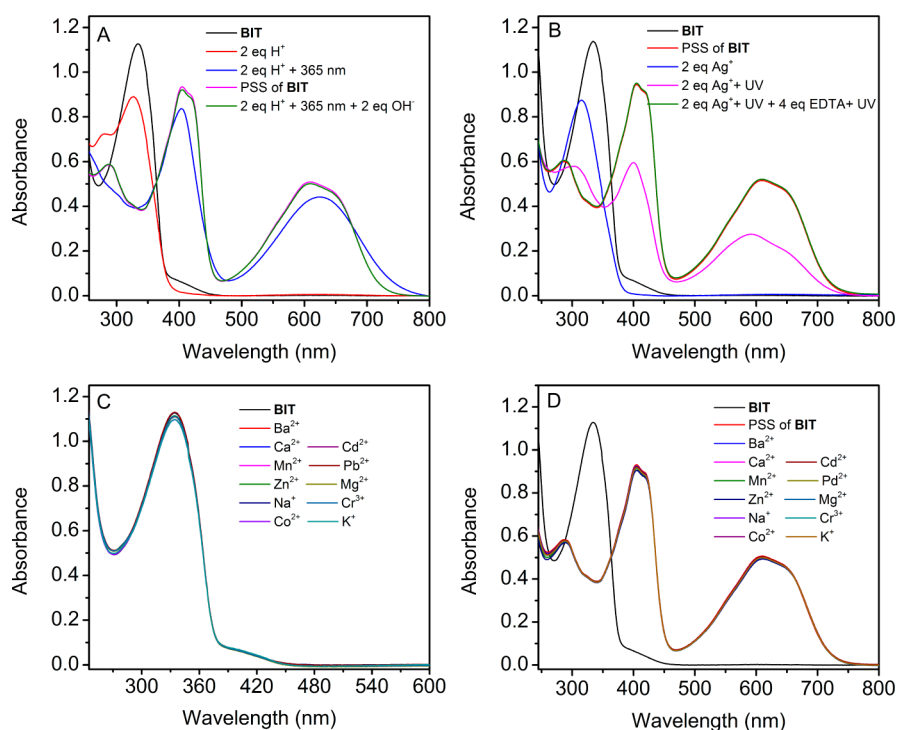
Figure 2. Absorption changes of **BIT** (2.07×10^{-5} M) in THF: (A) upon the addition of protons (H$^+$) and irradiation with 365 nm light, (B) upon the addition of Ag$^+$ ions, EDTA, and UV irradiation (365 nm), (C) upon the addition of different ions in the open state of **BIT**, and (D) upon the addition of different ions in the PSS state of **BIT**.

Pd^{2+}, Mg^{2+}, and Cr^{3+} (Figure 2), only the addition of Ag$^+$ with **BIT** exhibited the distinct absorption change (Figure 2B). Additionally, Hg^{2+} has a minor influence on **BIT**, which would be a result of the interaction between Hg^{2+} and imidazole and sulfur units (Figure S2 in the Supporting Information). We also tested the metal ions (Cu^{2+} and Fe^{3+}) with **BIT**. It was found that both of them caused distinct irreversible damage to **BIT**, which might be due to the possible radical reactions as previously reported (Figure S3 in the Supporting Information).[63,64] We checked **BIT** and the PSS of **BIT** coordination with Ag$^+$, both in a 1:2 stoichiometry. This is confirmed by the Benesi−Hildebrand method.[65,66] When assuming a 1:2 association between **BIT** and Ag$^+$, the Benesi−Hildebrand equation is given as follows:

$$\frac{1}{A_0 - A} = \frac{1}{K(A_0 - A_{max})[Ag^+]_0^2} + \frac{1}{A_0 - A_{max}} \quad (1)$$

A_0 is the absorbance of **BIT** or the PSS of **BIT**, A is the absorbance obtained with Ag$^+$, A_{max} is the absorbance obtained with an excess amount of Ag$^+$, K is the binding constant (M^{-2}), $[Ag^+]_0$ is the concentration of Ag$^+$ added (M). As shown in Figures S4 and S5 in the Supporting Information, the plot of $1/(A_0 - A)$ against $1/([Ag^+]_0)^2$ shows a linear relationship, indicating that **BIT** and the PSS of **BIT** indeed associated with Ag$^+$ in a 1:2 stoichiometry. Moreover, the job's plots exhibit a maximum at about 0.66 mol fraction, indicating that **BIT** and the PSS of **BIT** form a 1:2 complex with Ag$^+$. It further confirms the 1:2 binding stoichiometry (Figure S6 in the Supporting Information). The association constant, K, between **BIT** or the PSS of **BIT** and two Ag$^+$ is determined from the slope to be $2.36 (\pm 0.21) \times 10^9$ (M^{-2}) and $8.98 (\pm 0.81) \times 10^8$ (M^{-2}), respectively. The small binding constants of the PSS of **BIT** with Ag$^+$ may be due to the rigid structure of the closed

form of **BIT**. The possible 1:2 binding model between **BIT** and Ag$^+$ (Scheme 1) was further confirmed by the ESI mass spectrum (Figure S7 in the Supporting Information). A peak found at 1108.9430 was well consistent with the calculated data for $[2Ag + \mathbf{BIT} + ClO_4]^+$ (1108.9428).

Notably, upon further UV irradiation, only a half absorbance was achieved at the PSS in the presence of Ag$^+$ (**BIT-Ag**). The phenomenon cannot be observed from **BIT-H** with UV irradiation. Moreover, upon the addition of a strong chelate such as ethylenediamine tetraacetic acid (EDTA), the photochromic properties of **BIT** could be recovered from **BIT-Ag** (Figure 2B). In the case of **BIT-H** and **BIT-Ag**, the spectra change would be attributed to the change of the electron distribution of the whole molecule as a result of the protonation of imidazole units in **BIT** and the interaction between Ag$^+$ and **BIT**.

^{1}H NMR experiments further confirmed the coordination of Ag$^+$ and **BIT** (Figure 3). Due to the unsymmetrical ethene bridge, both hydrogens for imidazole (N-H) and thiophene (H_e and H_f, Scheme 1) in **BIT** are chemically nonequivalent. The two signals at 12.85 and 13.05 ppm as single peaks are ascribed to the imidazole hydrogens (N-H). Upon the addition of Ag$^+$, these two peaks became broadened and shifted significantly downfield around 13.45 and 13.67 ppm (Figure 3). The deshielding effect clearly confirms the coordination of Ag$^+$ with the imidazole nitrogen (Scheme 1).[67−69] Meanwhile, the protons of thiophene groups also underwent a downfield shift; that is, the signals of H_e and H_f changed from 7.72 and 7.93 ppm to 7.78 and 7.97 ppm, respectively. It is suggestive that, besides the imidazole nitrogen, the sulfur atom of the thiophene unit in **BIT** is also involved in the Ag$^+$ coordination (Scheme 1).[70] As shown in Figures 3 and S8 and S9 in the Supporting Information, there existed a very small change in both ^{1}H and ^{13}C NMR for benzene groups of **BIT** attached to
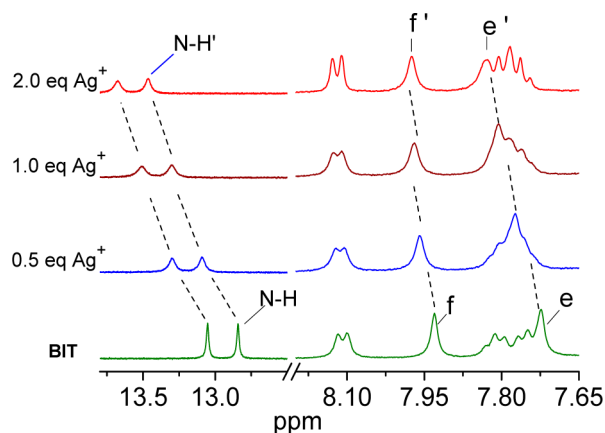
Figure 3. Partial ^1H NMR (400 MHz, 298 K, DMSO-d_6) spectra of **BIT** upon titration with Ag$^+$.

the imidazole unit during the titration of Ag$^+$, which might be reasonable since these protons are far away from the coordination site. Obviously, due to the joint interaction of the sulfur atom, the concerted coordination of S and N with Ag$^+$ might result in the above-mentioned lower absorbance at the PSS of **BIT-Ag** than **BIT-H** (Figure 2).

Here, the photochromism of **BIT** can be modulated by either protons or Ag$^+$. The conversion yield and the cyclization quantum yield from the open to the closed isomers in THF were 99.0 ± 0.6% and 45.0 ± 0.3% (**BIT**), 97.6 ± 0.5% and 46.0 ± 0.4% (**BIT-H**), and 91.2 ± 0.5% and 35.0 ± 0.3% (**BIT-Ag**), respectively (Table S1 and Figure S10 and S11 in the Supporting Information).[71,72] Notably, both the conversion yield and cyclization quantum yield of **BIT-Ag** were found to be smaller than those of **BIT**, possibly arising from the restriction of the photoactive antiparallel conformation due to the efficient interaction between Ag$^+$ and **BIT**. Since the conversion yield and the isomerization quantum yield are not significantly changed by the addition of Ag$^+$, the decreased PSS absorbance of **BIT-Ag** in the visible region (Figure 2B) might be due to a decrease in the absorption coefficient of the *c*-**BIT** complex to Ag$^+$. As calculated from Figure 2, the absorption coefficients at 365 nm of **BIT**, **BIT-H**, and **BIT-Ag** are 2.20×10^4, 1.64×10^4, and 1.01×10^4 M^{-1} cm^{-1}, respectively. Therefore, the product of the isomerization quantum yield and the absorption coefficient at 365 nm is 0.99×10^4 (**BIT**), 0.75×10^4 (**BIT-H**), and 0.35×10^4 (**BIT-Ag**). Obviously, the rate constant for the transformation from the open form to closed form is proportional to the mentioned product between the isomerization quantum yield and the absorption coefficient (Figure 4A). As a matter of fact, under irradiation with the same input light power for 1200 s (Figure 4A), the absorbance of **BIT-Ag** at 610 nm is 0.25, much lower than that of **BIT** (0.97) and **BIT-H** (0.92).

Constructing an INHIBIT Logic Gate and a Keypad Lock. Taking advantage of the multiple optical states of **BIT** with protons, Ag$^+$, and UV light, the multifunctional molecular logic gates such as an INHIBIT logic gate and a keypad lock were successfully constructed. First of all, the typical photocyclization restriction between Ag$^+$ and **BIT** was applied for the construction of the INHIBIT logic gate.[73,74] In the logic gate, irradiation by 365 nm light for photocyclization was chosen as input U, and Ag$^+$ (2 equiv) was utilized as another input A (Figure 5). The absorbance at 610 nm corresponding to the absorption of **BIT** at the PSS was defined as the output signal.
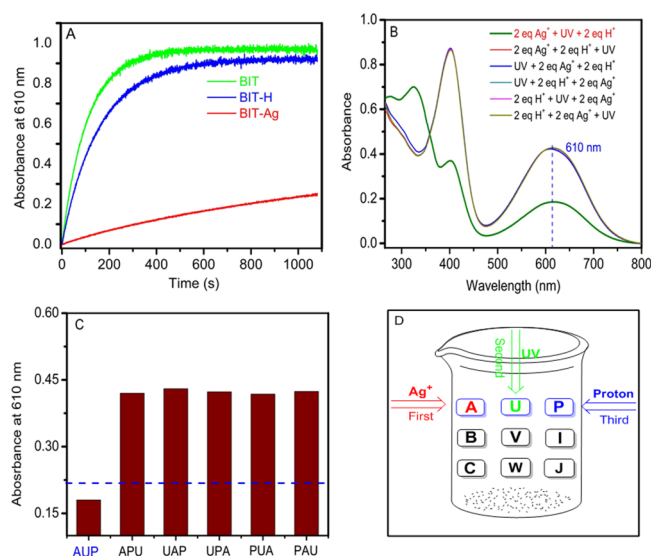

Figure 4. (A) Photochromism of **BIT**, **BIT-H**, and **BIT-Ag** under irradiation at 365 nm with the same input light power (0.81 mW cm^{-2}) and concentration (THF, 4.0×10^{-5} M). (B) Absorption changes of **BIT** (2.07×10^{-5} M) in THF upon the addition of Ag$^+$, protons, and UV irradiation (365 nm) in different sequences. (C) Bar presentation of the six possible output signals derived from absorbance at 610 nm. (D) A keypad lock with sequential inputs of Ag$^+$, UV irradiation (365 nm), and protons. Details are shown in the text.
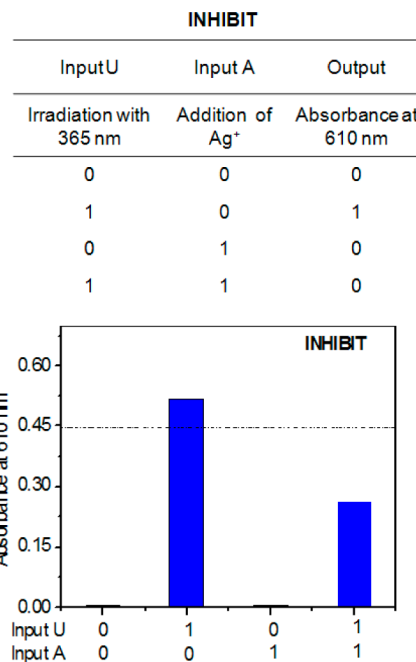
INHIBIT

Input U	Input A	Output
Irradiation with 365 nm	Addition of Ag$^+$	Absorbance at 610 nm
0	0	0
1	0	1
0	1	0
1	1	0

Figure 5. Truth table of INHIBIT gate (top) and **BIT** act as an INHIBIT logic gate (bottom). Note: The bar graph shows the experimental absorbance intensity following the listed inputs (absorption spectra shown in Figures S12 and S13 in the Supporting Information). The dotted line at an absorbance of 0.45 is the threshold level for the detection of an *on* response.

The threshold was set to be 0.45. As shown in Figure 5, only the irradiation at 365 nm (110 s) was carried out for **BIT** with the absence of Ag$^+$, and the absorbance value of **BIT** at 610 nm was higher than the defined threshold, that is, the output signal was "1". In that case, **BIT** was transformed into the closed form

by UV irradiation. However, for the other three situations, **BIT** was kept in the open form, or the photochromism of **BIT** was partly inhibited by Ag^+ with a low absorbance value relative to the threshold at 610 nm. Accordingly, the output signals for these three situations were "0". Taken together, the absorbance behavior at 610 nm coincides with the Boolean logic INHIBIT.

Further investigation of the photochromic behaviors of **BIT** was carried out with different combinational inputs of protons, Ag^+, and UV irradiation (Figure 4B). To simplify the discussion, the three inputs, protons (2 equiv), Ag^+ (2 equiv), and UV irradiation (365 nm, 110 s) were designated as "P", "A", and "U", respectively. Interestingly, only the "AUP" input gave a distinct different absorbance output at 610 nm among the six possible sequential input combinations (i.e., PAU, PUA, UPA, UAP, APU, and AUP). For the input sequential combination "AUP", the first addition of 2 equiv of Ag^+ (input "A") inhibited the photochromism of **BIT** to a great extent as a result of the efficient coordination between Ag^+ and **BIT**. Subsequently, the UV irradiation (input "U") gave a slight increase in absorbance. Finally, the absorbance intensity did not change much with the final addition of 2 equiv of protons (input "P"). For another input sequence "APU", after the first input of "A", the sequential addition of 2 equiv of protons might destroy the coordination between Ag^+ and **BIT** due to the protonation of the imidazole unit, resulting in the photochromic revival of **BIT**. Accordingly, the final UV irradiation (input "U") induced the full increase of the absorption band at 610 nm. In the case of "UPA" and "UAP", the photocyclization reaction was already induced by UV irradiation (input "U"); the following inputs "P" and "A" have little effect on the absorbance at 610 nm. For the sequence inputs "PUA" and "PAU", the presence of protons (input "P") can decrease the interaction between Ag^+ and BIT, resulting in the absorbance at 610 nm higher than the threshold (Figure 4C). It should be pointed out that, in the system of **BIT**, the observed sequence-dependent output with the proper order of inputs is a kinetic process, which resulted from the overall competition from the different absorbances for **BIT-H** and **BIT-Ag** with different effects on the photocyclization under the subsequent addition of the three inputs. As a kinetic process, the sequence-dependent phenomenon is always dependent upon the time scale.[19−21] Here, the established sequence-dependent system can stand or persevere beyond a reasonably long time scale (>4 h).

Inspired by the output dependence on the proper order of input signals, we can also utilize **BIT** to develop a specific molecular keypad lock with three inputs (Figure 4C). The corresponding output signals are defined as the absorbance at 610 nm ($A_{610\ nm}$), and the threshold is set as $0.05 < A_{610\ nm} < 0.2$. Herein, we defined that when the output signal fall in this threshold is "true", the output signal that is out of this threshold is "false". Obviously, only the input order "AUP" results in the "true" output signal ($A_{610\ nm}$), while the output signals from all other cases such as A, U, P, AU, UA, AP, PA, UP, PU, APU, PAU, PUA, UPA, UAP, or no inputs at all are out of the threshold region (Figure 4D and Figure S14 in the Supporting Information).

CONCLUSIONS

In summary, we report a novel multiresponsive photochromic switcher (**BIT**) that possesses two imidazole units specifically interacting with Ag^+ and protons. Its photocyclization reaction is restricted by the efficient interactions between Ag^+ and **BIT**,

demonstrated by NMR and UV/vis spectra. An INHIBIT logic gate was designed by using the absorbance at 610 nm as output signals with inputs of UV irradiation (365 nm) and Ag^+. Moreover, taking advantage of the specific basicity and coordination capability of the imidazole unit, **BIT** exhibits the characteristic sequence responses to the three combinational inputs of Ag^+, protons, and light, with several characteristics: (i) a light-triggered reversible photochromic bisthienylethene system with specific photoreaction; (ii) showing distinct multiple photochromic properties with three inputs such as light, Ag^+, and protons; (iii) exhibiting high selectivity to Ag^+, with high potential applications in sensing and labeling; and (iv) as a kinetic process, the established sequence-dependent system can stand or persevere beyond a reasonably long time scale. The potential incorporation into a multifunctional polymer matrix can provide a route toward all solid-state systems for fabricating a layer of logic.[75,76] Actually, the thin film solid-state systems for fabricating the layer of logic gates were also achieved (Figure S15 in the Supporting Information). It is also possible to incorporate the system into a cassette or microflowing cell to make a molecular device[77] or integrate this system with other chemical logic elements by making use of the inner filter effect or energy transfer strategies, which have already been utilized by Akkaya et al.[14] and Giordani and Raymo,[78] a further step toward data processing on the unimolecular platform with potential applications in sensing, small object recognition, and intelligent diagnostics as well as data manipulation.[1,6,25]

EXPERIMENTAL SECTION

Materials. All reagents were of analytical purity and used without further treatment. TLC analyses were performed on silica-gel plates, and flash chromatography was conducted using silica-gel column packages purchased from Qing-dao Haiyang Chemical Co. (China). In titration experiments of multiaddressable and sequence-dependent responses, $HClO_4$ and perchlorate salts were utilized as the sources of proton and metal cations. 2,3-Dibromobenzo[b]thiophene-1,1-dioxide and (5-(1,3-dioxolan-2-yl)-2-methylthioph-en-3-yl)boronic acid were prepared according to the established methods.[79,80]

Characterization. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz Spectrometer (^1H 400 MHz and ^{13}C NMR 100 MHz) at 298 K. The ^1H NMR and ^{13}C NMR chemical shifts are reported relative to residual solvent signals. Coupling constants (J) are denoted in hertz and chemical shifts (δ) in parts per million. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. Mass spectra were recorded on a Waters LCT Premier XE spectrometer with acetonitrile or methanol as the solvent. Absorption and fluorescence spectra were recorded on a Varian Cary 500 and Varian Cary Eclipse, respectively. The photochromic reaction was induced in situ by continuous wavelength irradiation using a Hg/Xe lamp (Hamamatsu, LC6 Lightningcure, 300 W) equipped with narrow-band interference filters of appropriate wavelengths. The photochromic quantum yields were determined by probing the sample with a Hg/Xe lamp during the photochromic reaction. Absorption changes were monitored by a CCD camera mounted on a spectrometer (Ocean Optics).

*Synthesis of **BTA**.* To a 100 mL two-necked bottle charged with nitrogen was added 2,3-dibromobenzo[b]thiophene-1,1-dioxide (0.324 g, 1.0 mmol), 2 M Na_2CO_3 (10 mL), 10 mL of THF, and $Pd(PPh_3)_4$ (0.1 g). The mixture was allowed to reflux for 15 min; then (5-(1,3-dioxolan-2-yl)-2-methylthiophen-3-yl)boronic acid (0.66 g, 3 mmol) dissolved in 10 mL of THF was introduced. The resulting mixture was allowed to reflux under the protection of nitrogen in the dark for 15 h. Then, the reactive mixture was allowed to cool to room temperature, and 3 M hydrochloric acid was added. After 4 h, the mixture was poured into H_2O and extracted with ethyl acetate. After concentration,

the compound was purified by column chromatography on silica (petroleum: ethyl acetate = 5:1 v/v) to yield 0.2 g (yield 39%) of white solid. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 2.12 (s, 3H, $-CH_3$), 2.21 (s, 3H, $-CH_3$), 7.30−7.32 (d × d, J = 8.4 Hz, 1H, benzothiophene−H), 7.62−7.67 (m, J = 8.4 Hz, 3H, benzothiophene−H, thiophene−H), 7.89−7.91 (d × d, J = 8.4 Hz, 1H, benzothiophene−H), 8.00 (s, 1H, thiophene−H), 9.86 (s, 2H, aldehyde−H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 15.46, 15.61, 122.18, 124.05, 124.54, 128.84, 130.97, 131.76, 134.00, 134.39, 134.89, 136.05, 136.62, 141.88, 142.25, 150.12, 152.26, 181.90, 182.27. Mass spectrometry (ESI positive ion mode for $[M + K]^+$) calculated for $C_{20}H_{14}O_4S_3K$: 452.9691. Found: 452.9696.

Synthesis of BIT. To a 50 mL bottle charged with nitrogen was added **BTA** (100 mg, 0.24 mmol), benzil (200 mg, 0.96 mmol), NH_4OAc (740 mg, 9.6 mmol), and 15 mL acetic acid. The resulting mixture was allowed to reflux under the protection of nitrogen in the dark for 15 h. Then, the reaction mixture was allowed to cool to room temperature and neutralized with 150 mL of $NaHCO_3$ (10%) solution. The resulting precipitate was collected, and the crude product was washed with water and recrystallized from dichloromethane to yield 0.1 g (yield 39%) of yellow solid. ^1H NMR (400 MHz, DMSO−d_6, ppm): δ 2.00 (s, 3H, $-CH_3$), 2.08 (s, 3H, $-CH_3$), 7.21−7.25 (m, J = 7.2 Hz, 2 H, benzene−H), 7.28−7.32 (t, J = 7.2 Hz, 4H, benzene−H), 7.37−7.51 (m, 14H, benzene−H), 7.58−7.62 (d, J = 7.2 Hz, 1H, benzothiophene-H), 7.72 (s, 1H, thiophene−H), 7.75−7.83 (m, J = 7.2 Hz, 2H, benzothiophene−H), 7.93 (s, 1H, thiophene−H), 8.10−8.12 (d, J = 7.2 Hz, 2H, benzothiophene−H), 12.85 (s, 1H, imidazole−H), 13.05 (s, 1H, imidazole−H). ^{13}C NMR (100 MHz, DMSO−d_6, ppm): δ 14.08, 14.25, 121.87, 123.01, 123.76, 124.10, 124.57, 126.67, 126.99, 127.06, 127.62, 127.84, 127.96, 128.10, 128.23, 128.63, 128.73, 130.71, 130.91, 131.55, 131.95, 132.01, 133.96, 134.03, 134.49, 134.61, 135.54, 136.90, 139.59, 140.65, 141.51. Mass spectrometry (ESI positive ion mode for $[M + H]^+$) calculated for $C_{48}H_{35}N_4O_2S_3$: 795.1922. Found: 795.1926.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
^1H NMR, ^{13}C NMR, and HRMS spectra of **BTA** and **BIT** and other optical properties of **BIT**. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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