

Dual-stimulus supramolecular luminescent switch based on cyanostilbene-bridged bis(dibenzo-24-crown-8) and a diarylethene derivative

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The development of multifunctional photo-controlled luminescent switch is of paramount significance, which provides versatile tools for smart systems and advanced organic luminescent materials. An intelligent supramolecular luminescent switch was fabricated based on cyanostilbene-bridged bis(dibenzo-24-crown-8) and a diarylethene derivative. The assembly act as a molecular plug-in, revealing fluorescence enhancement and reversible photo switching behaviour. Meanwhile, the plug-in's fluorescence was locked/unlocked by base/acid with apparent self-feedback fluorescence by reason of aggregation induced emission mechanics, which was further applied as multifunctional photoerasable fluorescent ink.

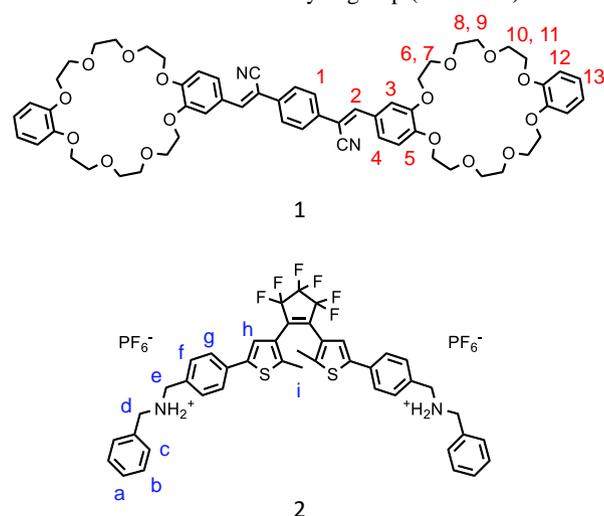
Organic luminescent materials are intensely studied because of their unique electronic structures and optical properties in expressing information with high resolution and sensitivity.¹ Among the most versatile fluorophores, cyanostilbene (CS) derivatives emerged as competitive options:² a) CS structures is tunable by substitution in either the aromatic rings or the doubled bond, allowing a wide variety of structural design; b) the substitution of cyan group makes CS molecules easy to be synthesized; c) aggregation induced emission (AIE) properties endow CS molecules with high quantum yield emissions in assemble or aggregate state.³ The intriguing photophysical features of CS are promoting more and more supramolecular scientists to incorporate it with various host (such as cucurbit[8]urils, chiral amino acid, polysiloxane), for potential applications of light harvesting,⁴ high performance aqueous fluorescence,⁵ sequential energy transfer,⁶ liquid crystal paints,⁷ and so on. Thus, CS derivatives contributed high performance molecules for supramolecular luminescent materials.

Photochromic molecular switches that can undergo reversible transformations are of great interest because the input is remote, instantaneous, clean and wavelength tunable,⁸ for the application of stereo-selective recognition,⁹ near-infrared photo responsive materials,¹⁰ single cell operation,¹¹ and so on. We constructed a dual-stimulus [2]pseudorotaxane based on an unsymmetrical diarylperfluorocyclopentene and Eu²⁺/terpyridinyldibenzo-24-crown-8 complex and revealed an excellent photochemical control of the luminescence of lanthanide.¹² Recently, we report a

supramolecular switch based on a symmetrical perfluorocyclopentene diarylethene derivative and a [Ru(bpy)₃]²⁺ complex, revealing highly efficient Förster resonance energy transfer (FRET) and applied as photoerasable fluorescent ink.¹³ To transfer the fluorescent information more intelligently and securely, it is vital important to develop an additional mechanism to “lock” or “unlock” the written luminescent characters. Furthermore, a self-feedback function is badly needed because it demonstrates the system states and the instruction of following

step actions for operators. Yet, “locking” or “unlocking” of photo controlled reversible fluorescence on/off materials with self-feedback functions haven't been reported to date, which is extremely powerful in transformation and protection of secret information.

Herein, we report a locking/unlocking function of photo switching process by integrating base/acid- and photo responsive properties into a two sites' bonded assembly, with a strong self-feedback ability, which is called supramolecular plug-in. The host molecule, cyanostilbene-bridged bis(dibenzo-24-crown-8) (**1**) was obtained by the dehydration reaction of p-phenylenediacetonitril and aldehyde substituted dibenzo-24-crown-8, while the guest molecule, diarylethene bis-ammonium salt (**2**) was obtained via condensation of amine- and aldehyde group (Scheme 1).



Scheme 1. Chemical structures of host molecule **1** (cyano-stilbene bridged bis(dibenzo-24-crown-8)) and guest molecule **2** (diarylethene bis-ammonium salt).

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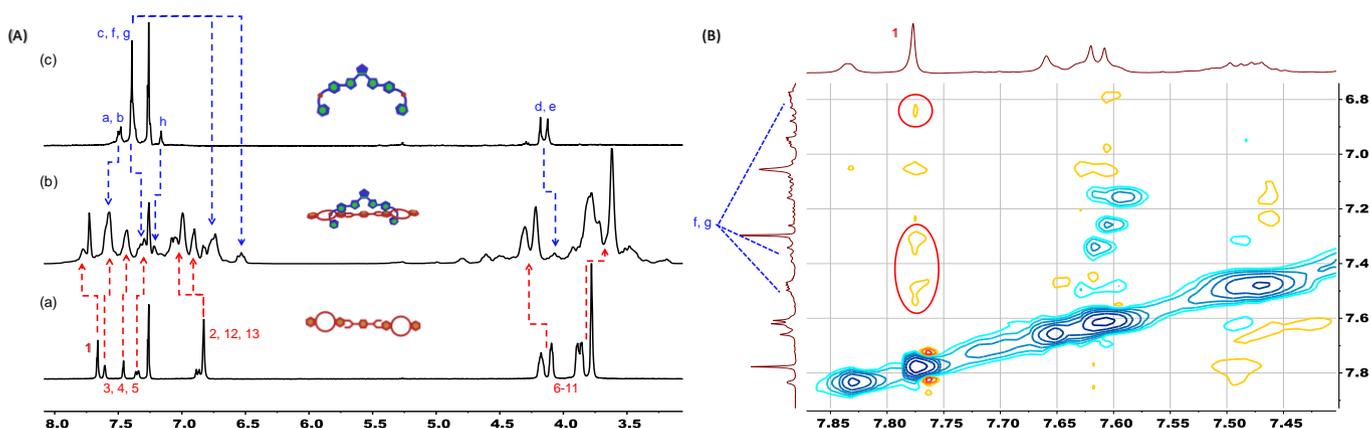


Figure 1. (A) ¹H NMR spectra (400 MHz, CDCl₃/CD₃CN = 10/1, 2 × 10⁻³ M) of (a) **1**, (b) **1** to **2**, (c) **2**. (B) 2D NOESY spectra (100 MHz, CDCl₃/CD₃CN = 10/1, 298 K) of **1** to **2**.

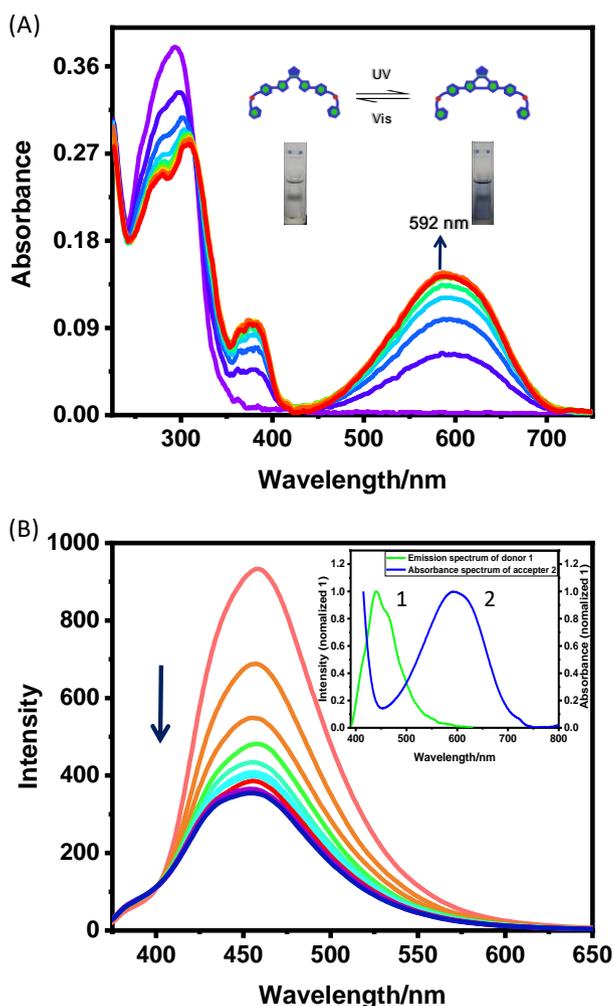


Figure 2. (A) UV/Vis spectra (CDCl₃/CD₃CN = 10/1, 2 × 10⁻⁵ M) of **2** irradiated by 254 nm light for up to 160s. (B) Fluorescence spectra (CDCl₃/CD₃CN = 10/1, 2 × 10⁻⁵ M) of **1** to **2** irradiated by 254 nm light for up to 4 min. Inset: Fluorescence spectra (CDCl₃/CD₃CN = 10/1, 2 × 10⁻⁵ M) of **1** (green) and UV/Vis spectra (CDCl₃/CD₃CN = 10/1, 2 × 10⁻⁵ M) of **2** (Closed form, blue).

Absolute conformation of assembly 1 to 2. It is well known that 24-crown-8 interacts intensely with ammonium salt by electrostatic- and dipole-dipole interactions.¹⁴ As shown in Figure 1A, when mixed **1** and **2** in the CDCl₃/CD₃CN solvents, signals of H_{d,e} near ammonium salt, and partial signals of H₆₋₁₁ in the crown ether moved to up field and down field respectively. Besides, it is also observed that signals of H_i in the benzene of **1**, and H_h in the thiophene of **2**, moved to down field obviously, indicating that aromatic part was also affected when **1** assembled with **2**. Thus, we speculated that **1** buttoned on the bottom of **2** parallelly (Figure S7, distance between the two cavities just match with distance between the two ammonium salts). To confirm this hypothesis, at first, bonding ratio was determined to be 1:1 by UV/Vis titration experiments (Figure S8, inset). Next, relative molecular mass of the assembly was determined to be mass of one host add one guest ($m/z = 1832.57, [M - 2PF_6^- - H^+]$) by matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-TOF, Figure S9), indicating that the assemble pattern was [1+1], not [n+n]. At last, direct evidence was found in the Nuclear Overhauser Effect Spectroscopy (NOESY) experiment (Figure 1B): signals of the middle benzene protons (H_i) of **1** correlated with signals from the middle part protons (H_{f,g}) in **2** by NOE effect, indicating that the spatial distance between the thiophene bridge and the cyanide stilbene bridge is very small. At this point, only one configuration can accord with all experiments, that we called the assembly as a supramolecular plug-in, as shown in Figure 5, with bonding constant determined to be 8.24 × 10⁵ M⁻¹ by UV/Vis titration experiments (Figure S10).

Photo-switching of supramolecular plug-in 1 to 2. Over the past years perfluoro-diarylethene derivatives have received much attention due to their promising properties of anti-fatigue, fast responsive speed, anti-photobleaching and convenient modification.¹⁵ As shown in Figure 2A, **2** performed well in photo-switching process: with 254 nm light irradiation, absorbance around 592 nm arose, and this process was reversible by ≥ 450 nm light irradiation, with good reversibility (Figure S11). Furthermore, the photo-switching property was also possessed by plug-in **1** to **2**. As shown in Figure 3A, signals of thiophene protons (H_h) and methyl protons (H_{d,e}) adjacent ammonium salt of **2** split into two peaks moving conformably to down field. While partial signals of ethylene glycol protons of **1** passivated a lot, indicating that ring-closure reaction occurred in plug-in **1** to **2**, and influenced

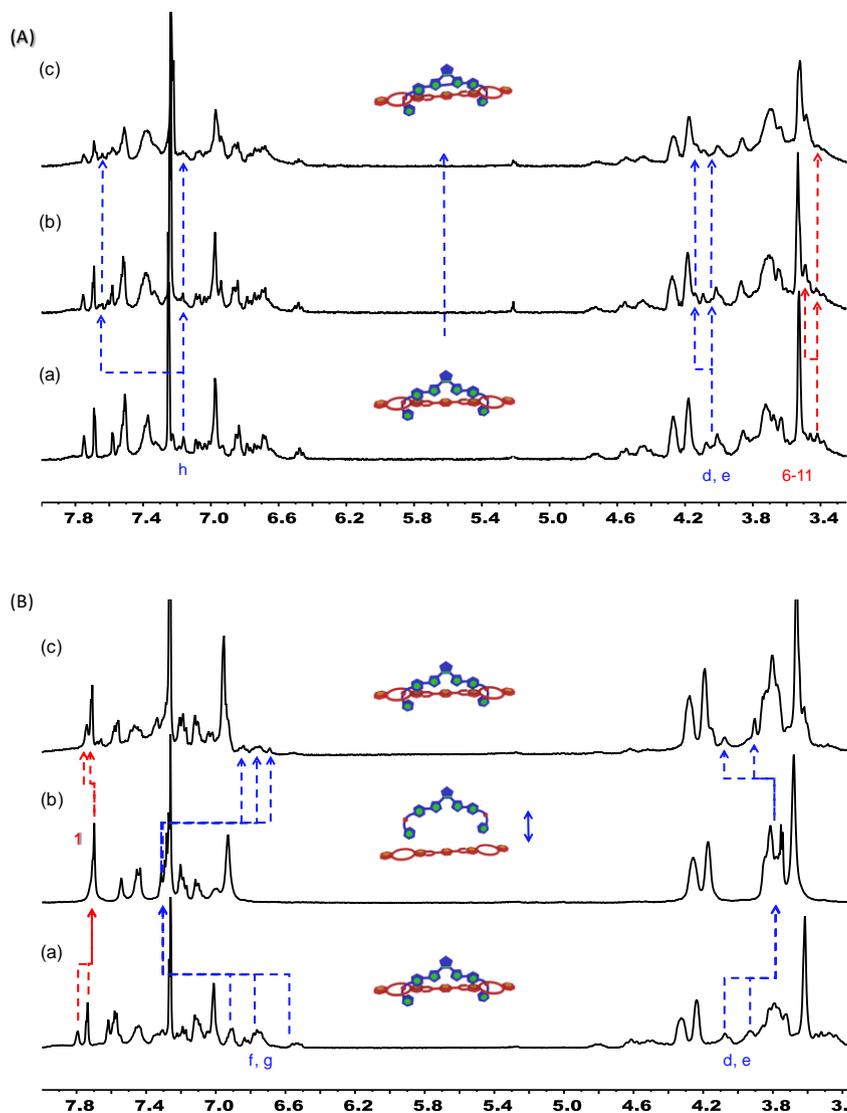


Figure 3. (A) ¹H NMR spectra (400 MHz, CDCl₃/CD₃CN = 10/1, 2 × 10⁻³ M) of 1-2 with 254 nm light irradiation for (a) 0 min, (b) 20 min, (c) 40 min. (B) ¹H NMR spectra (400 MHz, CDCl₃/CD₃CN = 10/1, 2 × 10⁻³ M) of (a) 1-2 treated with (b) base and (c) acid.

the interactions between **1** and **2**. Besides, absorbance of plug-in 1-2 arose consistently at 592 nm with 254 nm light irradiation regardless of stereo restriction by **1** (Figure S12).

FRET is fundamental important in photo-electronic systems in which delocalized exciton may form and diffuse over donor and acceptor.¹⁶ In our case, as shown in Figure 2B (Inset), the absorbance of closed form **2** overlapped with the emission of **1**. Besides, the distance between **1** and **2** was short enough (Figure S13, the distance was significantly shorter than Forster radius:¹⁷ R₀ = 30.7 Å) because the assembling process brought two components toward each other. That means **1**'s emission energy was able to transfer to **2**, and that the later has no emission spectra, indicating quenching effect of **1**. This process was shown in Figure 2B: with 254 nm light irradiation, the emission spectra of plug-in 1-2 declined a lot to a low level, and reversible conversion was realized by ≥ 450 nm light irradiation. Such a spectra change demonstrated that fluorescence of the plug-in can be switched by selective wavelength, providing a powerful photo-

switch for the dual-stimulus molecular device.

Base/Acid response of plug-in 1-2 and AIE property of host 1. Base/Acid stimulation was an effective method to switch the non-covalent interactions among crown ether and ammonium salt, leading to their moments along axle tracks.¹⁸ As shown in Figure 3B, with adding excess amount of base, the primarily split benzene signals (H₁) of **1** merged to one signal, and the primarily shifted methyl signals (H_{d,e}) adjacent ammonium salt of **2** vanished. The reversible process was performed by adding excess amount of acid, with all signals above recovered rapidly to original level. The variation of ¹H NMR spectra indicated that base/acid stimulation was able to modulate **2** to plug into or out of **1** effectively.

It should be noted that fluorophore **1** was an AIE¹⁹ molecule, benefiting from which plug-in 1-2 was an intelligent optical devices with assembly induced emission²⁰ and fluorescence enhancement properties in plug in/out form of solvent/solid state. As shown in Figure 4A, the fluorescence of **1** increased significantly when solvent's solubility decreased, due to the restriction of vibration and J-aggregation of **1**. As for the assemble process, when **2** plugged into **1**, **1**'s fluorescent strength doubled (Figure S14), due to the restriction of **2**. In a word, AIE property induced the fluorescence to be stronger and the fluorescent signals easier to be recognized.

Base/Acid stimulation provided a powerful chemical switch to modulate fluorescence of plug-in 1-2. As shown in Figure 4B, adding base led to the fluorescence of plug-in 1-2 decreased by half, on accounting of the plug-out process of **2** with removing of **2**'s restriction to **1**.

Reversible process was realized by adding acid to the solvents accompanying fluorescence recovered basically to original level, which can be performed in several cycles (Figure S15). In the solid state, the luminescent behaviour became a little different: when treated with base, fluorescence of plug-in 1-2 turned to be brighter with a distinctive yellow color (Figure 4C), on accordance with aggregate form **1** (Figure 4A, inset). This was interpreted as that when **2** plugged out from **1**, **1** had the chance to come nearer toward each other without obstacle of **2**, so the fluorescence was strengthened by reason of AIE mechanism. This magic yellow fluorescence strengthening provided a prominent self-feedback signals that **2** had plugged out from **1** to be a detached system.

Locking/Unlocking of the photo-switched plug-in 1-2 with self-feedback function. Smart materials with photo, thermal or chemical responsive functions were widely reported, but dual-stimulus responsive small molecular fluorescence switch was rarely reported, which is significantly important for micro enviro-

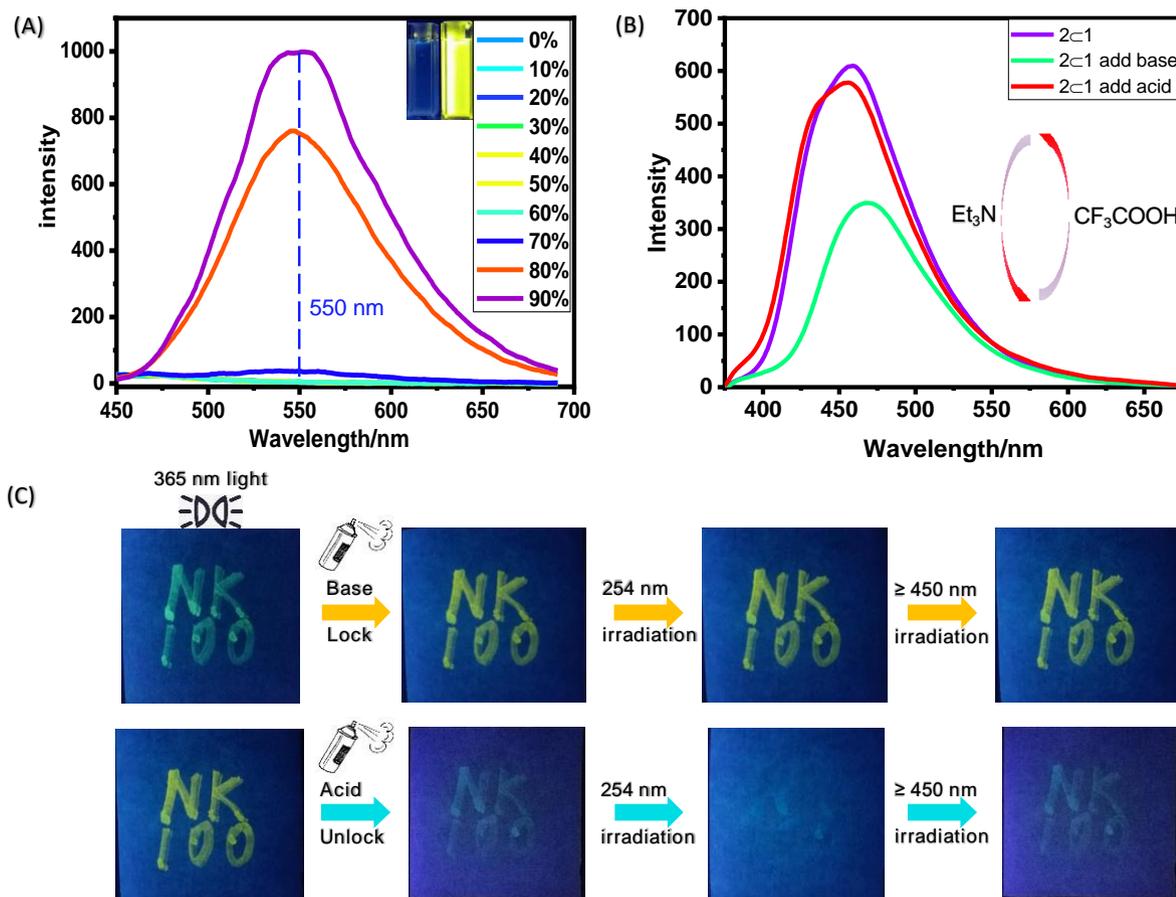


Figure 4. (A) Fluorescence spectra of **1** in different fractions of CHCl_3 and n-Hexane, 5×10^{-5} M; Inset: pictures of **1** in the fractions of 0% n-Hexane (left) and 90% n-Hexane (right). (B) Fluorescence spectra ($\text{CH}_2\text{Cl}_2/\text{CD}_3\text{CN} = 10/1$, 2×10^{-5} M) of **1-2** (purple) treated with base (cyan) and acid (red). (C) Characters written by fluorescence ink made of plug-in **1-2** solvents, which was treated by base and acid for 254 nm light and ≥ 450 nm light irradiation (Fluorescence character was displayed under 365 nm light source).

nment sensing and imaging. On the other hand, locking/unlocking informational with self-feedback function is vital important and eagerly needed, because it provides protection for information security and monitoring for system state. Photo-responsiveness led to photo erasable fluorescent ink for leaving secret information on papers. And the unique base/acid responsiveness led to **2** to plug into or out from **1**, sequentially locking/unlocking of the particular fluorescence information which we modulated to be visible or invisible. In addition, base treatment can also protect the information from sunlight bleach because of the FRET-off state (Figure 5). Furthermore, the special conspicuous yellow color change facilitated by AIE mechanism made it convenient to monitor or feedback the information of locking or unlocking state of plug-in **1-2**.

As shown in Figure 4C, when treated with base, the character was locked, and the bright yellow fluorescence feedback demonstrated that the information would not be changed, no matter which wavelength was applied. When treated with acid, the fluorescence recovered to blue-green, reflecting that the character was unlocked, and following that the information was able to be erased by 254 nm light or recovered by ≥ 450 nm light irradiation. All in all, the three independent synergistic mechani-

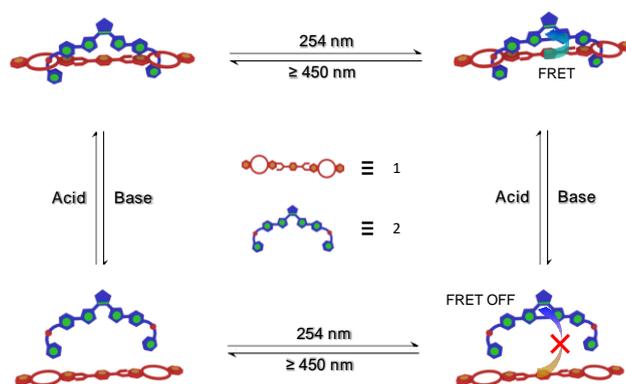


Figure 5. Schematic illustration of the dual-stimulus supramolecular luminescent switch.

isms achieved such intelligent luminescent materials. In summary, we demonstrated a photo-switched supramolecular luminescent plug-in, showing both AIE and photo/chemical dual responsive properties. Such an orthogonal stimulation allows for photo induced fluorescence on/off and information locking/unlocking by base/acid treatment, with apparent fluoresce-

nt color change for self-feedback function. This study realized the rarely reported but very important locking/unlocking information and self-feedback functions in one small molecular device, providing a promising step for multifunctional intelligent supramolecular luminescent devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

dual stimulus responsive, cyanostilbene, luminescent switch, locking/unlocking, self-feedback

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[1] (a) S. Yang, D. Streater, C. Fiankor, J. Zhang, J. Huang, *J. Am. Chem. Soc.* **2021**, *143*, 1061-1068; (b) Y. Z. Zhong, J. Zhan, G. H. Xu, Y. M. Chen, Q. Qin, X. Liao, S. D. Ma, Z. M. Yang, Y. B. Cai, *Angew. Chem. Int. Ed.* **2021**, *60*, 8121-8129; (c) S. Li, L. Y. Fu, X. X. Xiao, H. Geng, Q. Liao, Y. Liao, H. B. Fu, *Angew. Chem. Int. Ed.* **2021**, *60*, 18059-18064.
[2] (a) M. Martínez-Abadía, R. Giménez, M. B. Ros, *Adv. Mater.* **2018**, *30*, 1704161; (b) J. J. Tian, Y. R. He, J. T. Li, J. Wei, G. Q. Li, J. B. Guo, *Adv. Optical Mater.* **2018**, 1701337.
[3] (a) S. Y. Li, K. G. Gutierrez-Cuevas, X. F. Zhang, J. B. Guo, Q. Li, *Adv. Funct. Mater.* **2021**, *31*, 2007957; (b) H.-J. Kim, H. J. Lee, J. W. Chung, D. R. Wang, S. Y. Park, *Adv. Optical Mater.* **2019**, *7*, 1801348.
[4] H.-J. Kim, P. C. Nandajan, J. Gierschner, S. Y. Park, *Adv. Funct. Mater.* **2018**, *28*, 1705141.

[5] H.-J. Kim, D. R. Wang, J. Gierschner, S. Y. Park, *Angew. Chem. Int. Ed.* **2016**, *55*, 15915-15919.
[6] L. K. Ji, Y. T. Sang, G. H. Ouyang, D. Yang, P. F. Duan, Y. Q. Jiang, M. H. Liu, *Angew. Chem. Int. Ed.* **2019**, *58*, 844-848.
[7] J. Koo, J. Jang, S.-I. Lim, M. Oh, K. M. Lee, M. E. McConney, M. E. Sio, D.-Y. Kim, K.-U. Jeong, *Mater. Horiz.* **2021**, *8*, 1561.
[8] (a) M. Martínez-Abadía, B. Robles-Hernández, M. R. de la Fuente, R. Giménez, M. B. Ros, *Adv. Mater.* **2016**, *28*, 6586-6591; (b) D. Kim, J. E. Kwon, S. Y. Park, *Adv. Funct. Mater.* **2018**, *28*, 1706213; (c) N. F. König, D. Mutruc, S. Hecht, *J. Am. Chem. Soc.* **2021**, *143*, 9162-9168; (d) G. L. Niu, R. Y. Zhang, Y. Gu, J. G. Wang, C. Ma, R. T.K. Kwok, J. W.Y. Lam, H. H.-Y. Sung, I. D. Williams, K. S. Wong, X. Q. Yu, B. Z. Tang, *Biomaterials.* **2019**, *208*, 72-82; (e) Z. Q. Li, X. Liu, G. N. Wang, B. Li, H. Z. Chen, H. R. Li, Y. L. Zhao, *Nat. Commun.* **2021**, *12*, 1363.
[9] Y. Liu, Q. Zhang, S. Crespi, S. Y. Chen, X.-K. Zhang, T.-Y. Xu, C.-S. Ma, S.-W. Zhou, Z.-T. Shi, H. Tian, B. L. Feringa, D.-H. Qu, *Angew. Chem. Int. Ed.* **2021**, *60*, 2-12.
[10] Y. F. Han, Y. R. Yin, F. Wang, F. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 14076-14082.
[11] Z.-Y. Li, Y.-Y. Liu, Y.-J. Li, W. H. Wang, Y. Y. Song, J. J. Zhang, H. Tian, *Angew. Chem. Int. Ed.* **2021**, *60*, 5157-5161.
[12] H.-B. Cheng, H.-Y. Zhang, Y. Liu, *J. Am. Chem. Soc.* **2013**, *135*, 10190-10193.
[13] H. Wu, Y. Chen, Y. Liu, *Adv. Mater.* **2017**, *29*, 1605271.
[14] J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science.* **2004**, *303*, 1845-1849.
[15] (a) Z. W. Zhang, W. H. Wang, P. P. Jin, J. D. Xue, L. Sun, J. H. Huang, J. J. Zhang, H. Tian, *Nat. Commun.* **2019**, *10*, 4232; (b) C. B. Fan, L. L. Gong, L. Huang, F. Luo, R. Krishna, X. F. Yi, A. M. Zheng, L. Zhang, S. Z. Pu, X. F. Feng, M. B. Luo, G. C. Guo, *Angew. Chem. Int. Ed.* **2017**, *56*, 7900-7906; (c) S. Fredrich, R. Gçstl, M. Herder, L. Grubert, S. Hecht, *Angew. Chem. Int. Ed.* **2016**, *55*, 1208-1212.
[16] L. J. Patalag, J. Hoche, M. Holzapfel, A. Schmiedel, R. Mitric, C. Lambert, D. B. Werz, *J. Am. Chem. Soc.* **2021**, *143*, 7414-7425.
[17] P. Zhang, S. Rogelj, K. Nguyen, D. Wheeler, *J. Am. Chem. Soc.* **2006**, *128*, 12410.
[18] (a) X. Yang, Q. Cheng, V. Monnier, L. Charles, H. Karoui, O. Ouari, D. Gimes, R. B. Wang, A. Kermagoret, D. Bardelang, *Angew. Chem. Int. Ed.* **2021**, *60*, 6617-6623; (b) L.-S. Zheng, J.-S. Cui, W. Jiang, *Angew. Chem. Int. Ed.* **2019**, *58*, 15136-15141; (c) J.-S. Cui, Q.-K. Ba, H. Ke, A. Valkonen, K. Rissanen, W. Jiang, *Angew. Chem. Int. Ed.* **2018**, *57*, 7809-7814.
[19] Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Commun.* **2009**, *29*, 4332-4353.
[20] J. Wang, Z. Z. Huang, X. Ma, H. Tian, *Angew. Chem. Int. Ed.* **2020**, *59*, 9928-9933.