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Unsymmetrical diarylethenes as molecular keypad locks with tunable photochromism and fluorescence *via* Cu^{2+} and CN^- coordinations[†]

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New unsymmetrical diarylethenes were synthesized and their photochromic and fluorescent properties are tailored by Cu^{2+} and CN^- coordinations. A novel molecular logic keypad lock is constructed based on the fluorescence emission changes by the inputs of UV/visible irradiation, Cu^{2+} and CN^- .

Electronic devices play increasing roles in our daily lives and the development of data processing platforms using individual molecules mimicking the operation of electronic logic gates and circuits at the molecular level has been raised with wide interest.¹ Many researchers have therefore considered to build important molecular scale electronic logic devices keypad locks, which are capable of authorizing password entries, as they open new opportunities to protect information at the molecular scale.² However, it is still a great challenge to design delicate logic circuits and keypad locks using three or more inputs for the purpose of practical applications. As a basic binary unit, the photochromism offers a possibility for establishing such logic circuits and keypad locks.

Among all photochromic compounds, diarylethenes are one of the most promising candidates for photoelectronic applications owing to their excellent thermal-stability, remarkable fatigue-resistance, rapid response and fairly high photocyclization quantum yields.³ Much progress has been made to develop symmetrical diarylethenes with ions-modulated photochromic properties.⁴ Nevertheless, for the applications to electronic logic devices, it is essential to design unsymmetrical diarylethenes which exhibit good optical performances and multi-response to various ions due to their special structures.⁵ Furthermore, as one of the patterns that the fluorescence sensing of specific ions integrates into electronic logic devices, many fluorescence enhancement chemosensors have been designed to detect Cu²⁺ in the past few decades⁶ due to their more sensitive responses to Cu²⁺ than those of the fluorescence quenching chemosensors which arise from the paramagnetic nature of $Cu^{2+.7}$ Because the d^9 electronic configuration of Cu²⁺ displays strong binding tendencies towards CN⁻, it is rationally concluded that the complexes

with Cu^{2+} can recognize CN^- by ensuring high stabilization effects on the ligand field.^{8,9}

Herein, we report a convenient synthesis of two novel photochromic compounds possessing unsymmetrical molecular architectures, **P1** and **P2** shown in Scheme 1. Compound **P2** integrates the naphthalene moiety as a fluorophore with interaction sites for Cu^{2+} on both the ends of the dithienyl-cyclopentene to realize the photochromism and fluorescence modulated by Cu^{2+} and CN^- coordinations. Then, these functions can be incorporated into a more complex circuitry at the molecular level so that the logic circuit and the keypad lock are proposed.

Compound **P1** is used as reference to facilitate the research on the sensing mechanism between coordination sites and Cu^{2+} in CH₃CN solution. Addition of Cu^{2+} to the solution of **P1** produces a complex **P1–Cu²⁺**. The main absorption band at 363 nm decreased in intensity with the addition of Cu^{2+} (Fig. S1, ESI[†]). UV–vis titration profile of **P1** and Job's plot indicate that **P1** forms a 1 : 1 complex with Cu^{2+} in CH₃CN solution (Fig. S2 and S3, ESI[†], respectively). Unfortunately, the ¹H NMR spectrum of **P1–Cu²⁺** does not provide



Scheme 1 Proposed sensing processes of compounds P1 and P2 with Cu^{2+} , complex P2– Cu^{2+} with CN^{-} and the photochromic processes responding to light stimuli.

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useful information due to the paramagnetic nature of Cu^{2+} . To gain an insight into the stoichiometry of **P1–Cu²⁺**, the electrospray ionization (ESI) HPLC mass spectrum was carried out. When 1 equiv. of Cu^{2+} was introduced into the **P1** solution, a new peak appeared at m/z 475.9972 (Fig. S4, ESI†) that was assigned to **P1–Cu²⁺** with a 1 : 1 binding mode (the calculated $[C_{22}H_{20}NOS_2CICu]^+$ value was 475.9971).

The energy-minimized conformation of $P1-Cu^{2+}$ is simulated with the Gaussian 03 program package to support that P1 is coordinated to Cu^{2+} by a nitrogen atom in the imide group, an oxygen atom in the phenol group and a sulfur atom in the thiophene group, simultaneously, as shown in Scheme 1. As presented in Fig. S5 (ESI†), upon irradiation with 365 nm light, a new absorption band centered at 502 nm increased with the increase in irradiation time till the photostationary state of P1-Cu²⁺ was reached corresponding to the color change of the solution from colorless to pink (Fig. S6, ESI†), indicating the formation of the closed isomer. Upon irradiation with visible light (> 500 nm), the pink solution was bleached completely back to colorless solution, and the closed isomer converted to the open-ring isomer (P1-Cu²⁺).

Under alternative illumination with ultraviolet and visible light, P2 exhibits a typical photochromic response of diarylethenes in CH₃CN solution. Fig. S7 (ESI[†]) shows that a new absorption band centered at 607 nm appeared upon irradiation with the light of 365 nm, indicating the formation of the closed isomer (P3), accompanied by change of the colorless solution to blue (Fig. S8, ESI⁺). Upon irradiation with visible light (\geq 550 nm), the blue solution was bleached back to colorless solution and the original absorption spectrum was recovered. As depicted in Fig. 9^{+} , addition of Cu^{2+} to the solution of P2 produced a color change from colorless to vellow with a minor absorption change (Fig. S10, ESI⁺). Complex $P2-Cu^{2+}$ also performs photoisomerization with light irradiation. As seen from Fig. S11⁺, upon irradiation of $P2-Cu^{2+}$ with 365 nm light, the closed isomer $P3-Cu^{2+}$ formed. The absorption band at 354 nm decreased and a new band centered at 584 nm appeared, accompanied by the color change from yellow to blue (Fig. S9, ESI⁺). The blue solution returned to yellow solution with visible light (≥ 550 nm) irradiation and the original absorption spectrum was recovered. As expected, the results from UV-Vis titration profile, Job's plot and HRMS (ESI+) experiment suggest a 1:1 binding mode between **P2** and Cu²⁺ (Fig. S12–S14, ESI[†], respectively). The conformation of $P2-Cu^{2+}$ is also confirmed by the theoretical calculation shown in the ESI.[†]

It is noteworthy that the photochromic properties of $P2-Cu^{2+}$ can be modulated by CN^- . Fig. S15[†] shows that the bands at 354 nm decreased along with the addition of CN^- , indicating the formation of complex $P2-Cu^{2+}-CN^-$. It exhibits a typical photochromic response: upon irradiation of $P2-Cu^{2+}-CN^-$ with 365 nm light, the absorption band at 350 nm decreased, and a new band at 581 nm, which corresponded to the ring-closed isomer $P3-Cu^{2+}-CN^-$, appeared at the same time (Fig. S16, ESI[†]). This process was accompanied by a color change from yellow to blue. Upon irradiation with visible light (\geq 550 nm), the blue solution returned to yellow solution and the original absorption spectrum was recovered. To the best of our knowledge, it is the first report that anions



Fig. 1 (a) Fluorescence spectral changes of compound **P2** (10 μ M) with Cu²⁺ (0–12 μ M) in CH₃CN at 25 °C, $\lambda_{ex} = 360$ nm. (b) Fluorescence spectra of compound **P2** in the presence of various metal ions at 25 °C. [**P2**] = 10 μ M, [Cu²⁺] = 10 μ M, [M^{*n*+}] = 100 μ M in CH₃CN, $\lambda_{ex} = 360$ nm.

modulate the photochromism of diarylethene complexes by the coordination between anions and complexes.

Interestingly, the fluorescence response of compound **P2** is relative to Cu^{2+} concentrations, and the fluorescence intensity exhibits a more than 5-fold enhancement in the presence of 1 equiv. of Cu^{2+} (Fig. 1a). The C=N isomerization,¹⁰ which is the predominant decay process of excited states in **P2**, is inhibited through complexation of **P2** with Cu^{2+} , so compound **P2** shows a fluorescence enhancement in the presence of Cu^{2+} . Meanwhile, due to the reduced electron-donating ability of the phenol moiety after the coordination of Cu^{2+} , the photo-induced electron transfer (PET) quenching should be effectively suppressed and hence might yield a high fluorescence enhancement.¹¹ Fig. 1b demonstrates that only Cu^{2+} caused a prominent fluorescence enhancement of **P2**, whereas very weak fluorescence variations were observed for other metal ions. The detection limit for Cu^{2+} determined based on the S/B criteria is 91.1 nM (Fig. S17, ESI⁺).

As in a metal chelate-based sensing mechanism, copper complexes are useful for devising fluorescent sensors for CN^- detection due to the high affinity of copper for CN^- . The sensing properties of $P2-Cu^{2+}$ toward different anions using tetrabutylammonium as counter cation were investigated. As illustrated in Fig. 2, the addition of 3 equiv. of CN^- to $P2-Cu^{2+}$ caused a distinct increase in the fluorescence intensity, again indicating the formation of the complex $P2-Cu^{2+}-CN^-$, while the disturbance of fluorescence intensity for other anions could be neglected. Job's plot experiments reveal a 1 : 1 complex for $P2-Cu^{2+}$ with CN^- (Fig. S18, ESI†). Moreover, upon addition of excess CN^- (100 equiv.) to $P2-Cu^{2+}$, the increase in the fluorescence intensity is clearly observed (Fig. S19, ESI†), which indirectly suggests that CN^- does not form a strong enough complex to remove Cu^{2+} from $P2-Cu^{2+}$.



Fig. 2 (a) Fluorescence spectral changes of complex $P2-Cu^{2+}$ (10 μ M) with CN⁻ (0–30 μ M) in CH₃CN solution at 25 °C, λ_{ex} = 360 nm. (b) Fluorescent response of $P2-Cu^{2+}$ (10 μ M) to various anions at 30 μ M concentration in CH₃CN solution: 1, F⁻; 2, Cl⁻; 3, Br⁻; 4, I⁻; 5, HSO₄⁻; 6, NO₃⁻; 7, ClO₄⁻; 8, CN⁻; 9, HPO₄²⁻; 10, H₂PO₄⁻; 11, P₂O₇⁴⁻; 12, CH₃COO⁻; 13, OH⁻. λ_{ex} = 360 nm, λ_{em} = 448 nm.

Therefore, the significant fluorescence enhancement might result from the electrostatic interaction between CN^- and **P2-Cu²⁺**.^{8a,12} As shown in Fig. S20, the detection limit for CN^- is 22.5 nM and there is a fairly linear relationship between the fluorescence intensity and concentrations of CN^- from 4.0 to 20.0 μ M in CH₃CN solution (R = 0.993), which can be applied as a calibration curve for CN^- detection. Therefore, compound **P2** and its complex **P2-Cu²⁺** can serve as fluorescence enhancement chemosensors for Cu²⁺ and CN⁻ with high selectivity and sensitivity, respectively.

Additionally, there is no effect on the fluorescence intensity of **P2** and **P3** in the presence of CN^- only; nevertheless, sequentially adding Cu^{2+} to the solution can also induce a "turn-on" signal (Fig. S21 and S22, ESI†, respectively). Besides, the fluorescence of **P2–Cu²⁺** and **P2–Cu²⁺–CN⁻** is quenched when they are exposed to UV light (Fig. S23 and S24, ESI†, respectively), which is attributed to the efficient energy transfer from the excited fluorophore core to the attached closed-ring BTE unit that has a lower energy level.³

These studies inspire us to utilize compound **P2** to develop a complicated logic circuit for a molecular traffic signal with three inputs: UV irradiation, Cu^{2+} and CN^- as input-1, input-2 and input-3, respectively. The outputs are designated as output-1 ($I \le 100$), output-2 ($100 < I \le 150$) and output-3 (I > 150), respectively, where I is the value of fluorescence intensity at 448 nm. If the value of I locates in a specific range, the corresponding output is considered as the "1" state, otherwise, it is considered as the "0" state. Thus, according to the truth table (Table S1, ESI†), a logic circuit with AND, OR and NOT gates integrated within a single molecule is approached (Fig. 3a).

Depending on the different combinations of three inputs (UV irradiation, Cu^{2+} and CN^- designated as "U", "C" and "T", respectively), compound **P2** can switch between different fluorescence emission states "*On* and *Off*". A molecular keypad lock is constructed to visualize these sequence-dependent phenomena directly. Out of six possible input combinations *i.e.* UCT, UTC, CUT, CTU, TUC, TCU, only the UCT input combination (*i.e.* it is the password) gives birth to an instinct fluorescent output signal (Fig. S25, ESI†). As illustrated in Fig. 3b, when the sequence of three input keys UCT is inserted, the keypad lock "opens", corresponding to a strong fluorescence signal. All other sequences (as wrong passwords), which give weak fluorescence signal outputs, fail to open the lock.

In summary, two novel diarylethenes **P1** and **P2** with unsymmetrical structures have been successfully synthesized. The photochromic properties of compound **P2** and its complex **P2–Cu²⁺** can be easily modulated by employing Cu^{2+} and CN^- , respectively. **P2** and **P2–Cu²⁺** can be considered as fluorescence enhancement chemosensors for Cu^{2+} and CN^- , respectively.



Fig. 3 (a) A logic circuit and (b) a fluorescence keypad lock with inputs of UV irradiation, Cu^{2+} and CN^{-} . Details are shown in the text.

Besides, compound **P2** has been used to construct a logic circuit and a molecular keypad lock with UV irradiation, Cu^{2+} and CN^{-} as inputs, at the first time. This present work provides deeper insights for the future design of unsymmetrical photochromic compounds as multifunctional nanoscale logic devices.

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