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Chemical control of photochromism and a multiresponsive molecular switch based on a diarylethene derivative containing naphthol

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ABSTRACT

A photochemically inactive diarylethene derivative with a naphthol group bridging through the imidazole unit (**DIN**) was synthesized to characterize a multifunctional switch. Upon stimulation by radiation (UV and visible light), the target diarylethene derivative **DIN** was not photochemically inactive but photo-active, it can be photo-converted to keto compound. And moreover, the photochromic reaction of **DIN** was observed when it was stimulated by the addition of acid or methylation. Fluorescence quenching and the bathochromic effect occurred when **DIN** was stimulated by the addition of copper ions and base, respectively. Its optical properties could be regulated by various chemical stimulus. Thus, it could potentially be utilized as a multiresponsive molecular switch.

1. Introduction

Photochromic diarylethene compounds have attracted much attention in recent years since the first report by Kellogg et al.¹ and subsequent, extensive studies by Irie and coworkers²⁻⁶ on the photochromic properties of these systems. Several attempts to modulate the photochromic properties of diarylethenes for practical applications have recently been reported.⁷⁻¹⁹ Recently, it was found that the photochromic properties of some organic molecules can be induced by an external stimulus such as chemicals,²⁰⁻²² heat²³ or oxidation/reduction.²⁴ For instance, Irie²⁰ reported that photochemically inactive diarylethene derivatives having a N-(O-hydroxyphenyl)

group underwent photochromic reaction when they were esterified by the addition of acetic anhydride. Yam²¹ found that photochromic reactivity is highly suppressed in dithienylethene derivatives appended with 3- or 5-dimesitylboryl-2, 20-bithiophene, while it can be restored after F⁻ ion binding to the boron center. Such reactivity is indispensable to applications in display and memory technologies.

The imidazole and hydroxyl group account for the powerful coordination capacities of naphthol. The nitrogen atom in the imidazole ring is a good receptor for protonic acid, and the hydrogen atom in the hydroxyl group and the N–H groups in the imidazole ring are acidic. With these considerations in mind, we herein present an unprecedented example of a diarylethene derivative with a naphthol group bridged by an imidazole unit (**DIN**). In particular, we characterized multifunctional switches prepared from **DIN** and attempted to control the photochromic reaction by using specific chemical constituents.

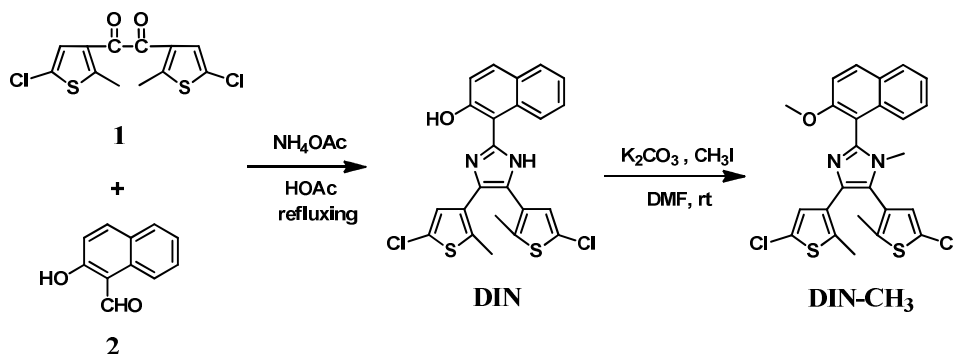
2. Materials and methods

2.1. Experimental

General: All manipulations were carried out under an argon atmosphere by using standard schlenk techniques, unless otherwise stated. DMF was dried with magnesium sulfate then distilled under vacuum. 1,2-Bis(5-chloro-2-methylthiophen-3-yl)ethane-1,2-dione (**1**) was prepared by methods described in the literature.²⁵ All other starting materials were obtained commercially as analytical-grade and used without further purification. The relative quantum yields were determined by comparing the reaction yield with the known yield of the compound 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene.²⁶ ¹H and ¹³C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or 600 MHz. ¹H and ¹³C NMR chemical shifts were relative to TMS. UV-Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were recorded on a Hitachi-F-4500 fluorescence spectrophotometer. UV light was irradiated using ZF5UV lamp (302 nm), and visible light irradiation ($\lambda > 402$ nm) was carried out by using a LZG 220 V 500W tungsten lamp with cutoff filters

2.2 Synthesis

Target compounds **DIN** and **DIN-CH₃** were prepared according to the synthetic route presented in Scheme 1.



Scheme 1 Synthesis of **DIN** and its derivative **DIN-CH₃**.

Synthesis of DIN: To a solution of ammonium acetate (1.2 g, 16 mmol) in refluxing glacial acetic acid (15 mL) was added 2-hydroxy-1-naphthaldehyde **2** (0.20 g, 2.0 mmol) under a argon atmosphere at 120 °C, and it was refluxed for 2 h. 1,2-Bis(5-chloro-2-methylthiophen-3-yl) ethane-1,2-dione **1** (0.64 g, 2.0 mmol) was added to the reaction solution above and continue to react further for overnight. The reaction mixture was allowed to cool to room temperature, and then transferred to ice water (200 mL), carefully neutralized with a 10% sodium carbonate solution to a pH of 6.5-7.0. The formed precipitate was collected and the crude product was washed with water, the dried solid was redissolved in DCM. Then dried over sodium sulfate, upon removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether / ethyl acetate (4:1) as the eluent to obtain the target compound as a white powder in a yield of 68%. ^1H NMR (400 MHz, CDCl_3): δ 2.15 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 6.79, 6.87 (s, 2H, thiophene-H), 7.31 (d, $J = 8.8$ Hz, 1H, Ar-H), 7.40 (t, $J = 7.2$ Hz, 1H, Ar-H), 7.58 (t, $J = 7.2$ Hz, 1H, Ar-H), 7.81 (d, $J = 8.8$ Hz, 1H, Ar-H), 7.87 (d, $J = 8.4$ Hz, 1H, Ar-H), 8.16 (d, $J = 8.8$ Hz, 1H, Ar-H), 9.50 (s, 1H, -OH), 13.03 (s, 1H, -NH). MS(m/z): 470 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{23}\text{H}_{16}\text{Cl}_2\text{N}_2\text{OS}_2$: C, 58.60; H, 3.42; N, 5.94. Found: C, 58.89; H, 3.29 ; N, 6.19.

Synthesis of DIN-CH₃: To a solution of **DIN** (0.20 g, 0.5 mmol) in *N,N*-dimethylformamide (10 mL) in the presence of potassium carbonate (0.28 g, 2.0 mmol) was added methyl iodide (0.12 mL, 2.0 mmol) under dark conditions for 12 h at room temperature. The reaction mixture was allowed to cool, transferred to about 100 mL of water. The formed precipitate was collected

and the crude product was washed with water, the dried solid was redissolved in DCM. Then dried over sodium sulfate, upon removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether / ethyl acetate (5:1) as the eluent to obtain the target compound as a light yellow solid in a yield of 90%. ^1H NMR (400 MHz, CDCl_3): δ 2.08 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.22 (s, 3H, N- CH_3), 3.91 (s, 3H, O- CH_3), 6.73, 6.86 (s, 2H, thiophene-H), 7.33-7.58 (m, 4H, Ar-H), 7.82 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.97 (d, $J = 10$ Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3): δ 13.87 (s, CH_3), 14.40 (s, CH_3), 31.51 (s, N- CH_3), 56.50 (s, O- CH_3), 112.90, 123.34, 123.97, 124.53, 126.58, 127.37, 127.44, 127.93, 128.95, 131.17, 131.68, 133.81, 134.34, 135.24, 138.09, 143.67, 156.01 (s, thiophene, ethene, naphthalene). MS (m/z): 498 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{Cl}_2\text{N}_2\text{OS}_2$: C, 60.12; H, 4.04; N, 5.61. Found: C, 59.95; H, 3.91; N, 5.71.

2.3 Crystallographic Details

Crystals suitable for X-ray diffraction were grown from a dichloromethane of solution **DIN** layered with hexane. A crystal with approximate dimensions of $0.20 \times 0.10 \times 0.10$ mm³ for **DIN** was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo $\text{K}\alpha$ radiation (0.71073 Å) at 298 K. The structures were solved by a combination of direct methods (SHELXS-97) and Fourier difference techniques and refined by full-matrix least squares (SHELXL-97). All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC 979718. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 544 0 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1 X-ray structure of **DIN**

The molecular structure of **DIN** (Fig. 1) was determined through X-ray crystallography. Its crystallographic details are given in Table S1. **DIN** crystallized with the approximate parallel conformation in the crystalline phase, which could not undergo photocyclization in the crystalline phase.²⁷ The dihedral angle between the naphthalene ring and the imidazole ring in **DIN** was

26.10°. The intramolecular distance between the two reactive carbons was 4.641 Å, which was too long for the cyclization reaction to take place in the crystalline phase; photochromic activity usually appeared when the distance between the reactive carbon atoms was less than 4.2 Å.²⁸ The distance between the hydrogen atom in the naphtholic hydroxy group and the nitrogen atom in an imidazole ring was found to be 1.875 Å, which was enough to form an intramolecular hydrogen bond.

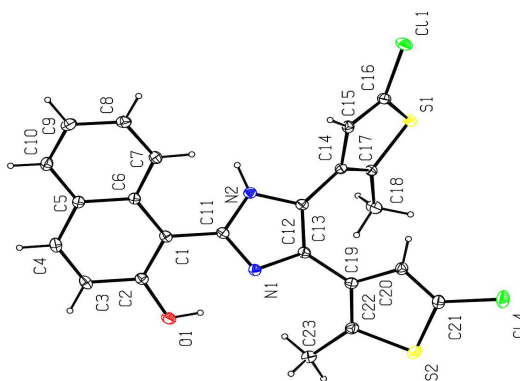


Fig. 1 Molecular structure of **DIN**. The H atoms have been omitted for clarity.

3.2 Optical behaviors of **DIN**

The absorption spectrum of **DIN** in acetonitrile solution at room temperature is shown in Fig. 2A. Before irradiation with 302 nm UV light, the absorption maximum of **DIN** was at 239 nm ($\epsilon = 3.92 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) because of a $\pi-\pi^*$ transition.²⁹ The other absorbance maximum of **DIN** appeared at 356 nm ($\epsilon = 1.15 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$), which is characteristic of the absorbance of naphthalene derivatives. When it was irradiated with 302 nm UV light, a new absorption band between 363 and 500 nm emerged, and the absorbance intensity at 239 nm gradually weakened. No absorbance of the closed-ring isomer was observed. It indicated that **DIN** did not exhibit any photochromism by cyclization and cycloreversion in acetonitrile upon irradiation with 302 nm light. Hence, the photochromism by cyclization and cycloreversion was inhibited by intramolecular proton transfer, but the permanent tautomerization took place, as shown in Fig. 2. Formation of an intramolecular hydrogen bond in the ground state between the naphthol hydrogen and the imidazole ring nitrogen is confirmed by the X-ray structure of **DIN**. The fluorescence spectrum of **DIN** in acetonitrile solution at room temperature was investigated. Upon excitation at

a wavelength of 356 nm, it exhibited emission at 458 nm (Fig. 2B). A small fluorescence quantum yield ($\phi_f = 0.047$) was detected by using quinoline sulfate ($\phi_f = 0.55$, in 0.1 M aqueous H_2SO_4) as a reference. The emission intensity of **DIN** rapidly decreased upon irradiation with 302 nm UV light. Such emission was mainly induced by intramolecular proton transfer from the naphthol hydrogen to the imidazole ring nitrogen, as shown in Fig. 2. Hydrogen bonding induced quenching of the excited state by proton transfer.¹⁵ To confirm further the intramolecular proton transfer, IR spectra of **DIN** before and after UV irradiation were obtained (Fig. S1). The characteristic absorption of the carbonyl group appeared at 1711 cm^{-1} after UV irradiation. It was accompanied by the disappearance of the characteristic absorption of the hydroxyl group at 3243 cm^{-1} , which was observed before UV irradiation. This result agrees with the crystal structure and results of the UV experiment on **DIN**.

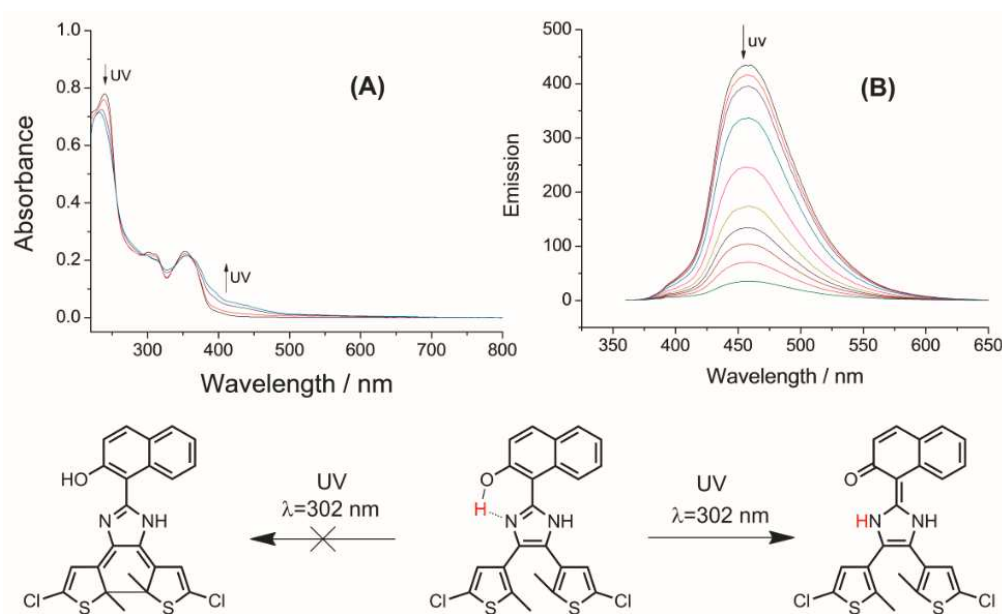


Fig. 2 Optical behaviors of **DIN** and the corresponding changes of structure.

3.3 Effect of metal ions on the optical properties of **DIN**

Absorbance and fluorescence changes in **DIN** in acetonitrile at room temperature due to the presence of various metal ions were investigated. Cu^{2+} had marked effects on the optical properties of **DIN**, but the binding of other metal ions (Ag^+ , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cu^+ , Hg^{2+} , K^+ , Mg^{2+} , Na^+ , Ni^{2+} , Sn^{2+} , Sr^{2+} , Fe^{3+} , Zn^{2+}) caused only slight changes in absorbance and emission under the same conditions (Fig. S2). As shown in Fig. 3A, the absorption maximum (352 nm) of

the open-ring isomer of **DIN** in the presence of Cu^{2+} shows a hypsochromic shift ($\Delta\lambda = 4 \text{ nm}$) relative to that of free **DIN** (356 nm) before irradiation with 302 nm UV light. This shift may be attributed to a change in the degree of conjugation of the diarylethene after binding Cu^{2+} . Meanwhile, the absorbance maximum of **DIN** in the presence of Cu^{2+} after UV irradiation was nearly unchanged compared with that of **DIN** upon UV irradiation in the absence of Cu^{2+} (Fig. S3). Thus, the photochromic property of **DIN** was not affected by the addition of Cu^{2+} . That is, **DIN**, which was photochemically inactive, did not exhibit photochromism in the presence of Cu^{2+} . As presented in Fig. 3B, the emission at 458 nm band decreased significantly upon addition of varying amounts of Cu^{2+} (0–4 eq), and the fluorescence quantum yield decreased from 0.047 to 0.013 when the amount of Cu^{2+} was varied from 0 to 4 eq. Fluorescence quenching of **DIN** upon addition of Cu^{2+} might have resulted from ligand-to-metal charge transfer, in which the electronic charge is transferred from the ligand toward the coordinating metal.³⁰ Thus, **DIN** is a potential molecular sensor for the detection of Cu^{2+} by fluorescence recognition.

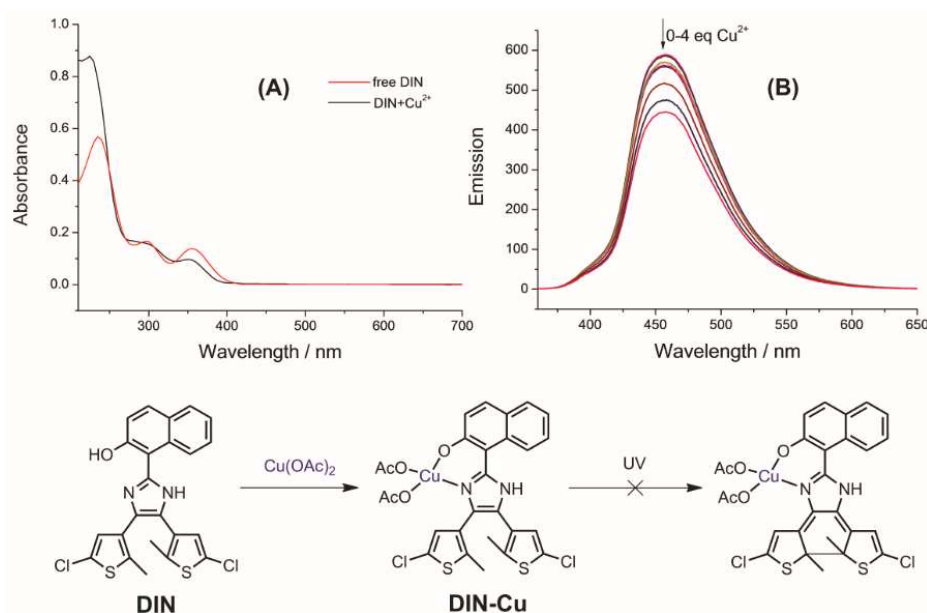


Fig. 3 Optical response of **DIN** in acetonitrile upon the addition of Cu^{2+} before irradiation with 302 nm and the corresponding changes of structure.

3.4 Photonic and pH control of the photochromic reactivity of **DIN**

Protonation of the open-ring isomer, **DINo**, by the addition of HCl in excess in acetonitrile ($c = 2 \times 10^{-5} \text{ mol}^{-1} \text{ L}$) afforded **DINo•H⁺** (Fig. 4), as indicated by a bathochromic shift of $\Delta\lambda = 7 \text{ nm}$ ($\lambda_{\text{max}} = 356 \text{ nm}$). This red shift was due to protonation-induced delocalization of the π system,

which stabilizes the positive charge.³¹ A new absorption band centered at 590 nm ($\epsilon = 1.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) appeared and the colorless solution turned blue when **DINo**•**H**⁺ was irradiated with 302 nm UV light. These changes are due to a ring-closure reaction, which produces the closed-ring isomer, **DINc**•**H**⁺. A well-defined isosbestic point at 257 nm was observed. Upon irradiation with visible light ($\lambda > 402 \text{ nm}$), the colored **DINc**•**H**⁺ underwent a cycloreversion reaction to the initial colorless **DINo**•**H**⁺. The quantum yields of cyclization and cycloreversion for **DIN**•**H**⁺ were 0.042 and 0.0013, respectively. Deprotonation of **DINo**•**H**⁺ with Et₃N led to the formation of **DINo**. When **DINc**•**H**⁺ was neutralized with Et₃N (1.5 eq vs. HCl) and subsequently irradiated with visible light ($\lambda > 402 \text{ nm}$), **DINo** was also regained. However, the fluorescence spectrum of **DIN** in acetonitrile solution was scarcely affected by the addition of HCl (20 eq), as shown in Fig. S4. The photochemically inactive **DIN** underwent photochromic reaction when it was acidified by the addition of HCl. Thus, this system may be used a novel dual-control molecular switch by the regulation of photoradiation and pH.

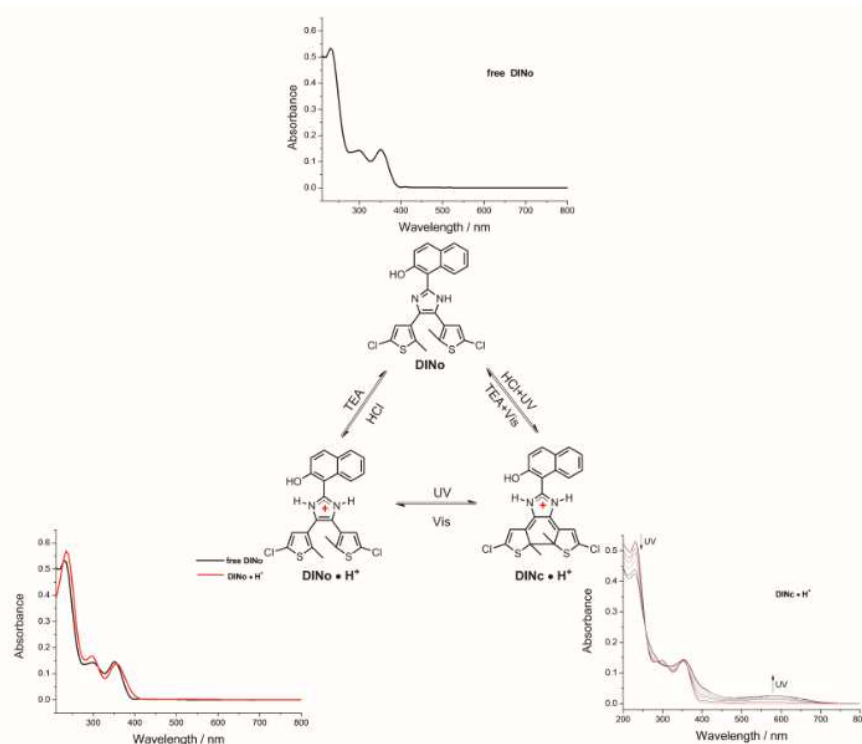


Fig. 4 Absorption spectra of **DIN** in acetonitrile ($c = 2 \times 10^{-5} \text{ mol/L}$) upon protonation with HCl (20 eq) and deprotonation with TEA (30 eq) and/or irradiation with UV/Vis light.

3.5 Effect of base on the optical properties of **DIN**

DIN solution in acetonitrile ($c = 2 \times 10^{-5} \text{ mol L}^{-1}$) formed **DIN•2Na** upon addition of excess alkali, as indicated by a bathochromic effect of $\Delta\lambda = 24 \text{ nm}$ ($\lambda_{\text{max}} = 356 \text{ nm}$; Fig. 5A). This red shift is due to π -system delocalization induced by deprotonation, which stabilizes the negative charge. **DIN•2Na** could be protonated to form **DIN** by adding acid to its solution. However, upon irradiation with 302 nm light and the addition of alkali to its solution, **DIN** did not exhibit photochromism, as shown in Fig. S5. Deprotonation of imidazole and naphthol in **DIN** also caused a significant difference in the emission. The emission of **DIN** at 458 nm decreased greatly with the addition of alkali. This efficient fluorescence quenching was a result of the photoinduced electron transfer from the deprotonated imidazole and naphthol to the diarylethene group (as shown in Fig. 5B).³²⁻³³ The fluorescence quantum yield decreased from 0.047 to 0.021 when the amount of alkali was varied from 0 to 10 eq. Fluorescent quenching upon addition of alkali to diarylethene **DIN** provides a potential application in alkali sensors. However, triethylamine had no effect on the optical properties of **DIN** (Fig. S6).

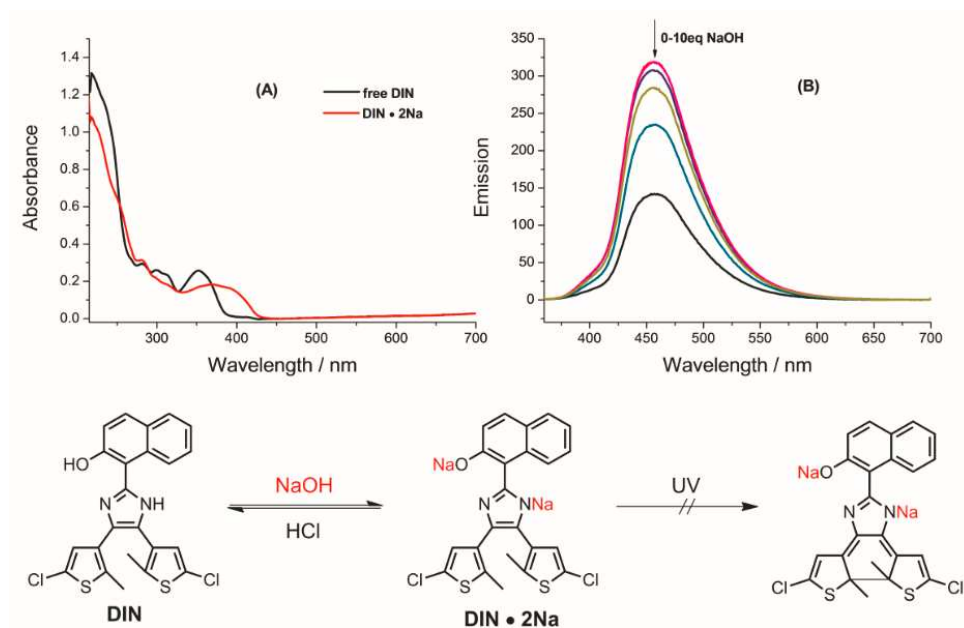


Fig. 5 Optical response of diarylethene **DIN** in acetonitrile ($c = 2 \times 10^{-5} \text{ mol/L}$) upon the addition of NaOH (10 eq) and HCl (15 eq) and irradiation with UV light.

3.6 Effect of methylation of NH and OH groups on the optical properties of **DIN**

According to the experiments above, the photochromic reactivity of **DIN** was strongly suppressed by intramolecular proton transfer. Therefore, the methylation of NH and OH groups

was utilized to disturb the hydrogen bonding between the naphthol hydrogen and the imidazole ring nitrogen. As shown in Fig. 6, the absorption maxima of **DIN•CH₃** showed a hypsochromic shift of $\Delta\lambda = 23$ nm ($\lambda_{\text{max}} = 356$ nm) relative to that of **DIN**. This shift may be attributed to a reduction in the degree of conjugation after N-methylation of the imidazole ring and naphthol group.³⁴⁻³⁵ The synthesized derivative **DIN•CH₃** had the same absorbance spectrum as that of the **DIN** solution when methyl iodide was added, confirming the methylation. A new absorption band centered at 563 nm ($\epsilon = 2.18 \times 10^3$ L mol⁻¹ cm⁻¹) appeared, and the colorless solution turned purple during irradiation with 302 nm UV light. These changes resulted from a ring-closure reaction that produces the closed-ring isomer, **DINc•CH₃**. Upon irradiation with visible light ($\lambda > 402$ nm), the colored **DINc•CH₃** underwent a cycloreversion reaction to the colorless open-ring isomer, **DINo•CH₃**. The quantum yields of cyclization and cycloreversion of **DIN•CH₃** were 0.12 and 0.0034, respectively. The properties of the open-form of diarylethene derivatives, especially for the photochromic cyclization reaction, is strongly dependent on the conformation of the open-isomer, such as the antiparallel (AP) or the parallel (P) forms. In the ¹H NMR spectrum of **DIN•CH₃**, the methyl signal of AP conformer was observed at 2.08 ppm, while that of P conformer at 2.32 ppm. The intensity ratio of the two signals indicates that the relative population of AP and P conformers is 1:1. The result is in accord with that of DFT calculations. DFT calculations showed the parallel and anti-parallel energy for **DIN•CH₃** was -2866.1883 and -2866.1898, respectively. The difference of their energy is small.

The methylation of imidazole and naphthol groups in **DIN** also had a great effect on the fluorescence spectrum. As shown in Fig. S7, the emission band of **DINo•CH₃** is significantly blueshifted ($\Delta\lambda = 25$ nm) relative to that of **DINo**. This shift is also attributed to a reduction in the degree of conjugation after N-methylation of the imidazole ring and naphthol group. The fluorescence intensity gradually decreased and combined with a bathochromic shift ($\Delta\lambda = 31$ nm) upon irradiation with 302 nm UV light because of the generation of **DINc•CH₃** (Fig. S8). And the fluorescence quantum yield of open and closed form were ϕ_f (**DINo•CH₃**) = 0.032 and ϕ_f (**DINc•CH₃**) = 0.014, respectively. Irradiation with visible light ($\lambda > 402$ nm) restored the original emission spectrum.

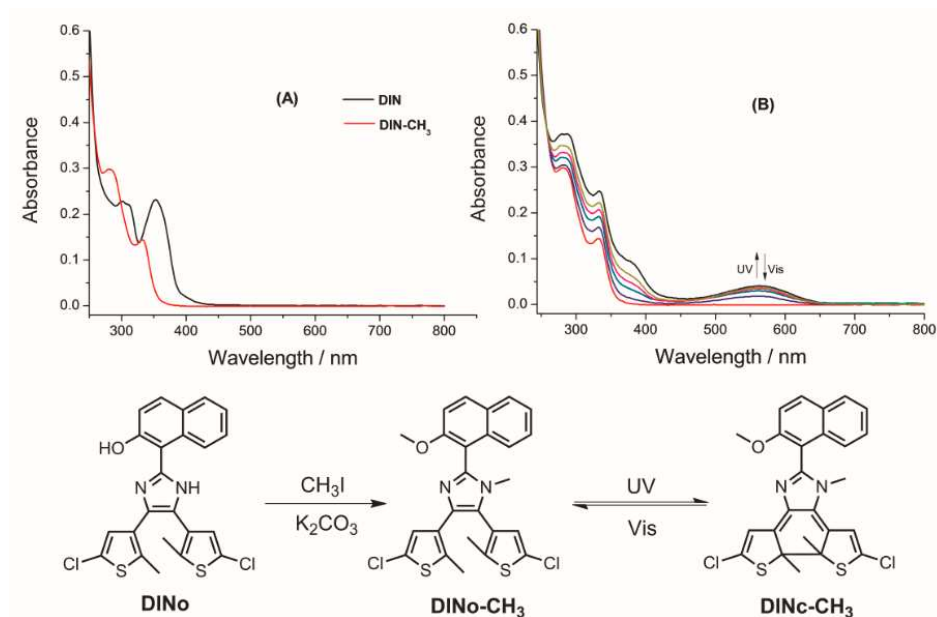


Fig. 6 Absorption spectra of diarylethene **DIN** and **DIN-CH₃** in acetonitrile ($c = 2 \times 10^{-5}$ mol/L) upon irradiation with UV/Vis light.

4. Conclusions

It was demonstrated that the photochromic reaction of the photochemically inactive diarylethene **DIN** could be controlled by the addition of acid and by the methylation of NH and OH groups. The addition of copper ions and alkali had a significant effect on the optical properties of **DIN**. Its photochromism reaction and optical properties could be easily regulated by various chemical constituents. Such chemically responsive systems have potential utility as multiresponsive molecular switches in display materials, memory media, as well as molecular logic gates.

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Supporting information available: IR spectrum, fluorescence responses to various ions, optical response to the addition of Cu²⁺ after irradiation, fluorescence response to HCl, absorbance responses and fluorescence responses to the addition of NaOH and NEt₃, fluorescence changes of diarylethenes **DIN** and **DIN-CH₃** before irradiation with UV light,

crystal data and structure refinement parameters.

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