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CB[8] gated photochromism of a diarylethene derivative containing thiazole orange groups†

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Photochromism in a diarylethene derivative (10) can be gated by a host–guest interaction where the thiazole orange groups are bound into the hydrophobic cavity of CB[8] in water. The closed-ring isomer (1C), which cannot be obtained freely in aqueous solution, survives even when the complex is dissociated by displacement from CB[8] by competition with 1-adamantanamine hydrochloride.

Photochromism is defined as a reversible transformation of a chemical species between two isomers having different absorption spectra induced in one or both directions by photoirradiation.^{1,2} Diarylethene derivatives are potential candidates as photochromic materials since they exhibit fatigue-resistant properties and both isomers have excellent thermal stability.^{3–5} Although much progress has been made in the development of diarylethene systems,^{1,2,6–8} a property that is very desirable but inadequately exhibited is gated photochromism.⁹ Gated photochromism is the property wherein the ON/OFF photoactivity of a molecule is dependent on external stimuli such as solvent,^{10,11} reaction,^{10,12–17} heat,¹⁸ coordination,^{9,19–21} acidity²² or host–guest interaction.^{23,24} For example, a methanol-enhanced photocyclization activity of a diarylethene compound in which intramolecular hydrogen bonds were formed has been reported by N. Kawai *et al.*²⁵ Zhu *et al.* recently reported BF₃-suppressed photochromism of a photoactive diarylethene compound resulting from the interaction between BF₃ and thiazide groups.⁹ Irie *et al.* reported that the host–guest inclusion between the diarylethene core and cyclodextrin increased the cyclization quantum yield and the induced CD signals.²³ Diarylethene derivatives with gated photochromic properties are indispensable for application to sensors, switches and memory technologies. However, the gated photochromism of diarylethene derivatives based on the host–guest inclusion between substituent groups and host molecules has not been reported.

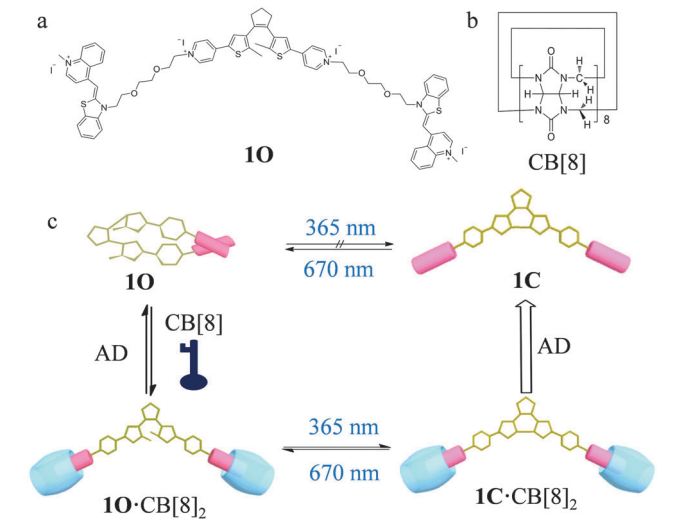
Cucurbit[*n*]urils (abbreviated as CB[*n*]), a family of unique pumpkin-shaped molecular structures, comprise a series of macrocyclic methylene-bridged glycoluril oligomers containing *n* glycoluril units.²⁶ CB[*n*] can be used to accommodate guests of certain molecular species through hydrophobic and ion–dipole interactions, leading to well-defined assembly systems that are not easily accessible by other methodologies.²⁷ The interaction between a spiroopyran and CB[8] was reported to influence the photochromic properties of the spiroopyran.²⁴ Recently, thiazole orange (TO), one of the cyanine dyes that can interact with single and double stranded DNA,²⁸ was found to form host–guest inclusions with CB[*n*] (*n* = 7 and 8) in different stoichiometries.^{27,29}

We have previously reported a TO-modified diarylethene (10) which shows weak fluorescence but no photochromic activity in aqueous solution as a result of twisted intramolecular charge transfer (TICT).⁴ The fluorescence of 10 is drastically enhanced upon binding to DNA and the photochromic activity is unlocked. Herein, we have found that the photochromism of 10 can not only be controlled by binding to DNA but also gated by a host–guest interaction through binding of the TO groups into the hydrophobic cavity of CB[8]. After interaction, the open isomer in the complex (10-CB[8]₂) can be successfully switched to its closed form (1C-CB[8]₂) upon UV irradiation. Moreover, the closed isomer, 1C, which is not easily obtained in aqueous solution, survives for at least 5 hours after the TO groups of 10 are displaced from CB[8] by competition with 1-adamantanamine hydrochloride (AD). Here, the details of the host–guest interaction between 10 and CB[8] and the gated photochromism of 10-CB[8]₂ are reported. This report provides a strategy to produce gated photochromic systems using host–guest interactions (Scheme 1).

The interaction between 10 and CB[8] was demonstrated *via* changes in the ¹H NMR spectrum after addition of CB[8] to a d₆-DMSO/D₂O(1 : 199) solution of 10 (Fig. 1). The assignment of the NMR signals of 10 is shown in Fig. S1 (ESI†). The signal for H_g, assigned to the methylene closest to the TO groups, was shifted upfield from 4.34 to 4.16 ppm after addition of 2 equivalents of CB[8] to 10. At the same time, signals from protons on the alkyl chains located at a higher magnetic field showed relatively small

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Scheme 1 The chemical structures of (a) **10** and (b) CB[8]; (c) the schematic diagram for the interaction of **10** with CB[8] and the photochromic process.

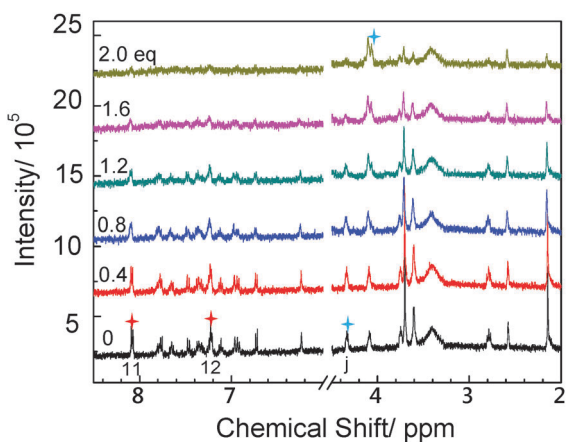


Fig. 1 ^1H NMR spectra of **10** with different equivalents of CB[8] in $\text{d}_6\text{-DMSO}/\text{D}_2\text{O}$ (1:199). The concentration of **10** was $100\ \mu\text{M}$ and that of CB[8] increased from $0\ \mu\text{M}$ (0 eq.) to $200\ \mu\text{M}$ (2 eq.). The peaks for the solvent (H_2O) and CB[8] have been omitted for clarity.

changes. The signals for H_{11} and H_{12} of pyridine located at 8.18 and 7.34 ppm, respectively, showed small changes, while the signals for other protons on the aromatic TO groups weakened and became broader after addition of CB[8] to the D_2O solution of **10**. These results indicated a strong interaction between the TO groups and CB[8].

As reported previously, TO groups display distinct electronic states with absorption maxima around 500, 470 and 430 nm for the monomer, H-dimer, and higher H-aggregates, respectively.^{28–31} In an aqueous solution of **10** at a concentration of $5\ \mu\text{M}$, the predominant form of the TO groups was the H-dimer with an absorption peak at 476 nm.⁴ As a result of the TICT state and the strong intramolecular interaction between the TO groups, which were proven by 2D NOESY spectra, **10** existed in a parallel conformation that was not photochromic in aqueous solution.⁴ It is interesting to note that after interaction with CB[8] the photochromism of **10** is unlocked. From the titration absorption spectra

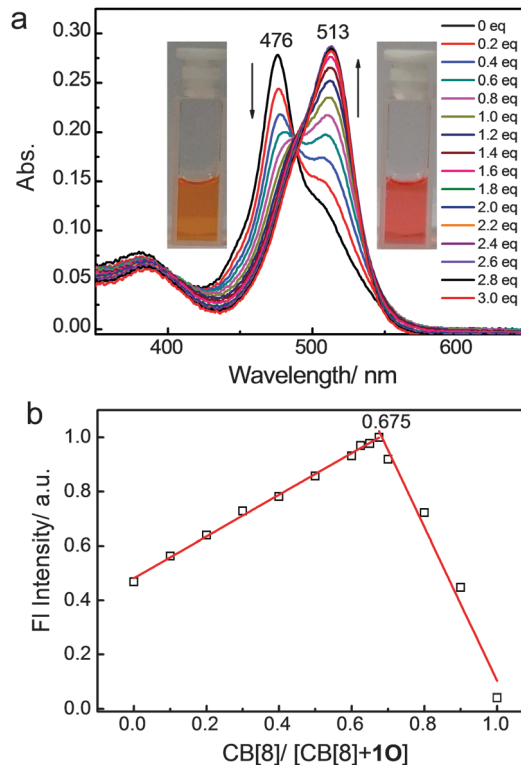


Fig. 2 (a) The UV-visible spectra of **10** ($5\ \mu\text{M}$) with addition of different equivalents of CB[8]; (b) Job plot of **10-CB[8]₂** for the emission intensity changes at a wavelength of 546 nm with a total concentration of **10** and CB[8] of $15\ \mu\text{M}$; square deviations of the fitted lines were 0.99721 and 0.97348, respectively.

(Fig. 2a), we can see that as CB[8] is added to **10**, the TO absorption band shifts from 476 to 513 nm with an isosbestic point at about 490 nm. The absorption at 513 nm was assigned to monomeric TO groups. The changes in the absorbance at 476 nm and 513 nm upon addition of different equivalents of CB[8] are shown in Fig. S2 (ESI[†]), which indicated that the absorbance tended to remain unchanged when the molar ratio of $\text{CB[8]}:\mathbf{10} \geq 2:1$. Furthermore, the fluorescence emission wavelength of **10** was hypsochromically shifted from 616 to 546 nm upon addition of CB[8] (Fig. S3, ESI[†]), which also suggested that the TO groups changed from the H-dimer to the monomer upon interaction with CB[8]. A Job plot was drawn for the different emission intensities at 546 nm with a total concentration of **10** and CB[8] of $15\ \mu\text{M}$ (Fig. 2b and Fig. S4, ESI[†]). The maximum emission intensity at 546 nm appeared at 0.675, indicating that the stoichiometric binding ratio of **10** with CB[8] was 1:2 (namely **10-CB[8]₂**). The binding constant was calculated to be $(3.36 \pm 0.75) \times 10^6\ \text{M}^{-2}$ from the nonlinear fitting of the equation in Fig. S5 (ESI[†]).^{28,32}

Comparing the UV-visible absorption and fluorescence spectra of **10** with **10-CB[8]₂**, we found that the host-guest interaction between the TO groups and CB[8] hindered the intramolecular interactions of **10**. The Stokes shift of **10** without CB[8] was 140 nm, a large value similar to those observed in many TICT molecules.^{4,33,34} The intramolecular electron transfer from the donor to the acceptor of a TICT molecule results in charge separated polarized states, in which the donor and the acceptor groups are in a perpendicular

geometry.³⁴ The Stokes shift of **10** drastically reduced from 140 to 33 nm upon addition of CB[8], indicating inhibition of the TICT process. Although free TO molecules have been reported to form J-aggregates or H-dimers in the cavity of CB[8],^{27,29} the TO groups of **10** changed from the intramolecular H-dimer in aqueous solution to the monomer in the cavity of CB[8]. Since the intramolecular interaction was blocked upon addition of CB[8], we assumed that the photochromism of **10** might be restored to a certain degree.

There was no photocyclization of free **10** in an aqueous medium and its closed form (**1C**) could not be generated.⁴ As a result of the host-guest interaction between the TO groups and CB[8], the complex **10**-CB[8]₂ became photochromic. The photochromic properties of **10**-CB[8]₂ (1:2) were monitored by UV-visible absorption spectroscopy (Fig. 3a). Upon irradiation with 365 nm UV light, the characteristic absorption peak at 685 nm of the closed form of diarylethene increased while the peak at 385 nm of the open form decreased. This indicated that **10**-CB[8]₂ was photochromic. The photocyclization efficiency of **10**-CB[8]₂ was 40.2% in the PSS as measured by HPLC (Fig. S6, ESI[†]) and the photocyclization quantum yield (Φ_{o-c})³ was determined to be 17.7% upon 365 nm light irradiation. This is the first example of a CB[8] gated photochromic diarylethene compound. The closed form, **1C**-CB[8]₂, could be reversibly converted to the open form, **10**-CB[8]₂, upon irradiation with 670 nm laser light for a period of 10 min (Fig. 3a inset and Fig. S7, ESI[†]), indicating high bistability for open and closed

forms of the host-guest complex. Even though the TO group of **10** has a large absorption band centered at 513 nm, no obvious spectral changes appeared in both **10**-CB[8]₂ and **1C**-CB[8]₂ upon irradiation with 515 nm light (Fig. S8, ESI[†]). The results demonstrated that CB[8] interacted with **10** via a supramolecular host-guest interaction and modified the photocyclization properties of **10**.

AD is a typical guest of CB[8] with a binding constant $((8.19 \pm 1.75) \times 10^8 \text{ M}^{-1})$ ²⁶ that is larger than that between **10** and CB[8]. To verify the host-guest interaction between the TO groups and CB[8], a displacement experiment was conducted by addition of AD aqueous solution to a mixture of **10**-CB[8]₂. The UV-Vis spectra showed that the absorption at 513 nm (TO monomer) decreased and the absorption at 476 nm (TO dimer) increased when AD was added to the solution of **10**-CB[8]₂ (Fig. 3b and (Fig. S9, ESI[†])). The fluorescence emission of the TO groups shifted from 552 to 606 nm, which was similar to that of free **10** (Fig. S10, ESI[†]). In addition, the mixture of **10**-CB[8]₂ and AD was not photochromic. These results indicated that the interaction between the TO groups and CB[8] was replaced by AD-CB[8] and the **10**-CB[8]₂ complex converted to free **10**. However, to our surprise, after irradiating the **10**-CB[8]₂ complex into its PSS, the **1C** form was maintained to some extent even after displacement by AD. After addition of AD to the PSS of **1C**-CB[8]₂, the absorption peak of the TO groups in **1C**-CB[8]₂ at 513 nm shifted to 476 nm, indicating that AD displaced TO from CB[8] (Fig. 3c). At the same time, the

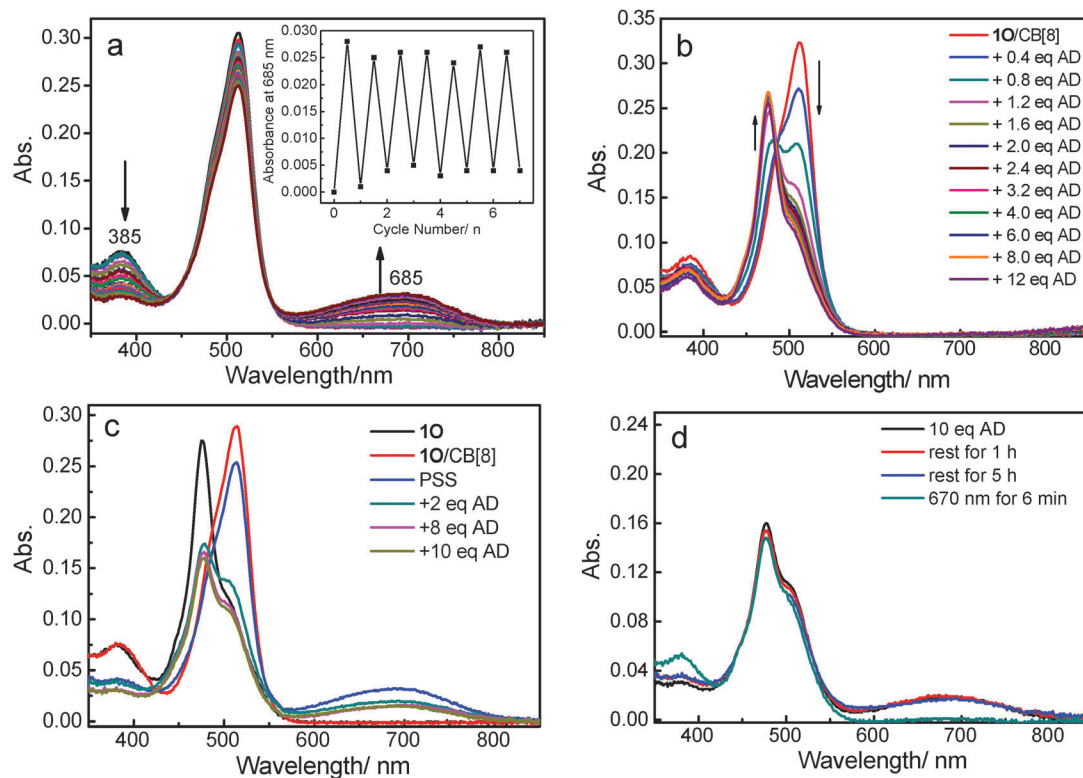


Fig. 3 The absorption spectra of (a) **10**-CB[8]₂ (5 μM) in aqueous solution upon irradiation at 365 nm from 0–40 min (inset: the absorbance changes at 685 nm upon alternate irradiation at 365 nm for 25 min and 670 nm for 6 min); (b) **10**-CB[8]₂ upon addition of different concentrations of AD; (c) PSS of **10**-CB[8]₂ upon addition of different amounts of AD; (d) standing for several hours followed by irradiation with 670 nm light for 6 min.

absorption at 685 nm of the **1C-CB[8]₂** generated upon UV light irradiation only decreased by 50%. This indicated that **1C-CB[8]₂** was dissociated into **1C** but only half of the closed-ring isomer converted to its open form (**1O**). The **1C** generated in this way was stable for at least 5 hours and could be converted to the open form again upon irradiation with 670 nm laser light (Fig. 3d and Fig. S11, ESI[†]).

In conclusion, we have developed CB[8] gated photochromism in a diarylethene thiazole orange compound (**1O**) and obtained its closed form (**1C**) *via* an indirect route. As a result of TICT and intramolecular interactions, photocyclization of **1O** in aqueous solution was not possible. Upon host-guest interaction between CB[8] and the TO groups of **1O**, the intramolecular interactions were blocked and the complex, **1O-CB[8]₂**, became photoactive. Here, CB[8] acted as the key to convert the parallel form of **1O** to the antiparallel form **1O-CB[8]₂**. **1O-CB[8]₂** could be photocyclized to **1C-CB[8]₂** upon irradiation with 365 nm light. Upon addition of a stronger guest, such as AD, free **1C** could be obtained from **1C-CB[8]₂**. **1C** was stable in aqueous solution for several hours and could be converted to **1O** upon visible light irradiation. This study provides a new method to generate gated photochromism.

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