

Selective response of cyclodextrin-dye hydrogel to metal ions

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Abstract The design and preparation of novel hydrogels have gained much interest recently, and in spite of the promising results to date, increasing pressure remains to develop novel gels based on stimuli-responsive systems. Here we present an anisotropic supramolecular gel of gamma-cyclodextrin and a simple azo dye in which physical gelation is completed through specific host–guest interaction. The obtained hydrogel exhibits respective morphological transitions based on supramolecular assembly and dissociation, leading to either precipitation or a sol-to-gel transition. It can identify different classes of metal ions, and, among them, naked-eye differentiation of lead ion is possible due to the coordination-induced unthreading of dye molecules. Gel-to-sol transitions can also be realized using chromium ions as a denaturing reagent. Accompanying structural changes were identified by various characterization techniques, including 2D-ROESY, HR-MAS, UV–Visible absorption, small-angle X-ray scattering, and induced circular dichroism measurements.

The hydrogel properties discussed here will be useful in analytical applications such as metal ion sensing and removal applications.

Keywords Supramolecular gel · Azo dye · Cyclodextrins · Anisotropy · Chemosensors

Introduction

Functional and stimuli-responsive organogels have gained much interest recently with the advent of adaptive multifunctional systems, i.e., smart materials. In particular, supramolecular hydrogels made of small organic molecules have attracted much attention due to their unique properties and the characteristics of their structures [1–7]. A myriad of gels have been prepared from the ordered aggregation of small molecules through non-covalent bonds to yield elongated supramolecules. Some of them respond well to external stimuli, showing high sensitivity to heat, light, pH, and chemicals, and thus have potential applications in drug-release systems and chemical sensors [8–12]. Therefore, the development of novel supramolecular hydrogels with stimuli-responsive properties is a challenging task of increasing importance. Several examples of promising results have been demonstrated recently.

The aggregation behavior of organic dyes, in the presence of host molecules, involves a combination of several non-covalent interactions. It is well known that cyclodextrins (CDs) have various chromophoric molecules in their cavity due to hydrophobic interactions and/or hydrogen bondings to form inclusion complexes [13–17]. Many dyes form inclusion complexes with α -cyclodextrin (α -CD) and β -cyclodextrin (β -CD), and dye-CD complexation is usually accompanied by peculiar spectral changes. γ -Cyclodextrin

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(γ -CD), which has a larger cavity size, can contain more than one molecule in its CD cavity; often leading to extended aggregates. Interesting experimental approaches have been made to study the nature of their aggregations, such as 2,5-diphenyl-1,3,4-oxadiazole (PPD) and 1,6-diphenyl-1,3,5-hexatriene (DPH), which self-assemble to form molecular aggregates that are held together by inclusion in the CDs [18–21]. All of these works sought to establish the formation of chromophore-anchored supramolecular aggregates and the effective role of CDs for nanotubular build-ups under appropriate conditions.

Here, we report an anisotropic supramolecular gel composed of a simple azo dye, dye **1**, and γ -CD, whose basis for anisotropy comes from noncovalent and ordered aggregates. We also reasonably envisaged that guest molecules would readily bind to metal ions, following the fact that 8-hydroxyquinoline (8-HQ), a coupling component of dye **1**, is well known as a ligand with high reactivity toward metals [22–25]. With this system we are able to distinguish several classes of metal ions and effectively identify a specific heavy metal ion with the naked eye. This process accompanies a change in its anisotropy and morphology. We use this characteristic recognition pattern and the effective binding in an aqueous environment to produce a simple, efficient detection system that does not require additional devices.

Experimental

Materials

The chemicals used in the synthesis of dye **1** and the hydrogel were 8-hydroxyquinoline, sulfanilic acid, γ -cyclodextrin, HCl (37%), NaNO₂, sodium acetate, HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), D₂O, and DMSO-d₆. All chemicals used in the syntheses were of laboratory reagent grade.

Dye **1** synthesis

The sulfanilic acid (1.221 g, 7.06 mmol) was dissolved in water (20 mL) and HCl (37%, 1.47 mL) was added while stirring the temperature was lowered to 0–5 °C, and a 5% NaNO₂ aqueous solution (7.06 mmol, 10 mL) was added dropwise. The solution was stirred for an hour at 0–5 °C to complete diazotization. 8-Hydroxyquinoline (1.025 g, 7.06 mmol) in 0.5 N NaOH (16 mL) was added dropwise for 1 h and stirring continued at room temperature overnight. After the reaction, the pH was adjusted to 7.5–8.0 using a dilute sodium acetate solution. The dye precipitate was then collected by filtration. The crude product was recrystallized three times in water (50 mL) and then dried

in a vacuum oven (yield 35%). ¹H NMR (500 MHz, DMSO-d₆): 9.3 (d, 1H), 9.0 (m, 1H), 9 (d, 2H), 7.8 (d, 2H), 7.7 (q, 2H), 7.2 (d, 1H).

POM measurement

Rubbed polyimide was used as a substrate for the POM measurements. A diluted polyimide solution was applied onto pre-cleaned glass slides, and this was spin-coated at 300 rpm for 1 min and then at 700 rpm for 30 s. The coated glass was dried at 90 °C (2 min) and post-baked at 230 °C (20 min). Both polyimide surfaces were rubbed in one direction with LCD rubbing fabric (HY-5318, Hyperflex). Several drops of warmed hydrogel were applied between two slides before observation using an Eclipse LV100 microscope (Nikon).

2D-ROESY and HR-MAS measurement

The 2D-ROESY spectrum was measured on a Bruker Avance II 900 spectrometer (900 MHz, Korea Basic Science Institute) with a relaxation delay of 2 s and a ROESY spinlock time of 250 ms. HR-MAS NMR experiments were recorded on a Varian UI500 spectrometer (500 MHz, Korea Basic Science Institute) with the spinning speed of the sample at 2300 Hz. All NMR measurements were carried out at 298 K using D₂O as a solvent.

UV–visible absorption

The UV absorbance spectra were collected using a Lambda 7 spectrometer (Perkin Elmer) in a 1 cm cuvette. For the pH adjustment, HEPES buffer solutions with a buffer strength of 5 mmol were prepared at pH 7.5. For metal ion titration, 5 min of standing was allowed before the measurement of the spectra to ensure complete mixing.

Small-angle X-ray scattering (SAXS)

SAXS measurements were carried out in transmission mode with synchrotron radiation ($\lambda = 1.20 \text{ \AA}$) at the 4C1 SAXS beamline (BL) of the Pohang Accelerator Laboratory. A two-dimensional (2D) charge-coupled detector (CCD) (Mar USA, Inc.) was employed. A sample-to-detector distance of 0.5 m was used. The magnitude of the scattering vectors q ($4\pi \sin\theta/\lambda$) was $0.3 \text{ nm}^{-1} < q < 5 \text{ nm}^{-1}$, where 2θ is the scattering angle and λ is the wavelength of the X-ray beam source. The scattering angle was calibrated with linear polyethylene, collagen (chicken tendon), and polystyrene-*b*-polyethylene-*b*-polybutadiene-*b*-polystyrene (SEBS) block copolymer standards. All scattering measurements were carried out at 25 °C.

Rheological measurement

Rheological properties were measured using Hakke Mars rheometer (Thermo Electron GmbH, USA) with a diameter of 15 mm using a solvent trap. The measurements were monitored by oscillatory time sweep experiments at 20 °C. During the time sweep experiments, the G' (storage modulus) and G'' (loss modulus) were measured for a period of 5 min at a frequency of 1 Hz under 1% strain.

Induced circular dichroism (ICD) measurement

The ICD spectra were recorded on a Jasco J-815 spectropolarimeter in a HEPES buffer solution (pH 7.5) with a 0.1 mm path length and a 1 nm spectral bandwidth at room temperature. All measurements were made at 25 °C.

Results and discussion

When aqueous solutions of dye **1** and γ -CD were mixed at low concentrations (up to 60 mM), a homogeneous, dark brown solution was obtained. As the concentration increased, its viscosity began to increase. At approximately 100 mM, the solution would not flow, this becoming a hydrogel (Fig. 1). Gelation occurred only in the presence of γ -CD. An anisotropic structure appeared before gelation, and its texture remained embedded in the gel matrix. When, for visual observation, it was examined with a polarized optical microscope, stripes of various colors and levels of brightness were observed under crossed polarizers. This reminds us of the mixture of Orange II with γ -CD, which reportedly forms a fibroid aggregate [26, 27]. No birefringence was observed when either dye **1** or γ -CD existed. When the mixture was heated above 60 °C, the anisotropy disappeared, leaving a clear isotropic solution. However, when cooled to room temperature, it reappeared. In SEM images, numerous fibrils appear to be crosslinked to form a randomly arranged network. The hydrogen bonds between the fibrils, mainly coming from the adjacent –OHs of the CD rings, act as physical cross-linkers.

The $^1\text{H-NMR}$ spectra show the interaction of the dye moiety in the γ -CD cavities. In the presence of CD, the resonance signals of aromatic protons decrease and the CD protons merge and broaden with slight chemical shifts. This demonstrates that the chromophores are trapped inside the γ -CD cavity and that their conformational flexibility is restricted by hydrogen bonds between the CDs and/or dye **1**. Under this environment, the dye experiences a shielding effect due to the change in the microenvironment. The 2D-ROESY NMR spectrum shows the rotational NOE interactions between the inner H_3 protons of γ -CD and the phenyl protons of the dye (Fig. 2a). However, almost no

NOE cross-peaks exist between the H_5 protons on the γ -CD ring and the protons of the 8-HQ unit in dye **1**. This indicates that the phenyl ring of dye **1** is tightly included in the hydrophobic cavity, but for the 8-HQ unit, only one side is included and the OH and N groups are excluded from the wide face of the γ -CD cavity. Measurement of the high-resolution magic angle spinning (HR-MAS) spectrum reveals a strong peak at 9.24 ppm, which is attributed to the hydroxyl group in 8-HQ (Fig. 2b). Compared to those of other aromatic peaks, its intensity is relatively strong, which confirms that OH is not included in the CD cavity. We noted that it acted as a binding site to metal ions, which will be discussed later.

The absorbance spectra of dye **1** change depending on the concentration of γ -CD with no fixed isosbestic points, which implies the existence of more than two environments for dye **1** (Fig. 3). The azo tautomer is favored in the presence of γ -CD, and thus the absorption maximum of the dye shifts gradually from 470 to 410 nm. A Benesi-Hildebrand plot reveals the preferential formation of a 1:1 (CD : dye) complex. The stability constant (K_f) was calculated to be $8.8 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$. From the high association constant, we note that the binding nature of the complex is strong.

The solution X-ray scattering measurements show overt evidence of an anisotropic dye/ γ -CD complex formation. SAXS data obtained using synchrotron radiation ($\lambda = 1.20 \text{ \AA}$) reveal three peaks at $2\theta = 2.9^\circ, 4.0^\circ, \text{ and } 5.8^\circ$, which are attributed to reflection at the (100), (110), and (200) planes, respectively, of the hexagonal packing of the CDs (Fig. 4a) [28–30]. It was noted that the intensity of the (200) plane becomes stronger with gelation. While scanning at a lower scattering vector, q , we observe three successive peaks at 0.045, 0.090, and 0.136 \AA^{-1} with a ratio of 1:2:3, which suggests the presence of a layered subunit in the gel with a regular spacing of 14.1 nm, corresponding to the stacking of 17.8 γ -CD ($0.79 \text{ nm} \times 17.8 = 14.1 \text{ nm}$) (Fig. 4b). In its dilution, as evidenced by a marginal shift in the peaks, the spacing slightly decreases to 13.2 nm ($0.79 \text{ nm} \times 16.7 = 13.2 \text{ nm}$). The γ -CD cavities stack on top of each other to form long cylindrical channels, and the hexagonal packing is reinforced by hydrogen bonding between the included guest molecules and neighboring γ -CD molecules in the CD stack, thereby producing anisotropic textures of the hydrogel in the current case.

Figure 5 shows the rheological properties of the mixture at different concentrations. The increase in the concentration from 60 to 100 mM leads to a considerable increase in the hydrogel strength, as demonstrated by a 550-fold increase of G' and a decrease in $\tan \delta$ from 3.19 to 0.14, indicating that the interactions which hold together the anisotropic structure become stronger at higher concentrations. Several previous studies noted the formation of

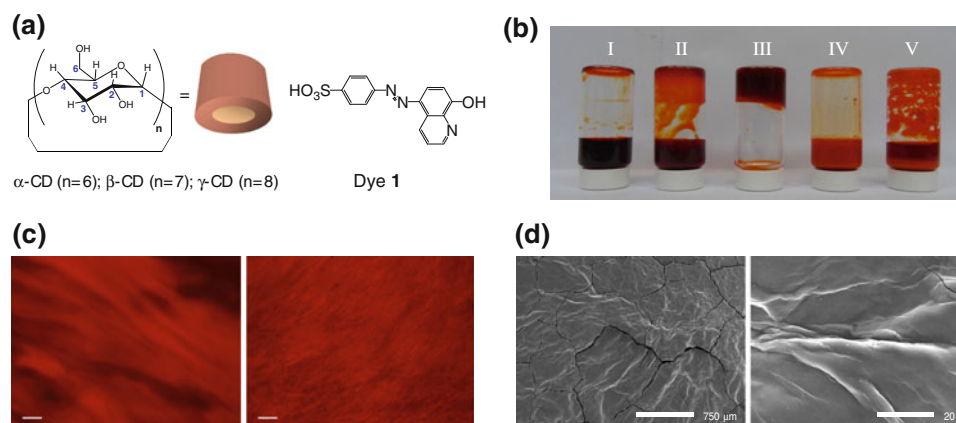


Fig. 1 a Chemical structures of cyclodextrins (CDs) and dye 1, b photographic images of the inclusion complex between dye 1 and CDs under HEPES buffer (pH 7.5): I (dye 1 20 mM + γ -CD 20 mM), II (dye 1 60 mM + γ -CD 60 mM), III (dye 1 100 mM + γ -CD 100 mM), IV (dye 1 100 mM + α -CD 100 mM), and V (dye 1

100 mM + β -CD 100 mM), c images from a polarized optical microscope between glass slides of rubbed polyimide of complex II (left) and complex III (right), respectively, with a scale bar of 100 μ m, and d SEM images of complex III after being air-dried, at lower and higher magnifications

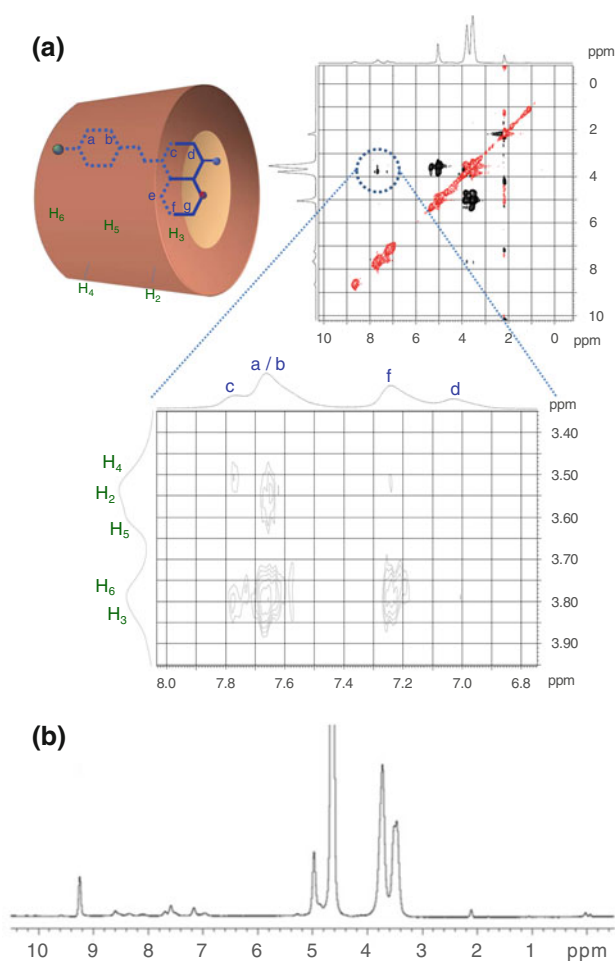


Fig. 2 a ROESY spectrum (spinlock time: 250 ms), and b ^1H HR-MAS NMR spectra of the hydrogel. In both cases, the concentrations of dye 1 and γ -CD were fixed at 100 mM. All measurements were made using D_2O as a solvent at 25 $^\circ\text{C}$. The possible binding mode of the inclusion complex is shown

CD aggregates in water in which the increased value of G' and the lower $\tan \delta$ of the hydrogel reveal that CD increases the cross-link density of the hydrogel [31–33]. The observation that an aqueous mixture of γ -CD molecules and dye 1 forms a hydrogel suggests, therefore, that CD molecules dramatically affect the hydrogel network structure and that the physical driving force of the gelation is related to the self-assembly of CD nano-aggregates made of host–guest inclusion complexes, which serve as strong cross-linkers in the supramolecular network.

Given the results above, we examined the influence of metal ions on the hydrogel. We intended to investigate whether and how a hydrogel having a guest molecule with 8-HQ behaves toward the metal ions. Three different responses could be identified: (a) no change in its appearance; (b) a gel-to-sol transition; and (c) the formation of precipitates. After examining various metal ions, we categorized them into three classes, as follows: (a) Mg^{2+} , Ca^{2+} and Li^+ ; (b) Al^{3+} , Fe^{3+} and Cr^{3+} ; and (c) Cu^{2+} , Ni^{2+} , Zn^{2+} , Hg^{2+} , Cd^{2+} and Pb^{2+} (Fig. 6). In a further investigation, for simplicity, we focused on two typical metal ions, Pb^{2+} and Cr^{3+} , to investigate their interactions with hydrogel.

Pb^{2+} can be distinguished from all other metals: it forms precipitates with an equimolar concentration of the hydrogel. In a dilute solution, it decolorizes the solution by precipitating the dye molecules. The response to Pb^{2+} occurs only in the presence of both dye 1 and γ -CD. No other metal in the (c) class shows this type of response in a dilute solution. We also noted that the gel becomes a sol upon the addition of equimolar Cr^{3+} in conjunction with a noticeable spectral shift into darker colors. In both cases, the anisotropic texture disappears completely with the addition of metal. In UV titration curves, the band centered

Fig. 3 **a** Absorbance spectra of dye **1** (4.0×10^{-5} M) upon the addition of different concentrations of γ -CD (0 – 4.6×10^{-3} M) at pH 7.5 (HEPES buffer), and **b** change in the absorbance at 470 nm with the addition of γ -CD

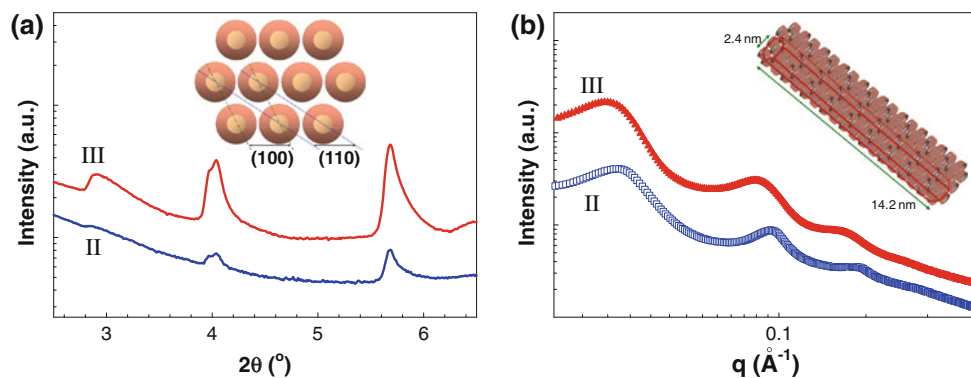
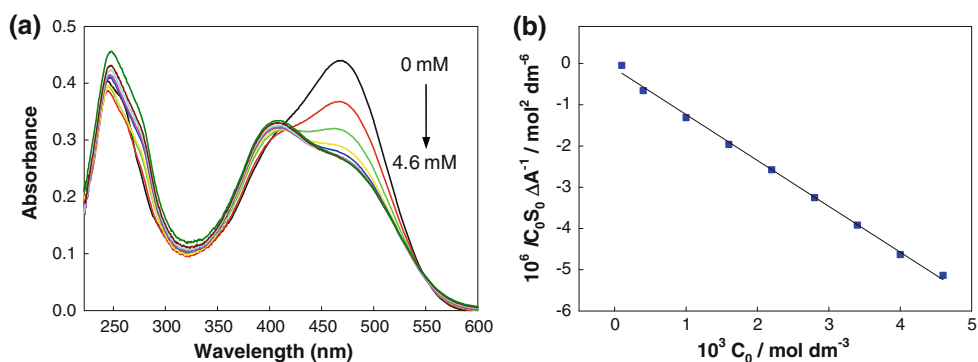


Fig. 4 **a** Small-angle X-ray scattering (SAXS) data of the complex in the range of 2θ under different concentrations of (II) 60 mM, and (III) 100 mM (numberings are identical to those in Fig. 1), and **b** SAXS data of complex (II) and complex (III) in regard to the q vector. Both

samples show three peaks, at 0.048 , 0.097 , 0.145 \AA^{-1} for (II) and at 0.045 , 0.090 , and 0.136 \AA^{-1} for (III), which suggests regular spacings of 13.2 nm and 14.1 nm, respectively

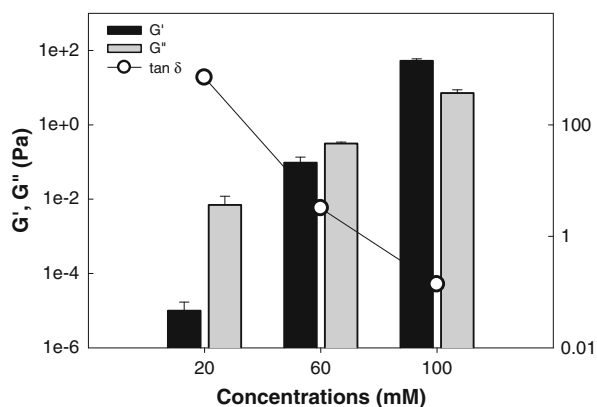


Fig. 5 Rheological properties of mixtures containing dye **1** and γ -CD at different concentrations. Left axis G' and G'' ; right axis: $\tan\delta$. Data are shown as averages with standard deviations. All measurements were done three times at 20°C , and all mixtures are composed of equimolar dye **1** and γ -CD

at 470 nm quickly drops with the addition of Pb^{2+} , showing that dye **1**- Pb^{2+} complexation has occurred (Fig. 7). The addition of Cr^{3+} , however, only slightly affects the absorbance curves.

The CD cavity provides a chiral microenvironment that induces circular dichroism (ICD) signals of complexed achiral groups. Therefore, circular dichroism spectrometry

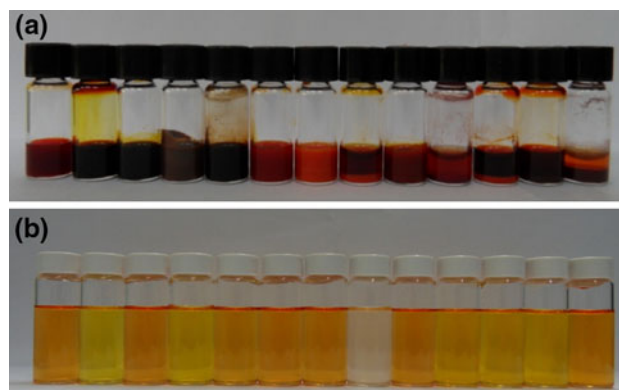
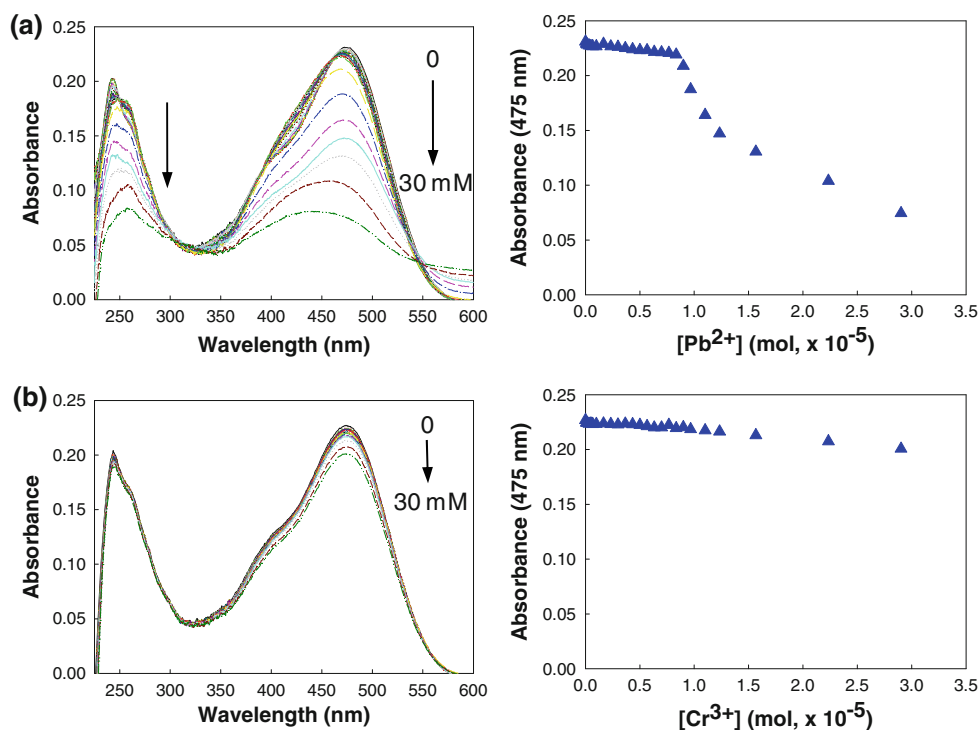


Fig. 6 Photographic images, upon the addition of metal ions, of **a** the hydrogel ($[\text{dye } \mathbf{1}] = 100$ mM, $[\text{g-CD}] = 100$ mM), and **b** the dilute solution ($[\text{dye } \mathbf{1}] = 5.0 \times 10^{-5}$ M, $[\text{g-CD}] = 5.0 \times 10^{-5}$ M). The order of the metal ions added was as follows: none, Al^{3+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Li^+ , Mg^{2+} , Pb^{2+} , Ca^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} (left to right). All solutions were prepared in HEPES buffer solution (pH 7.5)

has become an important tool in explaining the structure of CD inclusion complexes. In ICD spectra, as expected, no ICD signal was observed for dye **1** (Fig. 8). In the presence of γ -CD, the ICD spectra of the hydrogel reveal a positive cotton effect peak around 280 nm and a negative cotton effect peak around 380 nm. According to empirical rules

Fig. 7 **a** Absorbance spectra of dye **1** and γ -CD (1.0×10^{-5} M, both) at pH 7.5 upon the addition of **a** Pb^{2+} and **b** Cr^{3+} . All measurements were made in HEPES buffer at 25 °C. The right side shows the absorbance changes at 470 nm with the addition of metal ions



suggested in previous studies [34–37], the appearance of these signals indicates that the aromatic moiety penetrates the asymmetric locus of the CD cavity, thus experiencing restricted mobility. With the appearance of an anisotropic texture, a strong negative peak of the cotton effect around 330 nm develops. By adding Pb^{2+} , this ICD intensity then decreases completely toward the baseline, a phenomenon indicating the break-up of the hydrogel and the unthreading of the inclusion complex. Meanwhile, the addition of Cr^{3+} does not alter the ICD spectrum of the hydrogel. This implies that chromium ions act as a denaturing agent that inhibits the H-bonding between adjacent CDs while not giving rise to unthreading.

To estimate the structural features of the hydrogel with metal ions, we obtained the $^1\text{H-NMR}$ spectra of the hydrogel containing equimolar Pb^{2+} and Cr^{3+} in D_2O (Fig. 9). Upon the addition of Pb^{2+} , the proton signals of CD resolve into those of the pristine CD, which indicates that the addition of Pb^{2+} disrupts the inclusion complex of dye **1** and γ -CD by forming metal-dye bonds, ultimately leading to precipitated dye and uncomplexed CD molecules. The effect of Cr^{3+} is somewhat different; its NMR spectrum is nearly unchanged with broadened and merged resonance peaks of the CDs. This is identical to what was noted in the NMR spectra of a γ -CD and Cr^{3+} mixture. Thus, we conclude that Cr^{3+} complexes more with CD than with dye **1**. FT-IR spectrometry of the hydrogel strengthens this view (Fig. 10); when comparing the IR spectra, a shift of $\nu(\text{C}=\text{O})$ occurs from 1571 to 1560 cm^{-1}

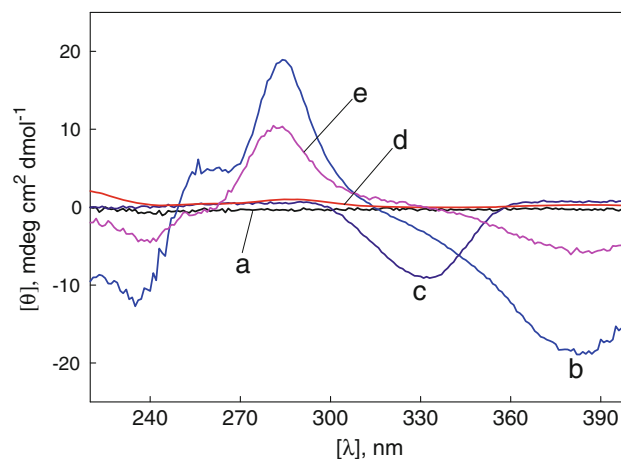


Fig. 8 Normalized ICD spectra of HEPES buffer solutions (pH 7.5) containing **a** dye **1**, **b** the mixture of dye **1** and γ -CD (20 mM), **c** the mixture of dye **1** and γ -CD (60 mM), **d** the mixture after adding Pb^{2+} (60 mM), and **e** the mixture after adding Cr^{3+} (diluted to 6 mM). All mixtures are composed of equimolar dye **1** and γ -CD. Due to the high absorbance, the ICD intensity of the hydrogel of 100 mM revealed a large experimental error. Therefore, it is not shown here. All measurements were made at 25 °C

after the addition of Pb^{2+} , indicating that the C–O stretching frequency of the C–O–M bond after dye **1** is coordinated with the metal ion. A noticeable shift of $\nu(\text{C}=\text{N})$ from 1223 to 1252 cm^{-1} also occurred. These facts show that coordination of dye **1** to Pb^{2+} takes place via both the oxygen and nitrogen atoms of 8-HQ group. After

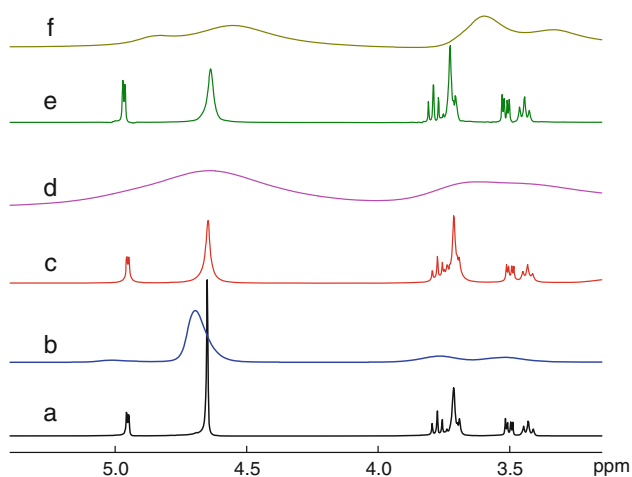


Fig. 9 Partial $^1\text{H-NMR}$ spectra of (a) $\gamma\text{-CD}$; (b) mixture made of dye **1** and $\gamma\text{-CD}$; (c) the mixture with Pb^{2+} ; (d) the mixture with Cr^{3+} ; e $\gamma\text{-CD}$ with Pb^{2+} ; and f $\gamma\text{-CD}$ with Cr^{3+} . The concentrations of all chemicals were fixed at 60 mM. Measurements were made at 25 °C using D_2O as a solvent

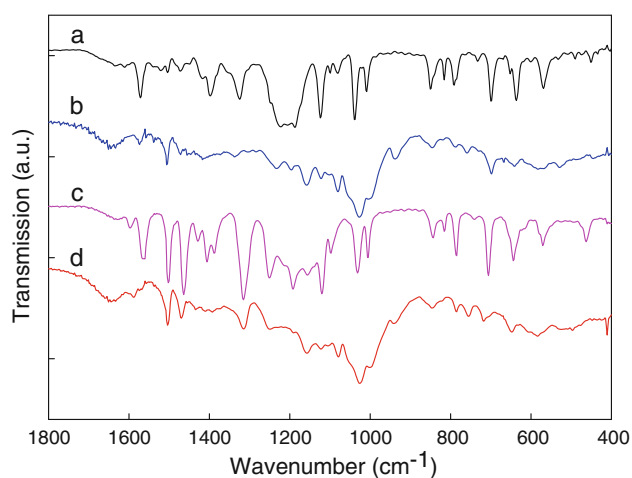


Fig. 10 FT-IR spectra of the hydrogels in the regions of $1800\text{--}400\text{ cm}^{-1}$ of (a) dye **1**, (b) mixture made of dye **1** and $\gamma\text{-CD}$, (c) the mixture with Pb^{2+} , and (d) the mixture with Cr^{3+} . Measurements were made after vacuum-drying the samples for a week

adding Cr^{3+} , in contrast, we did not observe such changes in the intensity and shape of the FT-IR absorption bands.

In summary, we have presented an anisotropic supramolecular gel of CD-azo dye, in which physical gelation is completed by a specific host–guest interaction. The obtained hydrogel exhibits respective morphological transitions based on supramolecular assembly and dissociation. It can identify different classes of metal ions, and, among them, naked-eye differentiation of lead ion is possible due to the coordination-induced unthreading of the dye molecules. Gel-to-sol transitions can also be realized by using chromium ion as a denaturing reagent. These hydrogel

properties will be useful in analytical applications involving metal ion sensing and removal.

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