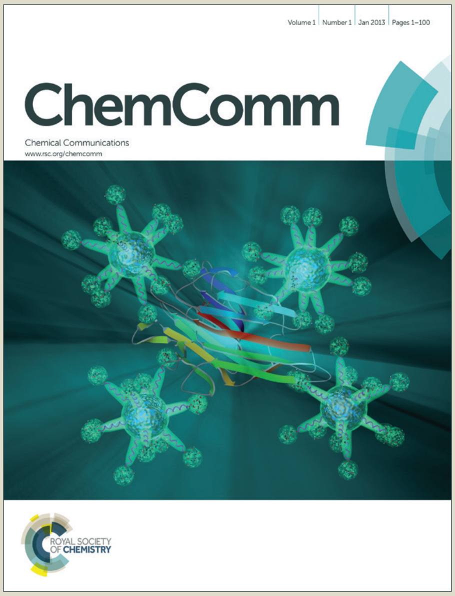

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ARTICLE TYPE

Photoresponsive Metallo-hydrogels based on Visual Discrimination of the Position Isomers through Selective Thixotropic Gel Collapsing

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Incoperating visual discrimination of 2,2'-bipyridine and self-healing ability, a novel photo-switchable metallo-hydrogel system is fabricated with pincer-type Cu(II) complex and 2,2'-azopyridine.

In consideration of slightly differences in skeleton with similar physical and chemical properties, the development of a simple discrimination protocol for positional isomers of small organic molecules constitutes an extremely intriguing and challenging task in chemistry, biology, pharmacology as well as environtology.[1] Although tremendous advance in the chemical analysis has been achieved along with the rapid development of analytic instruments such as NMR, chromatograph, electrochemistry and UV-fluorescence spectroscopy, the inexpensive, practical and reliable visual discrimination of structural isomers is still highly desirable. As one kind of smart materials, stimuli-responsive gels[2,3] have drawn increasing attention and regarded as intriguing platforms for molecular recognition,[4] however, the application of gels in visual discrimination of structural isomers has been somewhat neglected. Recently, Harada and co-workers demonstrated the macroscopic discrimination of the substituted positions on the naphthyl groups by polymeric gels modified with β-cyclodextrin on the basis of host-guest interactions.[5] In the case of molecular gels, Shinkai and co-workers realized the first example on visual colorimetric sensing of 2,6-dihydroxynaphthalene from its positional isomers by using hydrogen-bonding blocking approach.[6] With the similar strategy, Escuder and co-workers extended the naked-eye isomer detection to catechol from its structural analogues by using peptide molecular gels.[7]

Furthermore, incorporation of metal ions is intriguing to introduce the novel properties of the metal (such as redox, catalytic and coordination behaviors) into the gels,[8] and the resulting metallogels may have the potential applicability in visual isomers discrimination through metal coordination,[9] however, to our knowledge, the discrimination of positional isomers by using molecular metallo-hydrogels as a practical platform has been neglected so far. In addition, 2,2'- and 4,4'-bipyridines (bipys) are the most common forms among their six positional isomers, which demonstrated a variety of applications in a broad range of research fields. 2,2'-Bipy and its derivatives constitute one of the most useful bidentate ligands with strong coordination ability and have been applied as versatile building blocks in catalysis, photochemistry, supramolecular chemistry, macromolecular chemistry as well as nano sciences.[10] Besides their application of 4,4'-bipy and its derivatives in pharmaceuticals and pesticides, recently, they represent a widely useful tectons to construct metal-organic frameworks (MOFs).[11] However, straightforward visual-size recognition of bipyridines' positional isomers is still absent, especially by using the molecular metallogel matrix as a discrimination platform to date.

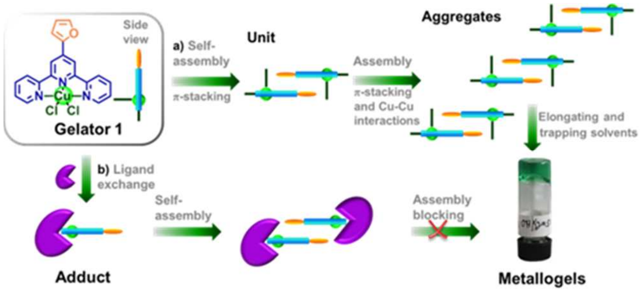

Fig. 1 Metallo-hydrogelator **1**; a) its plausible gel assembly and b) gel collapsing process *via* interaction blocking by using bulky ligands.

Recently, we have successfully developed several pyridine-bridged metal pincer complexes as efficient molecular metallo-gelators for a variety of organic solvents, ionic liquids and even water at extremely low gelator concentrations, and further demonstrated their potential applications in catalysis, solar cells as well as visual chiral recognition.[12,13] Among them, pincer-type terpyridine-Cu(II) complex **1** (Figure 1) constitutes a rare super metallo-hydrogelator, which can gelate pure water, alcohols and various aqueous media at the gelator concentration as low as 0.25 wt% even without obvious sticky sites.[12] Following our recent interests in developing novel metal complexes and their potential applications in catalysis and soft matter,[12-15] herein, we would like to incorporate the self-healing property and the coordination ability of hydrogel **1** into a practical discrimination platform for visual recognition of bipyridines' positional isomers, and further reveal their potential application in photo-responsive materials.

As shown in Figure 1, π-stacking and Cu-Cu interactions[8c] between metal-hybrid aromatic rings of terpyridine-Cu(II) complex **1** are rationalized as key forces for molecular assembly, which favor the further aggregation resulting in thixotropic metallo-hydrogel with self-healing ability.[12] In consideration of five-coordination number of Cu(II) center, the chloride ligands may be easily substituted by external *N*-containing ligands.[16] Therefore, structural modifications with additional ligands substitution may be a possible strategy to handicap these interactions (Figure 1b). Initially, rigid 1,10-phenanthroline (phen) was selected as a bulky ligand, in which two N atoms can efficiently chelate with the same Cu center. To our delight, the addition of one equivalent of phen to the 1 wt% stable green metallo-hydrogel **1** with subsequent heating to reflux and cooling to room temperature process resulted in a cyan solution (Figure 2). This result may be rationalized in terms of a substitution of the chloro ligands in complex **1** by phen further blocking the intermolecular π-stacking and Cu-Cu interactions which is hard for the further self-assembly leading to gel network collapse (Figure 1b). High-resolution mass spectrometry (HR-MS) study further confirmed ligands substitution and the adduct formation: $[M_{(\mathbf{1}+phen-2Cl)}]^+$ (*m/z* found: 542.1038; calculated: 542.1042). In addition, from the molecular structure of complex **2**, which was readily synthesized from complex **1** with phen in the presence of AgOTf and established by X-ray structure analysis (See ESI†, Figure S3), no obvious Cu-Cu interaction was observed between the molecules. Although, there is π-π stacking in a unit (3.55 Å), further assembly from the unit to form gel was apparently hampered by rigid bulky phen rings. From scanning electronic microcopy (SEM) morphologies, bulky crystalline rods (several μm long and ca. 200 nm wide) were found (Figure 1b), which were quite different from metallo-nanoparticles (MNPs) presented in Figure 2a.

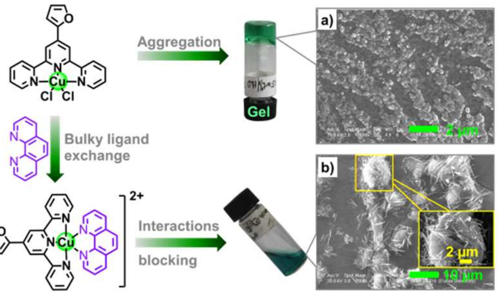

Fig. 2 SEM images of sol/gel formed by hydrogels **1**/H_2O (1 wt%): a) without any ligand substitution (gel); and b) with 1 equiv. phen (sol).

In terms of coordination abilities, 2,2’-bipy is similar to phen. Therefore, 2,2’-bipy is also involved the control test to further support the results from phen substitution experiment. Gladly, the addition of one equivalent of 2,2’-bipy to the gel with subsequent heating/cooling procedure also resulted in a collapse of the gel and a cyan solution was obtained (Figure 3). Crystalline rods were observed in the collapsed sol of [**1**+2,2’-bipy]/H_2O (ca. 150 nm wide and micrometers long, Figure 3a), which may be formed by crystallization of collapsed sol via vapouration during sample preparation. However, when its positional isomer 4,4’-bipy was added to the same metallo-hydrogel, after identical operation, the gel was stable and survived even with 2 equiv. bipy addition. In comparison with the corresponding SEM morphology of sol [**1**+2,2’-bipy]/H_2O, MNPs still existed in this case, although, they were glued closer than what were founded in the SEM images of mono-component metallo-gel **1**/H_2O (Figure 2a *vs.* 3b). With these results in hand, other bipys’ positional isomers (2,3’-, 2,4’-, 3,3’- and 3,4’-bipys) were also involved in the control tests. To our expected, similar as 4,4’-bipy, the metallo-hydrogel still survived the addition of all other selected positional isomers after routine heating/cooling gel preparation sequences (Figure 3c), which may be caused by these bipys hardly chelating the same Cu(II) center and unable to hamper the molecular self-assembly of pincer complex. Consequently, through selective metallo-hydrogel collapse with the ligands substitution and metal coordination strategies, we not only clearly demonstrated that π-stacking and Cu-Cu interactions were responsible for the gel formation, but also realized the first example of visual discrimination of the 2,2’-bipy out of its positional isomers by using metallogel as a convenient platform.

Fig. 3 a) Visual discrimination of 2,2’-bipy out of its isomers *via* selective gel collapse, and SEM images of sol/gel formed by hydrogels **1**/H_2O (1 wt%): b) with 1 equiv. 2,2’-bipy (sol) and c) with 1 equiv. 4,4’-bipy (gel).

Enlightened by the visual recognition of positional bipy isomers through selective metallo-hydrogel collapsing, we would like to combine these results with the self-healing property[12] of metallo-gel **1**/H_2O to fabricate a photo-responsive two-component hydrogel system with the special ligands, which have reversible chelation ability when stimulus were applied (Figure 4). Since the photochromatic properties of azobenzene and its derivatives making them as ideal candidates for numerous molecular devices and functional materials,[17,18] its N analogue, azopyridine (apy), is selected as suitable photo-dissociable ligand for this purpose. To the best of our knowledge, there is no example on photo-responsive molecular gels by using metal coordination strategy, especially with apy. The addition of one equiv. of *trans*-2,2’-apy to the stable transparent green metallogel **1**/H_2O (1 wt%) with subsequent heating/cooling process resulted in a turbid dark-brown gel (Figure 4b), obviously indicating the chelating of *trans*-2,2’-apy to Cu(II) center hardly blocked the interactions responsible for the gel formation. In consideration of the stable *trans* form of apy readily converting to its *cis* configuration upon irradiation with UV light (ca. 365 nm), which can be switched back to the *trans* form under visible light (ca. 440 nm),[16] a 1 wt% two-component hydrogel [**1**+apy]/H_2O prepared from pincer complex and one equiv. of *trans*-2,2’-apy was irradiated with 365 nm UV light. To our delight, the gel collapsed after more than 18 hours, and the resulting solution readily reformed a stable turbid hydrogel under visible light irradiation for a quater. After detailed study on UV behavior of 2,2’-apy in water, the gel collapse was realized within two hours, when UV irradiation at 320 nm was applied. The gel collapsing and reforming could repeat more than five times, indicating its potential in the field of molecular switches.

The visual photo-responsive behavior of metallo-gel [**1**+apy]/H_2O was further confirmed by the SEM and UV studies (See ESI†). Instead of the MNPs morphologies observed in Figure 4a, the images of [**1**+apy]/H_2O revealed dense long nanofibers, which were ca. 50 nm wide and several μm long (Figure 4b). Among these long and thin nanofibers, a small amount of crystal-like rods were found (insert view in Figure 4b). The coordination of *trans*-2,2’-apy with the Cu center of complex **1** to form a new adduct may be responsible for the difference in morphologies between the metallogels **1**/H_2O and [**1**+apy]/H_2O. After irradiation under UV light at 320 nm for 2 hours the gel collapsed, bulky and long crystalline rods were also found in the SEM image (Figure 4c). In assistance with HR-MS experiments, the substitution of two chloro ligands in complex **1** by *cis*-2,2'-apy *in situ* resulted in an adduct signal of $[M_{(1\text{+apy-2Cl})}]^+$ (m/z found: 546.1124; calculated: 546.1104), which indicated that apy coordinated to complex **1** in a 1:1 ratio. The results further proved that the small amounts of crystal-like rods in Figure 4b belonged to adduct of complex **1** and *cis*- 2,2'- apy, and also revealed that there were a small amounts of *cis*-form even containing in new prepared *trans*-apy. After resting under visible light (440 nm) for a quarter, a dark-brown gel reformed and similar SEM morphology like Figure 4b was observed (see ESI†), in which more crystalline rods existed indicating that there was a photostationary state between *trans*- and *cis*-apys, and not all *cis*-isomers could be switched back to its *trans* form under the irradiation of visible light. This was also consistent with the observation of a detailed UV studies on 1 × 10^{-5} M mixture of complex **1** and apy (1:1) in five irradiation cycles, except the first cycle, the intensity of absorption decreased ca. 10% between the original and reformed state, unobvious intensity decreasing was observed for the rest cycles (Figure 4d).

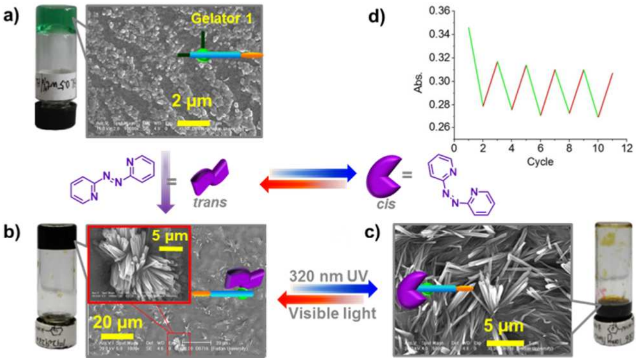

Fig. 4 Gel collapse and reformation process through reversible interaction blocking strategy by using photo-reversible apy. SEM images of a) hydrogel **1**/H_2O (1 wt%); b) hydrogel [**1**+*trans*-apy]/H_2O (1 wt%, 1:1 ratio); c) the collapsed sol after irradiation at 320 nm; and d) cycles of UV-visible absorption of the aqueous mixture of **1** and one eq. apy (1 ×10^{-5} M) under irradiation of 320 and 440 nm in turns.

Conclusions

Based on visual discrimination of 2,2'-bipyridine out of its positional isomers *via* selective thixotropic metallo-hydrogel collapsing, a novel photo-switchable two-component metallo-hydrogel system was fabricated with pincer type Cu(II) complex **1** and photo-responsive 2,2'-azopyridine. In assistance with SEM, HR-MS, UV and crystal analysis, the mechanism of gel collapse by addition of 1,10-phenanthroline, 2,2'-bipyridine and *cis*-azopyridine was explained, which not only further demonstrated that π-stacking and metal-metal interaction between molecular **1** are responsible for the gel formation, but also indicated the molecular assembly blocking strategy is a good approach to fabricate a new platform for visual discrimination and photo-responsive soft materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures and characterization data for new compounds, SEM morphologies of gels or sols, UV studies, biyridines' isomers recognition and photoswitch studies. See DOI: 10.1039/b000000x/

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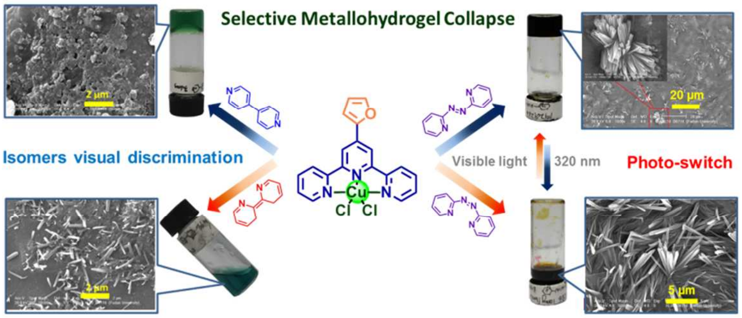

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