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A multi-responsive organogel and colloid based on the self-assembly of a Ag(I)-azopyridine coordination polymer;

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In this work, through the coordination of C_3 symmetric azopyridine ligands and Ag(I), coordination polymers with azo groups on the main chain were prepared. The *trans* coordination polymer formed an organogel with a network of nanofibers at low critical gelation concentrations, and it exhibited the abilities of self-healing and multi-stimuli response to heating, light, mechanical shearing, and chemicals due to the presence of dynamic coordinating bonds. On the other hand, the *cis* coordination polymer was found to assemble into nanoparticles to give a responsive colloid, which can produce fibrous precipitation in several days upon visible light irradiation due to the isomerization of the azo groups. This work provides a novel example for the design of a multi-responsive organogel and colloid based on the structural transformation of coordination polymers.

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1 Introduction

Stimuli-responsive materials showing dramatic property changes in response to external environmental stimuli have been attracting sustained attention due to the wide range of applications in soft robots,¹ tissue engineering,² biosensors,³ display,⁴ etc. This great interest has led to the development of numerous responsive materials wherein reversible transformations are achieved by introducing supramolecular interactions, such as hydrogen bonds, metal-ligand coordination, hydrophobic interactions, and π - π stacking.5 Among these supramolecular systems, coordination polymers have been of increasing interest in recent years, since they are mainly constructed from metal-ligand coordination that is not only thermodynamically stable but also kinetically labile, and this feature endows fast and precise stimuli-responsiveness to the materials.^{6,7} Generally, coordination polymers can be facilely synthesized through the coordination reaction of bridging ligands and metal ions, and their characteristics, e.g., the assembly structure, stability, and functionality, can be tuned by the metal ions and ligands utilized,8 which make them a promising prospect for potential applications in various fields.

Gels are a unique category of responsive materials with their entire three-dimensional network entrapping the solvent inside.^{9,10} If the network is built by the nano/micro assembly of coordination polymers, a so-called coordination polymer gel (CPG) forms.¹¹⁻¹³ Compared with other metallogels afforded from discrete metal complexes (metallogelators), CPGs benefit from the higher metal content and faster response of the coordination polymer, and thus they can be designed as a novel responsive material.^{14,15} In particular, CPGs in response to complex and multiple stimuli have become a focus of innovation in the design and fabrication of smart materials, as a single-responsive performance sometimes cannot ensure accurate and remarkable feedback in a complicated environment. To date, some studies have been reported to prepare CPGs that respond to many external inputs, including mechanical stress,¹⁶ change of temperature,¹⁷ sonication¹⁸ and chemicals.^{19,20} Recently, Mauro et al. introduced azobenzene groups into coordination polymers and fabricated a soft gel actuator with photosensitivity.^{21,22} However, to date, the incorporation of multiple responses to light, heating, mechanical force and chemicals into one CPG has not been reported.

In the last few decades, many kinds of stimuli-responsive colloids have been developed for drug delivery,²³ controlled release,^{24,25} *etc.* Traditionally, the response of these colloids is achieved by introducing some catalysts or agents to change the chemical structure of the matrix.^{26–28} However, this method leads to a complex procedure with additional reagents, which may contaminate the system. Therefore, the photo-responsive colloids based on a simple, clean, and efficient photochemical

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To demonstrate the strategy of preparing a stimuliresponsive gel and colloid by the assembly of a coordination polymer, herein, we report the fabrication of a multi-responsive organogel and colloid by employing two azo isomers of the Ag(1) coordination polymer. The azo groups were introduced into the main chain of the coordination polymer through the coordination of Ag(I) and azopyridine ligand, thereby affording the trans and cis conformers of the coordination polymer. The coordination polymer with trans configuration can produce a CPG constituted of the nanofiber networks, and its gel-sol phase transition can be triggered in response to multi-stimuli including light, heating, mechanical shearing, and chemicals. It was found that the photoisomerization of azo moieties on the coordination polymer was retarded significantly compared with that of azo ligands, showing the macromolecular hindrance effect. Meanwhile, the isotropic assembly of the coordination polymer with cis configuration produced a colloidal dispersion composed of nanoparticles, and both visible light irradiation and heating could change the nanoparticles into fiber aggregates due to the isomerization of the coordination polymer, and caused precipitation and demulsification. This research presents a novel example of a responsive colloid derived from the assembly transformation of coordination polymers.

2 Experimental

2.1 Materials and equipment

1,3,5-Benzenetricarbonyl trichloride, phenol, 3-aminopyridine, 4aminopyridine, sodium nitrite, sodium hydroxide, and 4dimethylaminopyridine (DMAP) were purchased from Shanghai Aladdin Co. Silver nitrate was supplied from Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), acetonitrile (MeCN), dichloromethane, cyclohexane and ethanol were purchased from Beijing Chemical Works. All other chemicals were of reagent grade or better. The synthesized compounds were characterized using ¹H NMR (Japan JEOL JNM-ECA600) and FT-IR (Bruker TENSOR II). The transmittance, particle size, and zeta potential were measured by dynamic light scattering (DLS) with a particle size analyzer (Litesizer 500 Anton-Paar). The gels were characterized using TEM (Japan JEOL JEM 2100, 200 kV), SEM (Japan Hitachi SU8010), X-ray diffraction (XRD) (Bruker AXS D8), and elemental analysis (Elementar Vario EL III). The rheological measurement was performed using a rheometer (Anton Paar Physica MCR-300). UV-vis absorption spectra were recorded with a UV-vis absorption spectrometer (Japan Shimadzu UV-3600). The light response was determined with a 365 nm UV lamp (Japan Iwata UV-201 SA, 200 mW cm $^{-2}$) and an LED lamp (>500 nm, 30 mW cm $^{-2}$).

2.2 Synthesis of 4-(3-pyridylazo)phenol

3-Aminopyridine (1 g) was dissolved in 20 mL of deionized water. Then, 4 mL of hydrochloric acid (30%) was added dropwise into the solution. The solution was kept in an ice-water bath, and 0.89 g of sodium nitrite dissolved in 10 mL of deionized water was added within 10 min under stirring. Subsequently, the reaction mixture was added to a 60 mL aqueous solution containing 3 g of phenol within 10 min. After continuing the reaction at 0 °C for 10 min, 1.6 g of NaOH was introduced and the resulting precipitate was filtered. The crude product was washed three times with deionized water and dried in vacuum for 12 h to give a yellow powder (1.73 g). Yield: 82%.

¹H NMR (600 MHz, 298 K, DMSO-d₆): δ = 10.45 (s, 1H, OH), 9.03 (s, 1H, pyridine 2-H), 8.68 (d, *J* = 4.4 Hz, 1H, pyridine 6-H), 8.11 (d, *J* = 8.4 Hz, 1H, pyridine 4-H), 7.84 (d, *J* = 8.8 Hz, 2H, phenyl 3-H), 7.58 (d × d, *J* = 4.8, 8.0 Hz, 1H, pyridine 5-H), 6.98 ppm (d, *J* = 8.8 Hz, 2H, phenyl 2-H) (Fig. S1, ESI†). FTIR (KBr, cm⁻¹): 3020, 3072, 1588, 1501, 1482, 1415, 1282, 1140. ESI-MS *m/z*: [M + H]⁺ calcd 200.07; found 200.1446.

2.3 Synthesis of tris(4-(3-pyridylazo)phenyl)benzene-1,3,5-tricarboxylate (*trans*-D)

First, 1 g of 4-(3-pyridylazo)phenol was dissolved in 50 mL of THF, and then 0.44 g of 1,3,5-benzenetricarbonyl trichloride dissolved in 10 mL of THF was added dropwise. Subsequently, 0.71 g of DMAP was added into the flask, and the solution was refluxed for 1.5 h. Afterwards, the solvent was rotary evaporated and 60 mL ethanol was introduced. The resulting precipitate was filtered and purified by column chromatography to give a yellow powder of ligand *trans*-D (0.37 g). Yield: 30%.

¹H NMR (600 MHz, 298 K, DMSO-d₆): δ = 9.16 (s, 3H, benzene H *J* = Hz), 9.12 (s, 3H, pyridine 2-H), 8.78 (d, *J* = 4.8 Hz, 3H, pyridine 6-H), 8.22 (d, *J* = 8.8 Hz, 3H, pyridine 4-H), 8.10 (d, *J* = 8.8 Hz, 6H, phenyl 3-H), 7.70 (d, *J* = 8.8 Hz, 6H, phenyl 2-H), 7.66 ppm (d × d, *J* = 8.8, 4.8 Hz, 3H, pyridine 5-H) (Fig. S2, ESI†). FTIR (KBr, cm⁻¹): 1752, 1590, 1494, 1420, 1214. ESI-MS *m/z*: [M + H]⁺ calcd 754.21; found 754.4189.

2.4 Synthesis of 4-(4-pyridylazo)phenol

NaOH (0.318 g) and phenol (0.747 g) were dissolved in 6 mL of deionized water (vial A), and 0.5 g of 4-aminopyridine was dissolved in 1.2 mL of hydrochloric acid (30%) (vial B). Subsequently, 0.383 g of sodium nitrite dissolved in 1 mL of deionized water was introduced into vial B at 0 $^{\circ}$ C within 1 min, and then the solution was carefully poured into vial A. After 5 min, 0.211 g of NaOH dissolved in 1 mL of deionized water was introduced and the resulting precipitate was filtered. The crude product was washed with deionized water three times and dried in vacuum for 12 h to give an orange powder (0.42 g). Yield: 40%.

¹H NMR (600 MHz, 298 K, DMSO-d₆): δ = 10.56 (s, 1H, OH), 8.73 (d, *J* = 6.0 Hz, 2H, pyridine 2-H), 8.34 (d, *J* = 8.8 Hz, 2H, phenyl 3-H), 7.64 (d, *J* = 6.0 Hz, 2H, pyridine 3-H), 6.94 ppm (d, *J* = 8.8 Hz, 2H, phenyl 2-H) (Fig. S3, ESI[†]). FTIR (KBr, cm⁻¹): 3043, 1580, 1469, 1403, 1295, 1135. ESI-MS *m*/*z*: [M + H]⁺ calcd 200.07; found 200.1446.

2.5 Synthesis of tris(4-(4-pyridylazo)phenyl)benzene-1,3, 5-tricarboxylate (*trans-Z*)

First, 0.3 g of 4-(4-pyridylazo)phenol and 0.159 g of triethylamine were dissolved in 15 mL of THF, and then 0.132 g of 1,3, 5-benzenetricarbonyl trichloride dissolved in 1 mL of THF was added dropwise. After 10 min, the solvent was rotary evaporated and the resulting solid was purified by column chromatography to give a yellow powder of ligand *trans*-Z (0.19 g). Yield: 51%.

¹H NMR (600 MHz, 298 K, DMSO-d₆): δ = 9.09 (s, 3H, benzene H), 8.82 (d, *J* = 6.0 Hz, 6H, pyridine 2-H), 8.10 (d, *J* = 8.8 Hz, 6H, phenyl 3-H), 7.75 (d, *J* = 6.0 Hz, 6H, pyridine 3-H), 7.69 ppm (d, *J* = 8.8 Hz, 6H, phenyl 2-H) (Fig. S4, ESI⁺). FTIR (KBr, cm⁻¹): 1749, 1589, 1495, 1204. ESI-MS *m*/*z*: [M + H]⁺ calcd 754.21; found 754.4459.

2.6 Preparation of coordination polymer gel

For a typical procedure, silver nitrate (2.1 mg, 0.0124 mmol) was added to vial A and dissolved in 0.2 g of DMF. Ligand *trans*-D (6.1 mg, 0.0083 mmol) was added to vial B and dissolved in 0.8 g of DMF by heating. Rapid mixing of A and B produced a *trans*-AgD organogel (0.8 wt%, Ag(i)/*trans*-D feeding ratio = 3 : 2). The gel was confirmed by the vial inversion test. Following a similar procedure, *trans*-AgZ precipitation was obtained by employing the ligand *trans*-Z.

2.7 Preparation of coordination polymer colloid

For a typical procedure, ligand *trans*-D (6.1 mg, 0.0083 mmol) was added to vial A and dissolved in 0.8 g of DMF by heating. The solution was irradiated by 365 nm UV light for 2 min to produce *cis*-D solution. Afterwards, silver nitrate (2.1 mg, 0.0124 mmol) dissolved in 0.2 g of DMF was added to vial A to generate *cis*-AgD solution, and then 5 mL of deionized water

was added. The yellow colloidal dispersion was immediately formed after shaking by hand.

3 Results and discussion

3.1 Formation of gel *via* self-assembly

In previous work, we reported several CPGs with various morphologies fabricated through coordination of metal ions and symmetrical ligands with pyridyl groups.³²⁻³⁴ To develop a CPG with multi-stimuli response, herein, azo-pyridyl groups were introduced into the C_3 -symmetric molecule, and the resulting ligands with meta-pyridine and para-pyridine were designed, namely ligand trans-D and trans-Z, respectively. The molecular structures of the synthesized compounds were characterized by ¹H NMR (Fig. S1-S4, ESI⁺), and their two-step synthetic routes are shown in Fig. S5 and S6 (ESI[†]). After the addition of the Ag(I) solution to the ligand DMF solution at room temperature, the corresponding coordination polymers trans-AgD and trans-AgZ immediately assembled and aggregated from the solution due to their poor solubility in the solvent. It is worth noting that only trans-AgD formed a stable gel an orange-yellow color (Fig. 1a and Movie S1, ESI†), while trans-AgZ produced a suspension under the same conditions (Fig. S7, ESI[†]). According to the observation of SEM and TEM (Fig. 1b and c), trans-AgD assembled into long fibers with a diameter in the range of 50-200 nm, and built the gel network by entanglement and interlacing with each other. Comparatively, the microstructure of trans-AgZ was composed of short thick fibers, which could not form a network (Fig. S7, ESI⁺). Although the crystal architecture analysis from a single-crystal XRD was not successful, their different morphologies might be deduced by the reported study on similar Ag(1) coordination polymers, as the meta-pyridine coordination polymer usually had a closer packing in topology than the para-pyridine



Fig. 1 Gel morphology of *trans*-AgD. (a) Photograph, (b) TEM image and (c) SEM image of *trans*-AgD gel. (d) The possible assembly structure of the *trans*-AgD coordination polymer.

Table 1 Gelation ability, CGC and $T_{\rm gel}$ of $\mathit{trans}\text{-}{\rm AgD}$ in various organic solvents

Entry ^a	Solvent	Status ^b	CGC^{c} (wt%)	T_{gel}^{d} (°C)
1	THF	Р	_	_
2	DMSO	S	_	_
3	DMF	G	0.33	93
4	DMAc	G	0.45	76
5	MeCN	Р	_	—

^{*a*} Molar ratio of AgNO₃/*trans*-D = 3:2. ^{*b*} P: precipitation; G: gel; S: solution. ^{*c*} Critical gelation concentration (CGC), *trans*-AgD mass percentage. ^{*d*} Gel-sol phase transition temperature, gel concentration 0.8 wt%.

coordination polymer, and that favored the one-dimensional assembly to form longer nanofibers.³⁵ In addition, under different feeding ratios of Ag(I)/trans-D, the elemental analysis of all organogel fibers showed a 1:1 ratio after the filtration of solvent (Table S1, ESI†), and that result was also consistent with the reported research.³⁵ Based on the above-mentioned results and reference, the possible assembly structure of the coordination polymer is proposed as shown in Fig. 1d.

All the nano aggregates displayed positive potential (9.3-11.2 mV)*via* zeta potential determination since Ag(ı) was distributed on the fiber surface (Table S2, ESI†). Notably, the increase of Ag(ı)/*trans*-D ratio (from 1:1 to 2:1) triggered the acceleration of gelation (Table S2, ESI†), while no gelation occurred at the ratio less than 1:1. This implied that the excessive Ag(ı) was beneficial to the nucleation and the fiber growth in the gelation process. From the TEM observation (Fig. S8, ESI†), with the increase of Ag(ı)/*trans*-D ratio, the gel fiber became thinner and the amount of gel fiber increased due to the increase of the nucleation concentration, which promoted the network density and enhanced the stability of the gel. To allow direct comparison, an Ag(ı)/*trans*-D ratio of 3:2 was used throughout the experiment.

The solvent also had great influence on the gelation process. In Table 1, several kinds of solvents are listed as candidates as they could dissolve in both AgNO₃ and ligand, but the *trans*-AgD gel could only form in some polar solvents such as DMF and DMAc. The gels could be obtained at very low concentrations with CGCs as low as 0.33 wt% in DMF and 0.45 wt% in DMAc, elevating *trans*-AgD to the category of supergelator.³⁶ The organogel was stable for months at room temperature,

whereas it featured obvious thermo-response with increasing temperature. The process of heating and cooling could trigger the reversible transition of the solution and gel states because of the inherent property of noncovalent bonds, where the temperature of gel–sol transition ($T_{\rm gel}$) was recorded during the heating process. $T_{\rm gel}$ in DMAc (76 °C) was lower than that in DMF because the coordination polymer had better solubility in DMAc (Table 1).

The kinetic growth of the fibers was characterized by DLS measurements at a concentration below CGC (0.2 wt%). The mean particle size increased up to 490 nm within 8 min along with a widened size distribution (Fig. 2). Taking into account its one-dimensional shape, the fiber length could be much longer. The single peak series in Fig. 2a suggests almost no secondary nucleation, inferring that the separation of nucleation and growth might facilitate a relatively uniform assembly of nano aggregates to nanofibers. With increasing time, the suspension became opaque and viscous as the fibers thickened and overlapped with each other (Fig. 2b). If a concentration above CGC was applied, the assembly process resulted in a gel.

3.2 Driving forces of gelation

The prominent gelation behavior of *trans*-AgD encouraged us to investigate the driving forces, and ¹H NMR, UV-vis spectroscopy, FT-IR, and powder X-ray diffraction (PXRD) were utilized in the characterization process. As shown in Fig. 3a, after the addition of Ag(1), the ¹H NMR signal of the pyridyl hydrogen (H_d, H_e, H_f, H_g) shifted downfield, while the peaks of the phenyl hydrogen (H_a, H_b, H_c) remained unchanged, proving the coordination of Ag(1) and the formation of *trans*-AgD. Comparing the infrared spectra of the *trans*-AgD xerogel with those of the ligand *trans*-D (Fig. 3b), the additional peak at 1662 cm⁻¹ was assigned to the stretching vibration of the coordinated pyridyl ring, while the peak at 1383 cm⁻¹ corresponded with the absorption of NO₃⁻, also the vibration peak of the pyridyl ring red-shifted from 1011 to 1027 cm⁻¹, reflecting the coordination of pyridine.

Besides coordination, the π - π interaction also played a critical role in gel assembly. Fig. 3c shows the UV-vis absorption spectra of *trans*-AgD in gel and sol states. A maximum absorbance peak at 325 nm was revealed in the DMAc solution, corresponding to the π - π * transition of free azopyridine



Fig. 2 Dynamic measurements: (a) particle size distribution weighted by number in solution over time; (b) the plot of mean particle size and transmittance against time (0.2 wt% solution concentration and 3:2 molar ratio).



chromophores,³⁷ whereas a hypsochromic shift of 27 nm was found in the gel state, demonstrating the formation of H aggregates by π - π stacking interaction.³⁸ Meanwhile, the PXRD pattern of *trans*-AgD exhibited a broad peak around $2\theta = 24.7^{\circ}$ (d = 0.36 nm), implying the loose π - π stacking in the xerogel (Fig. S9, ESI†). All these results proved that both the π - π interaction and the coordination were the key driving forces of gelation.

3.3 Mechanical response and self-healing property

Thanks to their dynamic cross-linking point, many gels were sensitive to mechanical stimuli and were able to "heal" themselves by the reconstruction of their 3D networks after mechanical destruction, which enables the gels to resist external damage.^{7,12,34} In our work, it was found that the trans-AgD gel changed into a turbid sol by vigorous shaking. After several minutes of resting, the gel could be regenerated, and no fluid flowed down during the vial inversion test (Fig. 6a). The mechano-responsive behavior of the gel was characterized in detail by the rheological measurements of the gel (0.8 wt% in DMF). As shown in Fig. 4a, the gel displayed a soft and elastic state under low strain (0.1%), as the storage modulus (G')was larger than the loss modulus (G'') in the frequency range of 1-100 Hz. As the oscillation strain was higher than 10%, the gel underwent a gel-fluid transition (G' < G''), showing a typical thixotropic behavior under mechanical shearing strain (Fig. 4b). Dynamic step strain testing was used to characterize the recovery property of the gel. As can be seen from Fig. 4c, when high strain was applied (90%), the gel was thoroughly disrupted as indicated by the lower values of G' than G''. Once low strain (0.1%) was reapplied, the elasticity (G' > G'') recovered in a few seconds. This recovery

behavior can be repeated in several cycles, demonstrating that the network of the gel was self-healable and can reversibly recover after the removal of mechanical stimuli. Furthermore, as the temperature raised above 90 °C, the *G*′ and *G*″ of the gel in DMF declined rapidly due to the destruction of the network, and this result was accorded with the T_{gel} measured in DMF, as shown in Table 1 (Fig. S10, ESI†).

3.4 Light response

The azo groups in trans-D were incorporated into the main chain of the coordination polymer through coordination, to give an example of azopyridine CPG with a unique light response. Under UV irradiation, the photoisomerization of the azopyridine of trans-D in the DMAc solution occurred as evidenced through the spectral change (Fig. 5a and b) and ¹H NMR chemical shift (Fig. S11, ESI[†]). By prolonging the irradiation time, the absorption intensity at 325 nm (π - π * transition) rapidly decreased, and the intensity of the peak at 435 nm concomitantly increased (n– π^* transition). According to these results, we speculated that the ligand transformed from the trans-isomer to the cis-isomer (denoted as cis-D) with an equilibrium time of 80 s (Fig. 5a). From the ¹H NMR analysis, the signal of the hydrogen on the ligand shifted to a higher field due to the isomerization, and 84% of the azopyridine turned into cis-isomer based on the integral calculation of ¹H NMR (Fig. S11, ESI[†]). Upon subsequent visible light irradiation, the time-dependent spectra of UV-vis (Fig. 5b) and ¹H NMR (Fig. S11, ESI[†]) showed an opposite tendency, since cis-D changed back to trans-D; nevertheless, it takes a longer time to reach the photoreaction equilibrium (240 s).

– G'

10

100

- G"



Fig. 4 Storage modulus G' and loss modulus G" values from the rheological experiments of (a) frequency sweep (strain = 0.1%) and (b) strain sweep (frequency = 1 Hz). (c) During the step strain measurement, the alternate step strain switched from low strain (0.1%) to high strain (90%) at a fixed frequency (1 Hz).



Fig. 5 UV-vis spectra at different irradiation times in DMAc. (a) The trans-D solution under UV light (365 nm); (b) the cis-D solution under visible light; (c) the trans-AgD gel (0.8 wt% in DMAc) dissolved in solution after UV light irradiation (365 nm); and (d) the cis-AgD solution under visible light.

When adding Ag(I) to the DMAc solution of *cis*-D, the *cis*-AgD coordination polymer was obtained, and the coordination between Ag(1) and cis-D was confirmed by the lower-field chemical shift of the pyridine hydrogen in ¹H NMR (Fig. S12, ESI[†]). On the contrary to the trans-AgD gel, cis-AgD was found to be soluble in DMF or DMAc because the cis conformer of the azo group possessed a larger dipole moment compared to its symmetrical trans conformer, which favored solubility in polar solvents.²² It is worth noting that, the photoisomerization rate of cis-AgD in solution was largely slower than cis-D under the same irradiation and concentration conditions with a remarkably prolonged equilibrium time of 45 min (Fig. 5d), which was also supported by the time-dependent spectra of ¹H NMR (Fig. S12, ESI⁺). This phenomenon coincided with the characteristics of the main chain azo supramolecular polymers,³⁹ as the macromolecular steric hindrance retarded the configurational transformation of the main chain azo group, thus the isomerization of the azopyridine group on the coordination polymer was "locked" by the coordination of Ag(1). Furthermore, from Fig. 5c, the dynamic isomerization in the trans-AgD gel was so significantly hindered that the system was still far from the photostationary state after 40 min of UV irradiation. Besides the macromolecular effect, we assumed that the trans-cis transformation of the azopyridine group was further hampered in the nano assemblies due to the close packing of the coordination polymer, resulting in the decrease of the isomerization rate.

As a consequence of the trans-to-cis isomerization of the coordination polymer, upon continuous UV irradiation, the gel gradually changed to a solution from its surface (Movie S2, ESI[†]). However, the corresponding solution was unavailable to recover its gel state under visible light stimuli (Fig. 6a). Different from the rapid gelation process in several seconds (Table S2, ESI⁺), the cis-to-trans isomerization of cis-AgD proceeded at a very slow rate to give great amounts of crystal nuclei to grow nanofibers, causing the larger aggregation of the coordination polymer as particles in microscale (Fig. S13, ESI⁺). Taking advantage of this feature, the trans-AgD gel could be designed as a smart UV-patterning material with visible light stability (Fig. 6b). For example, a layer of gel (0.8 wt%) was covered with a patterned mask, and then irradiated with UV light for 3 min. After removing the mask, the gel displayed the corresponding visual patterns. These patterns were stable under visible light for 2 days as the solution in the pattern could not convert back to gel. It is well known that heating can prompt the cis-to-trans isomerization of the azo motif.^{40,41} By heating up to T_{gel} and then cooling, the gel was regenerated and the patterns were erased. This process was repeatable, imparting the CPG with the UV-heating rewritable function.

3.5 Chemical response

The CPGs contain great amounts of metal ions. These ions can be used as reactive sites and render potential applications to the gels, such as catalysts,⁴² sensors,⁴³ absorbents⁴⁴ and so forth. The as-prepared *trans*-AgD gel was also chemically responsive, as the Ag(I)-azopyridine coordination bonds were chemically dynamic, and can be destroyed by adding other



Fig. 6 Behaviors of the *trans*-AgD organogel. (a) Photographs of the gel in response to heating, shaking, UV/vis light, and chemicals. (b) Patterned images generated by a repeatable write (UV light)-erase (heating-cooling) process.

competing ligands, causing the disassembly of the nanofibers and the destruction of the gel. As demonstrated in Fig. 6, after introducing a small amount of ammonia (0.8 mg), the gel (0.8 wt% in DMF) quickly changed into a clear solution in several seconds, since ammonia could compete with ligand *trans*-D by coordinating with Ag(1) to form the Ag(NH₃)₂⁺ complex. The resulting solution was still reactive as a further addition of Ag(1) could regenerate the gel. Another example of the chemical response was derived from the reaction between Ag^+ and H_2S . When engaging hydrogen sulfide gas, the gel turned into a dark suspension, and the black particles were ascribed to the precipitation of Ag₂S. This process was irreversible since the pyridyl ligands were consumed by the reaction with H_2S , thus the addition of Ag(1) in dark suspension did not result in a gel (Fig. 6a). The chemical responsive behaviors described above provided intuitive examples to demonstrate the multi-sensitivity of the trans-AgD gel.

3.6 Coordination polymer colloid

Besides organogel, the multi-responsive behavior of the coordination polymer was also discovered in its dispersing colloidal state. Different from the one-dimensional packing of *trans*-AgD, the assembly of *cis*-AgD favored the amorphous mode in phase



Fig. 7 Responsiveness of the *cis*-AgD colloid. (a) Photographs of the preparation and the stimuli-response of the *cis*-AgD colloid. (b) SEM image of *cis*-AgD before visible light irradiation. (c) SEM image of the precipitate after 3 days of visible light irradiation. (d) Illustration of the assembly structural transformation of the coordination polymer.

separation due to the distorted stacking of the cis isomer,40 giving dispersing particles in aqueous dispersion. When the solution of cis-AgD was poured into deionized water, a yellow colloidal dispersion was produced upon slight shaking (Fig. 7a and Movie S3, ESI[†]). The cis-AgD colloid consisted of spherical nanoparticles with a diameter of 80-160 nm (Fig. 7b), and its selfemulsification might come from the Ag(1) ions distributed on the particle surface as inferred by the positive zeta potential (+21.0 mV). It is worth noting that both the visible light irradiation and heating (>90 $^{\circ}$ C) triggered the irreversible coalescence and precipitation (Fig. 7a). During this process, the coordination polymer gradually transformed from nanoparticles to fiber-like aggregates (Fig. 7c), implying that the demulsification was caused by the change of the assembly structure of the coordination polymer. The morphological transformation should be attributed to the cis-to-trans isomerization expedited under visible light and heating. The mechanism of the light/heating response is illustrated in Fig. 7d. It was a prominent example of the controlled demulsification based on the morphological transformation, where the isomerization of cis-AgD was greatly slower than ligand cis-D because of the macromolecular "lock on" effect.

Upon light irradiation by an LED lamp (0.1 W m⁻²), the dispersing colloid of *cis*-AgD slowly turned into precipitation in 4 days at room temperature. It can be seen from Fig. 8 that the



Fig. 8 Precipitate percentages in the *cis*-AgD colloidal dispersion for different times with or without light exposure.

amount of precipitate increased much faster under light exposure than in dark storage. After 80 h of irradiation, most of the coordination polymers precipitated, while the colloidal dispersion without light exposure remained relatively stable with a very small amount of precipitation.

4 Conclusion

In summary, the coordination polymers bearing azo groups on the main chain were obtained through Ag(I)-pyridine coordination. As a supergelator, the coordination polymer trans-AgD could form a stable organogel constituted by the network of nanofibers, where both coordination and π - π stacking interaction played important roles in self-assembly. The self-healing behavior of the gel was characterized, and the gel-sol transition of the organogel in response to multiple external triggers including temperature, mechanical shearing, light, and chemicals was systematically investigated. Compared with the ligand, the photoisomerization of the azo groups in the coordination polymers was remarkably hindered due to the macromolecular steric hindrance. Besides, different from the one-dimensional packing of trans-AgD, in the self-assembly of the cis coordination polymer, cis-AgD isotropically assembled into colloid nanoparticles. Upon visible light irradiation or heating, the nano assembly of cis-AgD transformed from particles to fibrous aggregates due to the cis-totrans isomerization, causing precipitation and demulsification. This work provides a new strategy to design a multi-responsive organogel and colloid with potential applications in responsive materials.

Conflicts of interest

There are no conflicts of interest to declare.

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