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RESEARCH ARTICLE

Zn^{2+} cation triggers self-assembly of cyclen into a stable metallogel

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A novel type of ligands contained 1,4,7,10-tetrazacyclododecane and functionalized by two azobenzene moieties grafted with two alkyl chains was designed and synthesized. The ligands with long alkyl chains can form metallogels in the presence of Zn^{2+} cations. The formation of metallogel was followed by NMR and electronic spectral detection. The morphology of the xerogels is varied with the equivalent of Zn^{2+} cations and the concentration of the gel. Spectral and structural analysis indicated that the driving forces of the gel formation were attributed to intermolecular hydrophobic interactions between alkyl chains and π-π interaction between azobenzenes.

Keywords cyclen, metallogel, self-assembly, azobenzene

1 Introduction

Supramolecular architectures that are formed by artificial self-assembly of small molecules under equilibrium conditions have great potentials for selective guest inclusion and molecular recognition [1–7]. Crown ethers are particular charming in the field of supramolecular architectures because of their simplest but most attractive ligand combining with cation (Na^+, K^+, Cs^+) [8,9]. Such performance results in potential usage as ion-carrier [10,11]. Moreover, macrocyclic polyamines, like1,4,7,10-tetrazacyclododecane (cyclen) derivatives, can be combined with compatible cation-diameter, such as Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Pd^{2+}, into a stable host-guest system [12–17]. It has been proven that Zn^{2+} complexes of macrocyclic tetraamine derivatives, such as Zn^{2+}-cyclen, are good models for Zn^{2+} enzymes. They form 1∶1 complexes with anions, including phosphate monoesters, imidates (e.g., thymine), and thiolates in aqueous solution at neutral pH [18–27]. Kimura et al. have done a lot of work in cyclen compounds in the field of biochemistry [28–33]. Zn^{2+}-cyclen derivatives have been found to be useful in elucidating and understanding the intrinsic properties of substrate or inhibitor recognition by zinc ions at the active centers of carbonic anhydrase and carboxypeptidase [28–33]. However, all of these works were carried out solely in a solution; the aggregation properties of those complexes rarely attracted attention.

Organogels are of increasing interest in recent years because of their numerous potential applications, such as hardeners of solvents, adaptive materials, drug delivery systems, and sensors [34–47]. Most of the gels are assembled by means of hydrogen bond, hydrophobic interaction, π-π stacking, and Van der Waals forces [48–52]. So far there have been some researches in the field of metallogel [53–58]. For instance, organometal gels have been reported by MacLachlan's group that zinc salphen complexes can form stable gels in certain solvents [59]. Also, Xu's group investigated that calix[4]-arene can gelate DMSO in the presence of Pd^{2+} [60,61]. A metallogel of palladium pincer complex has been reported for catalytic application [62]. In those metallogels, the center metal ions are generally posited at a planer environment with four coordination numbers in most cases, which may be in favor of the formation of the gel aggregate. To our knowledge, there is few investigation of organogels containing cyclen complexes in which the metal cations are not in a planar position. Our strategy makes use of cyclen, which is connected with 2,4,6-trichloro-1,3,5-triazine featuring azobenzene with flexible trails, to produce different supramolecular specie (Scheme 1). It has been reported that azobenzene chromophore has an excellent response to external stimulation because of the *N* = N *trans* and *cis* interconvertion when illuminated by ultraviolet radiation and undo [63–71]. Here, we report that the novel cyclen derivatives containing azobenzene can form metallogel by the induction of Zn^{2+}. The reaction shows color change in response to UV light.

2 Experiment

2.1 General

All starting materials are acquired from commercial suppliers. 4-aminophenol, acetic anhydride, and 1,4,7,10-tetraazacyclododecane were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai); di-tert-butyl dicarbonate were obtained from Aldrich. Other solvents were provided by Shanghai No.1 chemical reagent. ^1H NMR and ^{13}C NMR spectra were recorded on a Mercuryplus NMR spectrometer at 400 and 100 MHz, respectively. Proton chemical shifts are reported in

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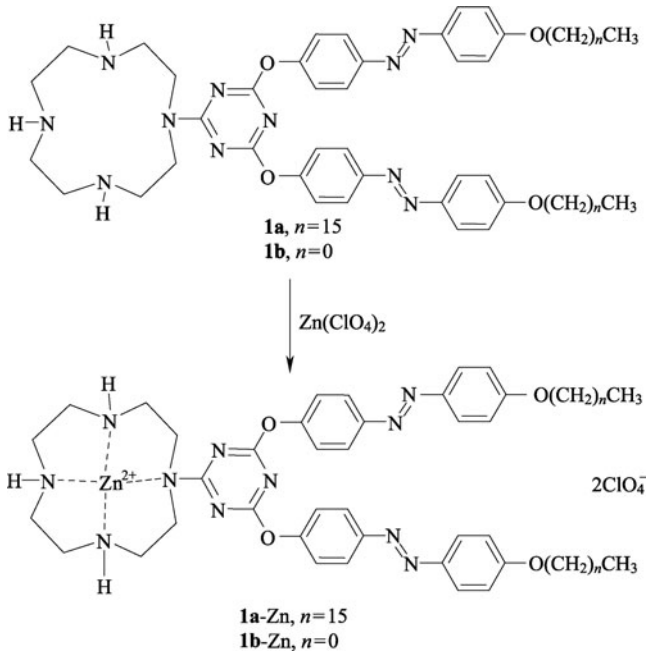


Scheme 1 Chemical structure of the ligands and complexes.

parts per million (ppm) downfield from tetramethylsilane (TMS). High-resolution mass spectra were recorded using a 4700 peoteomic analyzer (Applied biosystems, USA). Melting points were determined on a hot-plate melting point apparatus XT4-100A without being corrected.

2.2 The synthesis of the ligands

Compound **2** was synthesized according to Ref. [72].

2a Mp: 109°C–110°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.85 (t, 4H), 7.00–6.94 (q, 4H), 4.03 (t, 2H), 1.81 (m, 2H), 1.33–1.26 (m. 26H), 0.88(t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 158.0, 124.9, 124.8, 124.6, 116.0, 116.0, 115.0, 68.6, 31.1, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 14.2.

2b Mp: 134°C–136°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.83 (q, 4H), 7.00–6.99 (d, 2H), 6.95–6.92 (d, 2H), 3.89 (s, 3H), 1.81 (m, 2H), 1.33–1.26 (m. 26H), 0.88 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 157.9, 147.1, 147.0, 124.6, 124.4, 115.8, 114.2, 55.6.

Compound **3** was synthesis based on Ref. [73]. Mp: 178°C–180°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (bs, 4 H), 3.49–3.42 (m, 12 H), 1.47 (s, 9 H,), 1.43 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 165.0, 157.8, 156.4, 80.8, 80.6, 51.8, 50.7, 50.0, 49.2, 28.7, 28.6.

2.3 Synthesis of **4a**–**4b**

3 was slowly added (0.5 g, 0.81 mmol) in 15 mL acetone into a mixed solution of **2b** (0.55 g, 2.42 mmol) and anhydrous K_2CO_3 (3.3 g, 24.17 mmol) in acetone (50 mL) at room temperature. The reaction mixture was stirred for 48 h under nitrogen atmosphere. Then the solvent was removed under reduced pressure, and the residue was subjected to column chromatography (PE/EA = 4/1, *v*/*v*) on silica gel to yield **4b** as an orange powder. Yield 43%. Mp: 95°C–98°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.89 (q, 8H), 7.29–7.27 (d, 4H), 7.02–6.99 (d, 4H), 3.90 (s, 6H), 3.55 (bs, 4H), 3.38–3.35 (bs, 12H), 1.43 (s, 9H), 1.35 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 171.9, 162.1, 153.7, 150.2, 147.0, 124.8, 123.7, 122.3, 114.2, 80.4, 80.0, 69.5, 55.6, 53.9, 50.2, 49.8, 31.8, 29.3, 28.5, 28.4.

Ligand **4a** was obtained through a same process as **4b** by reaction between **2a** and **3.** Yield 51%. Mp: 63°C–65°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.86 (q, 8H), 7.29–7.27 (d, 4H), 7.00–6.97 (d, 4H), 4.04 (t, 4H), 3.56 (bs, 4H), 3.39–3.35 (bs, 12H), 1.84–1.79 (m, 4H), 1.43 (s, 9H), 1.36 (s, 18H), 1.31–1.27 (m, 52H), 0.88 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 162.0, 156.3, 153.9, 150.4, 147.1, 124.6, 123.8, 122.4, 116.0, 115.0, 80.5, 80.2, 68.6, 50.6, 50.3, 49.9, 32.1, 29.9, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 28.7, 28.6, 26.2, 22.9, 14.2.

2.4 General synthesis of **1a**–**1b**

Acetyl chloride (5 mL) was carefully added into methanol (20 mL) under stirring in ice water bath. The mixture was withdrew from the bath after continuous stirring at 0°C for 3 min. Then compound **4a**–**b** dissolved in THF (as little as possible) was slowly added into it. The reaction mixture was stirred at room temperature overnight and then neutralized with aqueous $LiOH \cdot H_2O$ to pH 8–9. The precipitated product was filtrated and dried in vacuum to yield the raw production, followed by chromatograph on silica gel (chloroform/methanol = 50/1, *v*/*v*) to yield **1** as an orange solid.

1a: Mp: 153°C–157°C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.90–7.86 (q, 8H), 7.28–7.26 (d, 4H), 7.00–6.98 (d, 4H), 4.03 (t, 4H), 3.81 (s, 4H), 2.98–2.94 (d, 8H), 2.71 (s, 4H), 2.00 (s, 2H), 1.82 (t, 6H), 1.41–1.26 (m, 50H), 0.87 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.0, 167.6, 161.8, 153.3, 150.4, 146.7, 124.8, 123.5, 122.3, 114.7, 68.4, 53.7, 51.5, 50.5, 47.8, 47.6, 42.3, 31.9, 29.7, 29.6, 29.4, 29.2, 26.0, 22.7, 14.1, HR-MS calcd for $C_{67}H_{102}N_{11}O_4$ $[M + H]^+$: 1124.8116, found: 1124.8042.

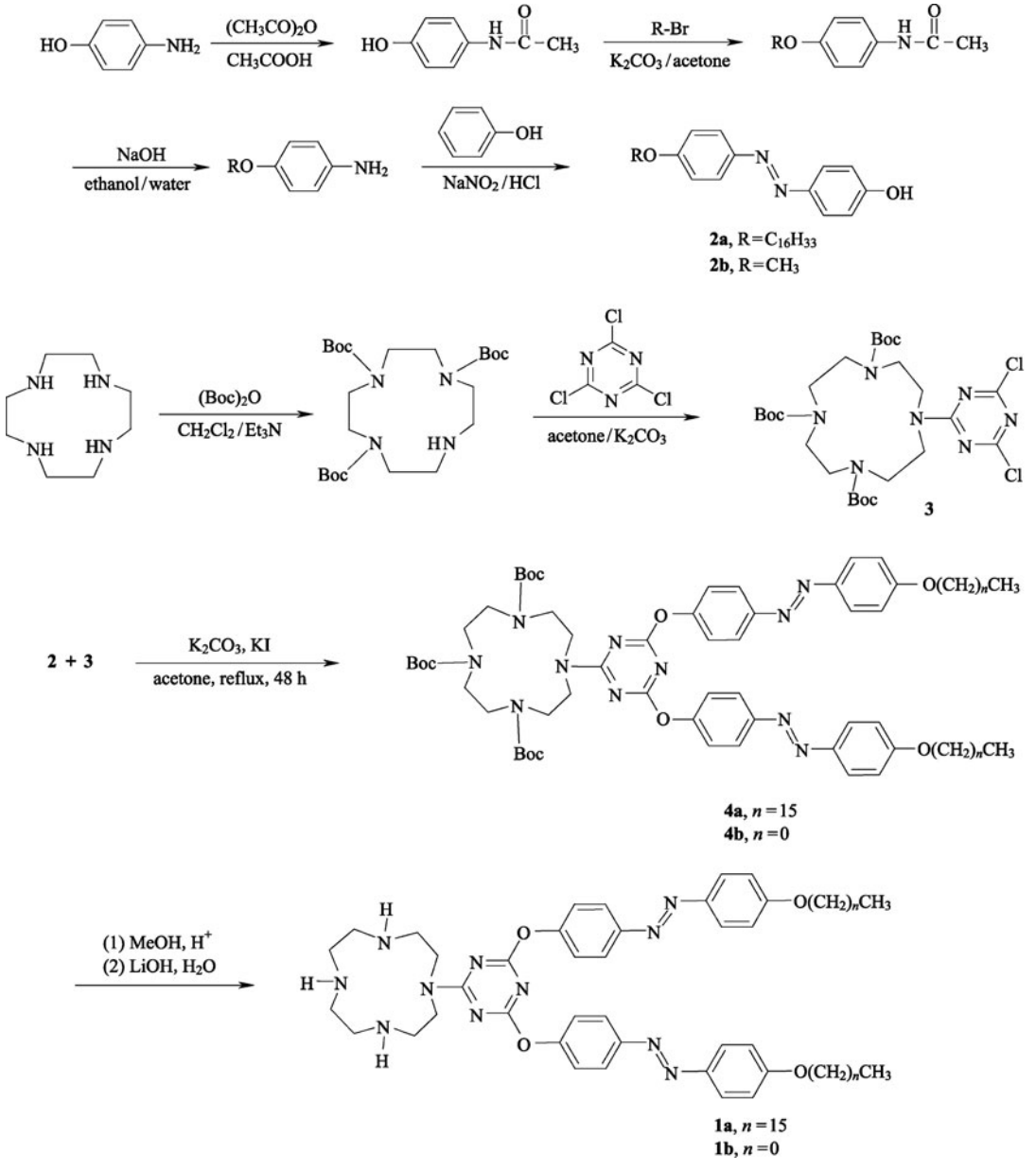
1b: Mp: 190°C–192°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.88 (q, 8H), 7.28–7.26 (d, 4H), 7.02–6.99 (d, 4H), 3.90 (s, 6H), 3.00–2.99 (m, 8H), 2.74 (w, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 166.8, 162.3, 153.4, 150.5, 146.9, 124.9, 123.7, 122.3, 114.3, 55.6. HR-MS calcd for $C_{37}H_{42}N_{11}O_4[M + H]^+$: 704.3421, found: 703.9861.

2.5 Gelation test of organic fluids

The gelators and the solvents were put in a septum-capped test tube and were heated until the solid was dissolved. The sample vial was cooled to 25°C and left for 2 h under ambient conditions. Qualitatively, gelation was considered successful if no sample flow was observed upon inverting the container at room temperature.

2.6 Techniques

^{1}H NMR titration spectra were acquired on a DMX 500 NMR spectrometer at 500 MHz (Bruker). UV-Vis spectra were recorded on a UV-Vis 2550 spectroscope (Shimadzu). Scanning electron microscope (SEM) images of the xerogels were obtained using an SSX-550 (Shimadzu) with an accelerating voltage of 15 kV. Samples were prepared by spinning the gels on glass slices and coating with Au. Microspectral images were obtained using an OLYMPUS IX81 confocal laser scanning microscope equipped with a 60X oil immersion objective lens. X-ray powder diffraction (XRD) spectra were carried out by a D/max-γB X-ray scattering instrument (Rigaku Industrial Corporation) using Cu Kα radiation source (λ: 0.1542 nm) with the power of 40 kV and 60 mA at room temperature.



Scheme 2 Synthesis process of the ligands.

3 Results and discussion

3.1 Gelation studies

The ligands **1a** and **1b** were synthesized according to Scheme 2. The target molecules were characterized by ^{1}H, ^{13}C NMR, and high-resolution mass spectroscopy. In particular, **1b** is the consult compound that could provide us the model on how Zn^{2+} react with the cyclen. Ligands **1a** and **1b** has nice solubility in chloroform but has poor solubility in other common solvents at room temperature. However, **1a** of low concentration ($< 10\ mg \cdot mL^{-1}$) generates viscous solution in DMSO, acetone, and toluene after a heating-cooling process, but yields a deposit with higher concentration. This means that even though **1a** incline to gelation in those solvent, the balance of the driving force for aggregation is not in an optimized state. It is interesting that **1a** can form a stable gel in the presence of Zn^{2+} ion in DMSO. In fact, Zn-**1a** has a better solubility in DMSO than **1a**. As an example, a clear solution can not be observed even heating 10 mg of **1a** in 0.5 mL DMSO to 150°C. However, a clear yellow solution was obtained when 1.0 equiv of $Zn(ClO_4)_2$ was added into this **1a** solution at about 100°C. When clear solution was slowly cooled down to room temperature, a stable gel was obtained (Figure 1(a)). The gel-sol transition temperature (T_g) of Zn-**1a** has been measured at different concentrations (Figure 1(b)). It is clear that the higher concentrated the gel is, the higher the T_g is. T_g values of 20 and $80\ mg \cdot mL^{-1}$ gel are 14.5°C and 48°C, respectively.

The efficiency that Zn-**1a** gelates DMSO may be based on the combination of the cyclen ring to metal ion. Such combination allows aggregation of the complex by inter-molecular π stacking, possibly enhanced by van der Waals interactions between the alkyl chains. Zn^{2+}-titration ^{1}H NMR spectral studies of Zn-**1a** at 60°C were performed to probe the role of cyclen ring in the gelation process (Figure 2). By adding Zn^{2+} from 0.25 equiv to 1.0 equiv, it is clear that the

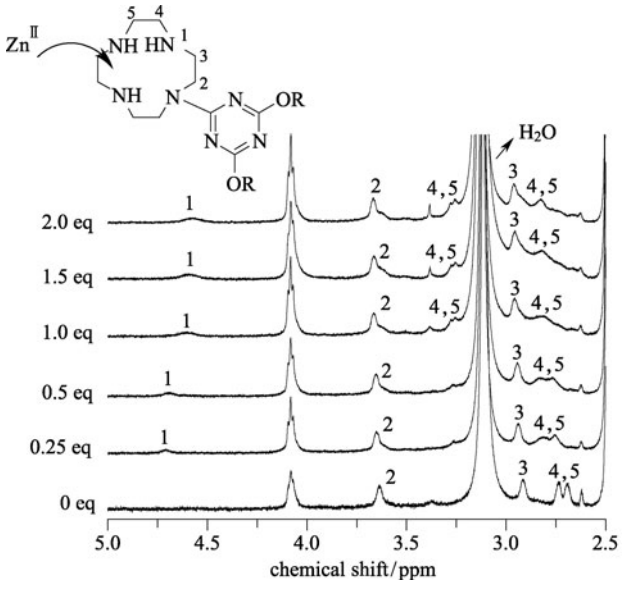


Figure 2 Partial ^{1}H NMR (500 MHz) spectroscopy of **1a** under Zn^{2+}-titration in d-^{6}DMSO at 60°C ([**1a**]: 12 $mg \cdot mL^{-1}$, Zn^{2+} from 0 equiv to 2.0 equiv).

ring of 1,4,7,10-tetrazacyclododecane is the reactive spot, which has strong interaction with Zn^{2+}. For example, the intensity of ^{1}H NMR signal of **1a** became stronger as the Zn^{2+} was added; it would indicate the enhanced solubility of the complex. Meanwhile, a notable shift of amino proton H1 at 4.69 ppm to high field (4.57 ppm) was observed. At the same time, the chemical shift of H2 has shifted downfield notably from 3.63 to 3.66 ppm. The chemical shifts of H3, H4, and H5 protons are also moved downfield likewise. The NMR data indicated that the isolated-pair electron density of nitrogen atom must decline as interacting with Zn^{2+} and therefore increase the shield effect on amino proton (H1) and cause the chemical shift moving to high field. In contrast, the protons of methylene (H2–H4) in the cyclen shifted downfield. The chemical shift had little change after the Zn^{2+} reached to 1.0

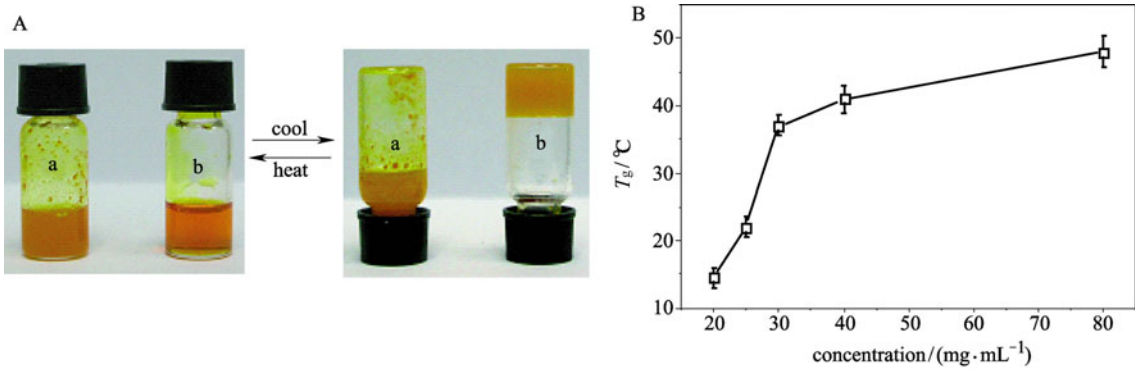


Figure 1 (A) Photographs of **1a** (10 mg) in DMSO (0.5 mL) at room temperature, **a** is in the absence of Zn^{2+}, **b** is in the presence of Zn $(ClO_4)_2 \cdot 6H_2O$ (1.0 equiv). (B) Concentrations variation T_g in gels of (1.0) Zn-**1a**.

equiv, which means that the cyclen ring reacted with Zn^{2+} as molar ratio 1∶1.

To characterize the function of the azobenzene chromophore, the UV-Vis spectra were investigated. Two films of **1a** with and without Zn^{2+} were made about 16.5 μm thick. Then the absorption spectra of the two films were measured before and after irradiation of light (365 nm) at the same circumstance. From the spectra, we can find that **1a** has a notable absorption decrease at 370 nm (π-π^*) and an absorption increase at about 450 nm (n-π^*) under irradiation, indicating a photo isomerization of azobenzene group (Figure 3(a)). However, the π-π^* absorption of Zn-**1a** belonging to the *trans* isomer has a blue-shift of 60 nm by comparison with that of **1a** even though the n-π^* absorption for the *cis* isomer posited at the same wavelength (450 nm) (Figure 3(b)). It indicates that there is strong aggregate between *trans* azobenzene groups in the gel state. Further study was done related to short-chain compound **1b** to give more evidence for aggregation. From the absorption spectra of **1b** and Zn-**1b** in DMSO solution (Figure 3(c) and 3(d)), we can see that the formation of the complex does not cause distinct change in the absorption spectra. Thus, the drastic shift of the absorption in Zn-**1a** gel should be deduced by the gelation. We also noted that the UV irradiation did not cause the gel to sol transformation as mentioned in some previous report [64,65], even though the color of the gel changed from brown to nut-brown (Figure 3(b), inset). This may be due to incomplete photo isomerization in the gel state.

3.2 The morphology of the gels

To gain a better insight into the molecular organization in the gel specimens, the morphology of the xerogels of Zn-**1a** in DMSO were analyzed by SEM. Honeycomb-like three-dimensional vesicles of about 4–6 μm in diameter were observed in the deposition of the ligand without Zn^{2+}

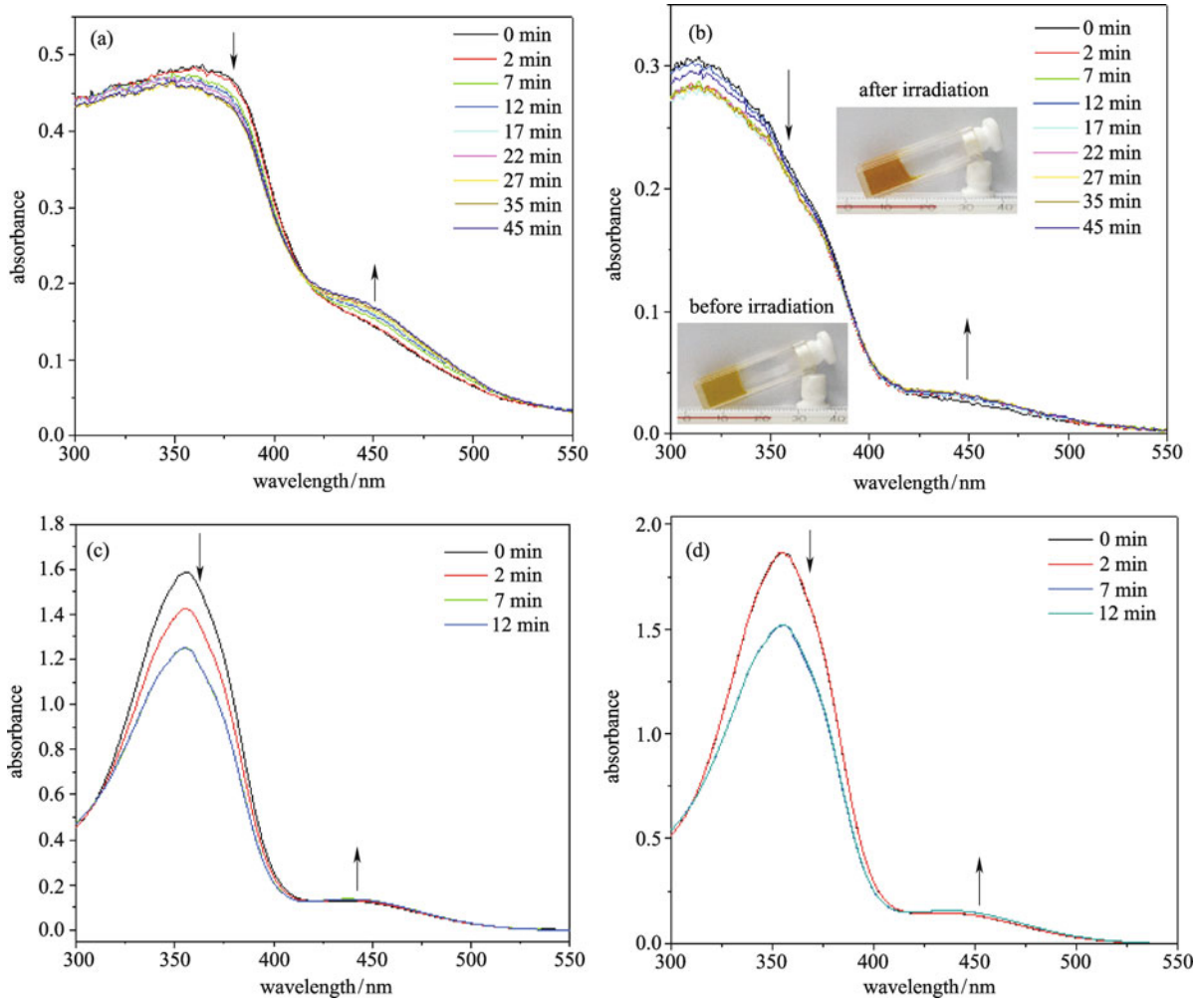


Figure 3 Absorption spectra of the thin films of (a) **1a** and (b) Zn-**1a** (16.5 μm); and the solution of (c) **1b** and (d) Zn-**1b** ($c = 1 \times 10^{-3}$ mg·mL^{-1}, $l = 0.1$ cm) in DMSO upon 365 nm irradiation.

(Figure 4(a)), with regular intertexture holes of about 0.2–0.5 μm in size distributed on the surface of the spheres. After the addition of Zn^{2+}, the honeycomb structure was destroyed to flakes when the ratio of Zn^{2+} was up to 0.4 equiv (Figure 4(b), 4(c)). With further addition of Zn^{2+}, fibrous intertexture morphology was observed in Zn-**1a** complex with a ratio of 1∶1 (Figure 4(d)–(f)). The morphology change of the complex with concentration was further studied by optical micro image, as shown in Figure 5. In a concentration lower than the critical gelation concentration, spherical morphology was observed, which may represent the initial stage of the gelation. With the increase of concentration, we observed the morphology evolution from flakes to fibers.

3.3 Structural study of the gel

The structure and dimensions of the gel network of Zn-**1a** and the powder of **1a** were studied by X-ray diffraction (Figure 6). From the diffraction pattern of **1a**, *d* values of 9.08 and 4.49 nm (*d*/1: *d*/2) suggests a lamellar structure [74,75]. However, only one clear peak at 7.66 nm was observed in the small angle range for the xerogel of Zn-**1a**. This diffraction length is just twice of the extended molecular length from the center Zn ion to the long alkyl chain in CPK model (Figure 6 (b)). This data can not give the definite structure of the gel but can provide the relationship between molecules in the aggregation network with the assistance of spectral analysis. Before being coordinated to Zn^{2+} ion, the ligands aggregated to two dimensional structures by hydrophobic interaction between alkyl chains and hydrogen bonds between triazine and amines. However, the hydrogen bond was weakened when Zn^{2+} was coordinated to the ligand. The hydrophobic interaction between the long alkyl chains and π-π interaction between azobenzene groups became the main driving force for the aggregation. The H type aggregation between azobenzene groups was evidenced by

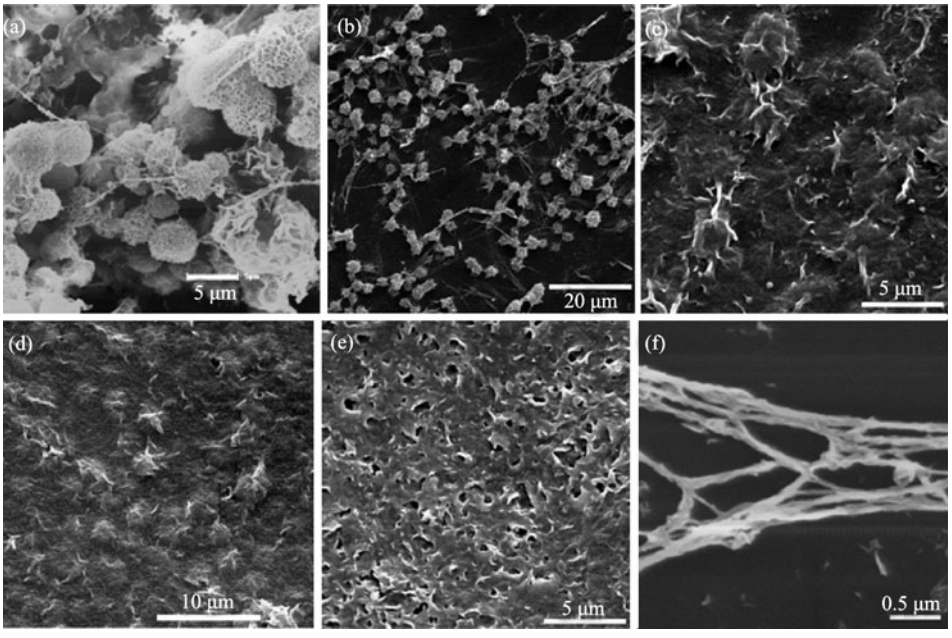


Figure 4 SEM images of Zn(*m*)-**1a:** (a) *m* = 0 equiv, (b) *m* = 0.2 equiv, (c) *m* = 0.4 equiv, (d) *m* = 0.6 equiv, (e) *m* = 0.8 equiv and (f) *m* = 1.0 equiv from DMSO (40 mg·mL^{-1}).

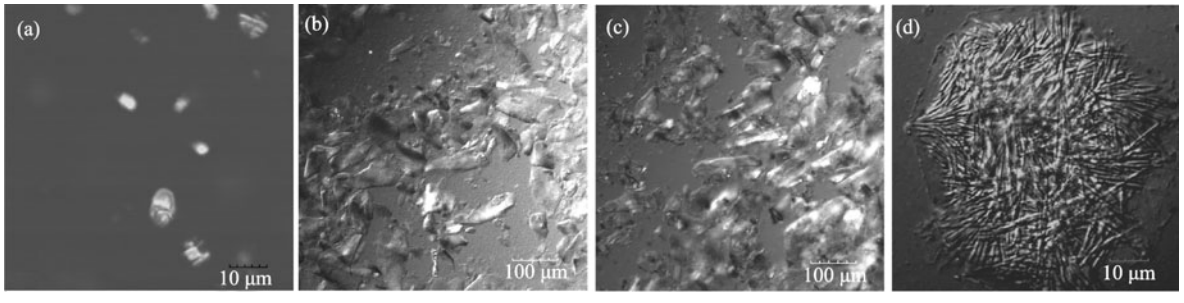


Figure 5 Micro image of the gels (Zn-**1a**) with concentration of (a) 10, (b) 20, (c) 40, and (d) 80 mg·mL^{-1}, respectively.

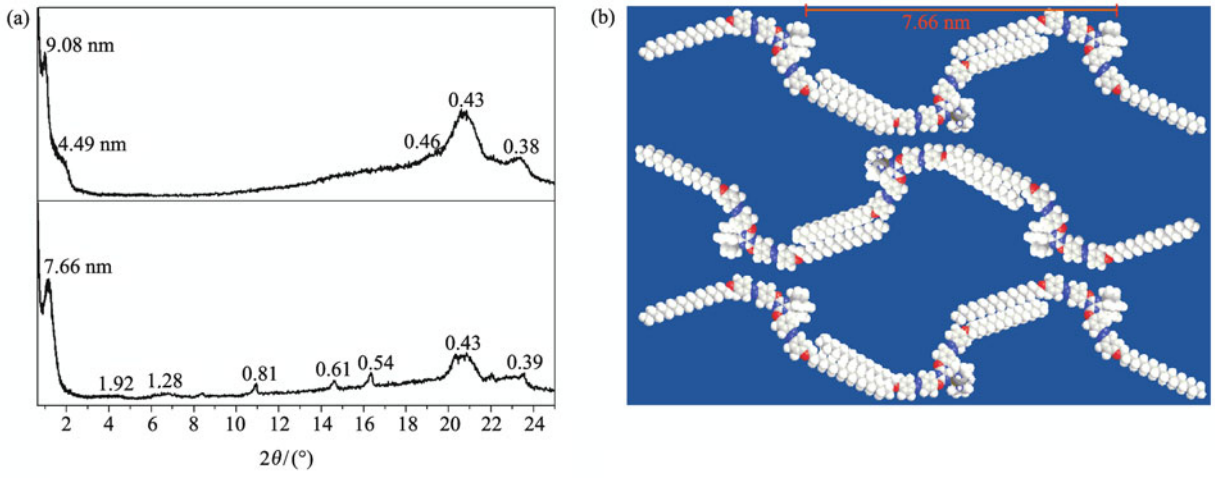


Figure 6 (a) Powder X-ray diffraction spectra of **1a** powder and Zn-**1a** xerogel from DMSO. (b) The perspective aggregation of Zn-**1c** gel in DMSO.

the absorption spectra. Thus the complexes form one-dimensional fiber structure by hydrophobic interaction and π-π interactions with the structure parameter of 7.66 nm, as shown in Figure 6(b).

4 Conclusions

In conclusion, a novel type of ligands containing cyclen ring and two azobenzene groups grafted with two long alkyl chains was designed and synthesized. In the presence of Zn^{2+}, the complex gelates DMSO into a stable metellogel. The morphology of the xerogels is varied with the equivalent of Zn^{2+} cation and the concentration of the gel. Spectral and structural analysis indicates that the driving force of the gel formation is intermolecular hydrophobic interaction between alkyl chains and π-π interaction between azobenzene. This is the first example of low molecular weight metellogel containing nonplanar cyclen ligand. The zinc(II) cyclen complexes are important sensors to nucleobase, phosphorylated amino acids or peptides, and carboxylates. The present system will be useful in designing novel supramolecular complexes and their applications in bioinorganic chemistry and other related scientific fields.

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