Photoreversible dendritic organogel†

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A photoreversible organogel made from dendrons was reported.

Bridging the gap between polymeric and small molecular gelators, dendritic gelators are attracting more and more attention due to their well-defined and readily controllable structures.[1] Like traditional gelators, most of them are thermo-reversible. No photoreversible dendritic gel has been reported so far. Moreover, smart dendritic systems that could respond to more than one kind of external stimuli at the same time are rare.[2] On the other hand, organogelators containing azobenzene moieties are a large family.[3] However, only a few of them could produce photoreversible organogels.[3b] The reason may be that the photoisomerization of azo groups was suppressed in the gel state. Previously, we found that a dendron made of natural amino acids, poly(Gly-Asp) dendron, could gel solvents.[4] Here we present for the first time a photoreversible dendritic organogel by incorporating azobenzene into the focal point of the second-generation poly(Gly-Asp) dendrons (**1**) (Fig. 1a: see the Supporting Information for the

synthesis†), demonstrating that dendrons could be a new candidate for the construction of smart gels.

As illustrated in Fig. 1(b), like many traditional organogels, gels formed by **1** converted into a clear solution upon heating and then returned to the gel state upon subsequent cooling. Moreover, upon irradiation at 365 nm, the gel gradually changed into clear solution at room temperature, and re-formed as gel after the above obtained solution was exposed to ambient light. The time needed for the sol-to-gel and gel-to-sol transitions depends on the concentration of the gelator and the solvent used. The solvents that **1** could gelate at a concentration below 2.5 mg mL^{-1} (0.25 wt%) included ethyl acetate, chloroform, acetone, toluene, acetonitrile, methanol, ethanol, tetrahydrofuran, 1,4-dioxane, and 1,2-dichloroethane. For instance, 1 mg of **1** could gelate 1 mL ethyl acetate (0.1 wt%) in two minutes after being dissolved by heating. Thus, amazingly, one gelator molecule could gelate some 1.3×10^{10} molecules of ethyl acetate. The gels of **1** were stable at room temperature for many months.

Similar to poly (Asp-Gly) dendritic gels,[4] the driving forces for **1** to gelate can be attributed to the hydrogen bonding and aromatic stacking, as evidenced by the results from FTIR, UV-vis and ^{1}H-NMR spectroscopy. For the homogeneous solution of **1**, the IR results displayed the N–H stretching, amide II and I bands at 3447, 1522, and 1644 cm^{-1}, respectively. In the gel state, the hydrogen bonding was revealed with the stretching frequencies of N–H bonds at 3373 and 3294 cm^{-1}, a shoulder in the amide I band at 1662 cm^{-1} to the main peak at 1633 cm^{-1}, and the amide II band shifted to 1538 cm^{-1} (Supporting Information Figure S-1 to S-4†). Compared with the dilute solution, the absorption corresponding to π–π* electronic transitions of the azobenzene chromophores at 338 nm in UV-vis spectrum blue shifted 10 nm in the gel state, indicating that the azobenzene groups packed in H-aggregates.[5] (Supporting Information Figure S-5†) In ^{1}H-NMR spectra (Supporting Information Figure S-6†), the amide upshifted a little and *trans*-azo benzene signals shifted downfield when the gel changed into solution at high temperature, which may be related to destroying of the hydrogen bonding and aromatic stacking.[6]

UV, ^{1}H-NMR and CD measurements confirmed that the reversible *trans/cis* isomerization of the azobenzene chromophores of **1** is responsible for the observed photoreversible gel-to-sol and sol-to-gel transitions. In the UV spectra of **1** from gel-to-sol state (Fig. 2a), UV irradiation at 365 nm resulted in photoisomerization of the azo moieties from the *trans*- to *cis*-isomer, as evidenced by the decrease of 329 nm band (π–π* transition of the azobenzene chromophores) and the increase of 440 nm band (n–π* transition). The sol-to-gel process shows the opposite tendency (Fig. 2b), in consistence with the rule that *cis*-azobenzenes isomerize back to the
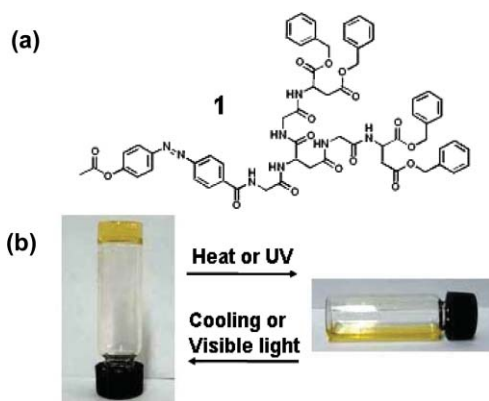

Fig. 1 (a) The structure of focal azobenzene modified second generation poly(Gly-Asp) dendrons. (b) Representative photographic images of the ethyl acetate gel of **1** (0.1 wt%), and the solution of **1** obtained from the gel.

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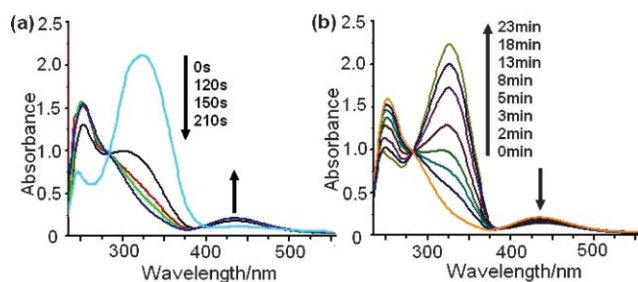
Fig. 2 Changes in the UV-vis absorption spectra of **1** in ethyl acetate (0.1 wt%, 0.5 mm path length): (a) the process from *trans*-rich gel state to *cis*-rich solution induced by irradiating at 365 nm; (b) the subsequent process from *cis*-rich solution to *trans*-rich gel upon exposure to room light.

trans isomers. The same isosbestic point at 287 nm in Fig. 2a and 2b suggests that only two absorbing species, namely *cis*- and *trans*-isomers, of the azobenzene groups exist in the reversible gel-to-sol and sol-to-gel transition. In the ^{1}H-NMR spectra (Supporting Information Figure S-7†), the signals at 7.37–7.13 and 7.89–8.02 ppm are attributed to phenyl protons in *trans*-**1**, and the sharp peak at 2.35 ppm is assigned to the –CH$_3$ protons related to the *trans* azobenzene. In the *cis* form, these signals shifted to 7.74–7.77, 6.97–6.83, and 2.24 ppm, respectively. From gel to sol with UV irradiation, the *trans* peaks decreased. Upon exposing to ambient light, *cis*-*trans* isomerization of the azobenzene moieties also occurred, leading to the sol-to-gel transition, which resulted in the enhanced *trans* signals. The gel already re-formed when the content of *trans* isomer was still below 50% as determined from the ratio of the integrations of 2.35 to 2.24 ppm signals. The final content of *trans* reached 85% after a prolonged time, which is the same as the *trans* content of the stable gel before UV irradiation. For the CD measurements, significant Cotton effect was observed in the gel state. It decreased and finally disappeared as the gel-to-sol transition proceeded under UV irradiation (Fig. 3a). As the solution returns to the gel state, the Cotton effect is restored (Fig. 3b). Such a process could be repeated many times. Since they were only observed in the gel state, the dichroic signals should not be attributed to the chirality of the molecules, but to the supramolecular chirality in the gel state.[7,8] However, it was difficult to ascertain whether the assembled fibers are twist helices based on atomic force microscopy data. (Supporting Information Figure S-8†.)
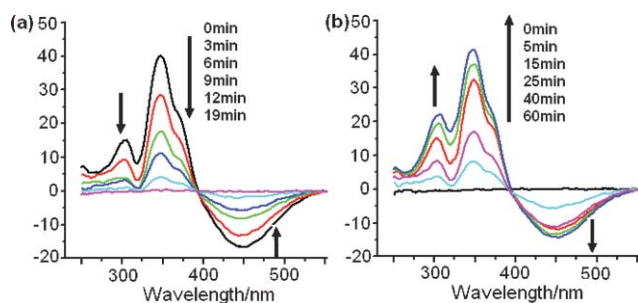
To further elucidate the self-assembly structure of **1**, X-ray measurement was performed. No useful information was obtained from the X-ray diffraction of **1** in the native gel state. On the other hand, wide-angle X-ray diffraction (WAXD) (Fig. 4) of the xerogel offers some insights on the self-assembly of **1**. It was found that the xerogel dried from gel before UV irradiation displayed the same WAXD patterns as the xerogel obtained from the re-formed gel with exposure to room light (Supporting Information Fig. S-9†). At room temperature, the xerogel displayed two major diffraction peaks with $d = 3.69$ and 2.48 nm in the low-angle range and two halos with the scattering maximums at $d = 0.48$ and 0.42 nm in the wide-angle range. Differential scanning calorimetry (DSC; Supporting Information Fig. S-10†) measurement of xerogel showed no phase transition occurred below 90 °C. Therefore, we recorded the WAXD patterns of the xerogel at different temperatures up to 80 °C, wherein the samples were annealed during a slow heating process. As shown in Fig. 4, besides the diffraction intensity increase with increasing temperature, two more diffractions with $d = 1.60$ and 1.49 nm appeared clearly at 80 °C. For those low angle diffractions, the scattering vector ratio is 1 : 1.49 : 2.30 : 2.48, which can be indexed as (110), (200), (310), and (230) in a two-dimensional (2-D) columnar centered rectangular lattice with $a = 4.96$ nm and $b = 5.52$ nm. As to rectangular dendritic system, both primitive *P2mm* and centered *C2mm* 2-D lattices for tapered dendrons were proposed by Percec *et al.*[7] Aida *et al.*[8] also reported a rectangular phase in dendritic gels. For the completely dried xerogel of **1**, the experimental density was 1.303 g cm^{-3}. Based on the structural and retro-structural analysis of supramolecular dendrimers as elegantly developed by Percec,[7] assuming that 0.48 nm of the first scattering halo maximum represents the average repeat distance along the column, our density measurement supports an average of about 4.5 dendrons in a stratum of the column. Thus, the results suggest that the focal azo moieties of **1** are located at the center of the column and the dendrons are radiating out from the center with benzyl rings pointing towards the periphery of the column, although the definitive arrangement of **1** in gels needs further evidence.

In summary, we have described an efficient photoreversible gelator based on azo-modified poly(Gly-Asp) dendron, **1**. Further investigation is in progress to prepare a series of new dendritic compounds based on the structure of **1** and to gain deeper insight into the mechanism and the supramolecular chirality of this thermal and photoreversible gelator system. We are also exploring the potential applications of this "smart" gelator system as a multi-addressable template for ordered inorganic materials.
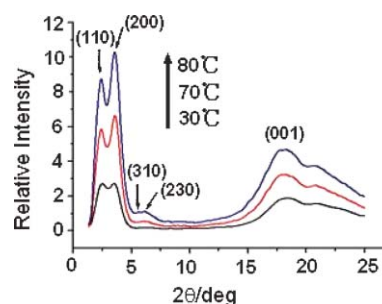

Fig. 3 CD spectra of **(a) 1** gel (0.1 wt%) in ethyl acetate induced by irradiating at 365 nm and (b) **1** *cis*-rich solution in ethyl acetate upon exposure to room light for different periods of time. A 1 mm optical path length cell was utilized.

Fig. 4 WAXD patterns of the **1** xerogel with increasing temperature.

Notes and references

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