

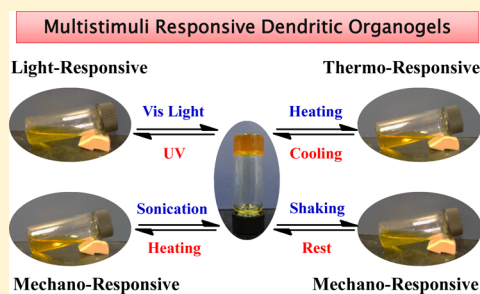
Multistimuli Responsive Dendritic Organogels Based on Azobenzene-Containing Poly(aryl ether) Dendron

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S Supporting Information

ABSTRACT: A new poly(benzyl ether) dendritic organogelator Azo-G3 containing azobenzene in its inner layer was designed and synthesized, and fully characterized. The dendron Azo-G3 was found to be a highly efficient and versatile organogelator toward various apolar and polar organic solvents with the critical gelation concentrations (CGCs) approaching 0.05 wt %, indicating that the dendron belongs to the category of supergelators. Further studies revealed that the intermolecular multiple π – π stacking interactions might be responsible for guiding the self-assembly processes and the gel formation. Most interestingly, these dendritic organogels exhibited multiple stimuli-responsive behaviors upon exposure to environmental stimuli including temperature, sonication, light, and shear stress.

KEYWORDS: dendritic organogelator, azobenzene, multiresponsiveness, sol–gel processes, supramolecular chemistry



■ INTRODUCTION

Recently, stimuli-responsive materials showing dramatic property changes in response to external environmental stimuli have been attracting considerable attention due to their wide ranges of potential applications in biomaterials, sensors, displays, surface science, etc.^{1,2} Among them, stimuli-responsive supramolecular organogels are one kind of the most attractive examples.² They are formed by assembly of low molecular-weight gelators (LMWGs) into physically cross-linked three-dimensional networks with solvent molecules entrapped inside through noncovalent intermolecular interactions such as H-bonding and π – π stacking. The weak nature of these forces allows external triggers to modulate their physical behaviors easily. In addition to temperature, other stimuli such as light, chemicals and/or mechanical force have also induced reversible gel–solution phase transition by the integration of suitable responsive modules into LMWGs.³ For example, light-responsive organogels have been achieved by incorporating photoresponsive moieties (e.g., azobenzene and stilbene) into the corresponding LMWGs.^{4,5} Most recently, Zhang and co-workers developed multistimuli-responsive organogels based on a new organic gelator featuring electroactive tetrathiafulvalene and photoresponsive azobenzene groups.⁶ Despite the great progress made recently in this field, multistimuli-responsive organogels still remain rare.^{6,7}

Dendrimers and dendrons are highly branched macromolecules with well-defined molecular architecture that are of great interest in the self-assembly of supramolecular gel-phase materials.⁸ To date, a number of physically thermoreversible organogels based on dendrons or dendrimers with different

chemical functionalities have been reported.⁹ On the other hand, unlike the small molecular gelators, dendritic architectures render them capable of being incorporated with different stimuli-sensitive functional groups (e.g., azobenzene) into the core, the inner and/or outer layers, leading to dendrimers showing property changes in response to external stimuli.¹⁰ Dendrimers are therefore ideal candidates for the development of stimuli-responsive smart materials. Surprisingly, dendritic gelators with stimulus (except for temperature) responsive properties are rarely reported.¹¹ To the best of our knowledge, there have been no reports of dendritic organogels responsive to more than dual external triggers.

Following our continued pursuit of developing efficient organogelators,^{12,13} herein we report a new dendritic gelator Azo-G3 (Scheme 1) with photoresponsive azobenzene groups located in the inner layer. The resulting dendritic organogels exhibit reversible gel–solution phase transition in response to external environmental stimuli including temperature, sonication, light, and shear stress. This molecular design was made on the basis of the following considerations. First, the azobenzene chromophore has been widely used to fabricate photoresponsive materials due to its simple, clean, and efficient photochemical isomerization. Second, we found recently the peripherally dimethyl isophthalate (DMIP) functionalized poly(benzyl ether) dendrons to be highly efficient organogelators.^{12a} Both the multiple strong π – π stacking interactions

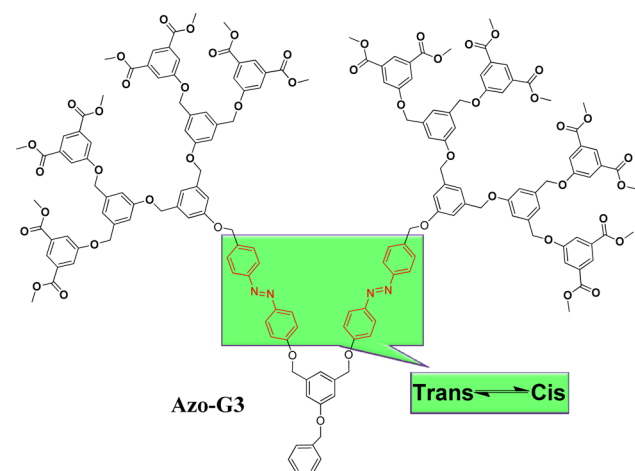
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Scheme 1. Chemical Structure of Dendritic Organogelator Azo-G3



due to the peripheral DMIP motifs and the dendritic architecture are critical in forming the self-assembled gel. Thus, incorporating azobenzene units into the inner layers can render the peripheral DMIP motifs unchanged. This modification will also provide enough space around the azobenzene groups and thus facilitate reversible trans–cis isomerization in the assembled gel state. Most importantly, the trans to cis isomerization of the azobenzene group triggered by light irradiation is anticipated to result in a large conformational change throughout the dendrimer.^{10b,g,h} Accordingly, the intermolecular noncovalent interactions will be altered, leading to photoresponsive dendritic organogels.

RESULT AND DISCUSSION

Molecular Design and Synthesis. The dendritic gelator Azo-G3 (Scheme 1) was first synthesized via a semiconvergent strategy modified from our previous method,¹⁴ and the synthetic details and characterization data are provided in the Supporting Information (SI). Its purity and chemical structure were confirmed by ¹H NMR, ¹³C NMR, and MALDI-TOF mass spectroscopy, as well as elemental analysis.

Organogelation Behavior. With Azo-G3 in hand, its gelation behavior was then evaluated in various organic solvents and mixed solvents. It was found that stable organogels were formed in most organic solvents through heating–cooling process. The critical gelation concentrations (CGCs) were collected in Table 1. Interestingly, Azo-G3 formed a translucent orange gel in tetrachloromethane or its mixed solvents at very low concentrations with CGCs as low as 0.05 wt %, elevating Azo-G3 to the category of supergelator.¹⁵ Notably, Azo-G3 gels could be formed only upon ultrasonic treatment in some polar solvents, such as 2-methoxyethanol, 2-ethoxyethanol, acetone, ethyl acetate, and mixture of anisole/hexane.^{3b,j,16} For example, when the heated solution of Azo-G3 in 2-methoxyethanol was cooled to room temperature, an orange suspension instead of a stable gel was observed. However, if the suspension or its hot solution was submitted to sonication irradiation for minutes, a translucent gel was formed rapidly (Figure 1a). To understand the effect of sonication on the gelation process, the aggregate morphologies before and after the sonication were studied by means of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Figure 1, and Figure S2 in the SI). The results suggested that the prominent

Table 1. Critical Gelation Concentration (CGC) Values and Gelation Ability of Supergelator Azo-G3 in Various Organic Solvents and Mixed Solvents

solvent	CGC (T-Gel) ^a [g L ⁻¹]	CGC (S-Gel) ^b [g L ⁻¹]	CGC (S-Gel) ^b [wt %]	CGC (S-Gel) ^b [mol L ⁻¹]
toluene	G (5.8)	G (5.8)	G (0.67)	1.92×10^{-3}
benzene	G (3.8)	G (3.8)	G (0.43)	1.26×10^{-3}
anisole	G (18.0)	G (18.0)	G (1.80)	5.96×10^{-3}
pyridine	G (3.6)	G (3.6)	G (0.37)	1.19×10^{-3}
benzylalcohol	G (5.6)	G (5.6)	G (0.54)	1.86×10^{-3}
cyclohexanone	G (3.5)	G (3.5)	G (0.37)	1.16×10^{-3}
2-hexanone	G (1.8)	G (1.8)	G (0.22)	6.0×10^{-4}
3-pentanone	G (2.0)	G (2.0)	G (0.24)	6.6×10^{-4}
acetone	P	G (5.6)	G (0.71)	1.85×10^{-3}
ethyl acetate	P	G (8.5)	G (0.94)	2.82×10^{-3}
2-methoxyethanol	P	G (4.0)	G (0.41)	1.32×10^{-3}
2-ethoxyethanol	P	G (6.5)	G (0.69)	2.15×10^{-3}
1,2-dichloroethane	G (31.6)	G (31.6)	G (2.51)	1.05×10^{-2}
tetrachloromethane	G (0.8)	G (0.8)	G (0.05)	2.6×10^{-4}
CHCl ₃ /CCl ₄ = 1/9	G (1.1)	G (1.1)	G (0.07)	3.6×10^{-4}
anisole/CCl ₄ = 3/2	G (7.5)	G (7.5)	G (0.63)	2.48×10^{-3}
anisole/hexane = 1/1	P	G (5.0)	G (0.60)	1.66×10^{-3}
THF/MeOH = 3/1	G (1.9)	G (1.9)	G (0.22)	6.3×10^{-4}

^aThe gelation test was proceeded based on heating–cooling process.

^bA short-term sonication (0.40 W/cm², 40 kHz, 1–5 min) was involved at the beginning of the cooling process for the gel formation.

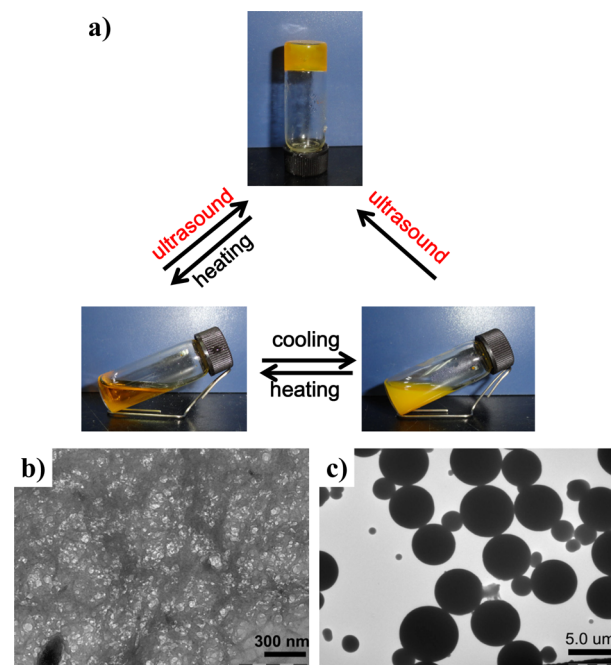


Figure 1. (a) Reversible sol–gel phase transition of the gel of Azo-G3/2-methoxyethanol triggered by sonication. TEM images of the xerogels after (b) and before (c) treatment with ultrasound.

morphological changes from microspheres to nanofibers were responsible for the gelation process triggered by sonication.

Gel–Sol Phase Transition Temperature. In addition, these dendritic organogels were found to be stable for months at room temperature. The gel–solution phase transition temperatures (T_{gel}) increased with increasing in the dendron concentrations in toluene, cyclohexanone, or benzylalcohol,

indicating higher stability of the gel networks under higher concentrations (Figure 2).

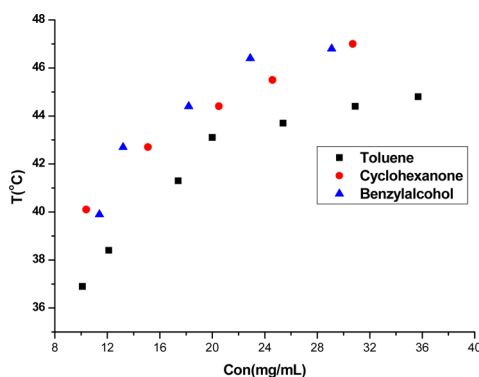


Figure 2. Plots of T_{gel} against the concentration of Azo-G3 in toluene, cyclohexanone, and benzylalcohol with the heating rate 2 °C/min in water bath.

Morphologies of Organogels. The morphologies of the xerogel with respective solvents were investigated by TEM and SEM. A very dense fiberlike morphology for Azo-G3 in different organic solvents was observed by TEM. For example, the xerogel from toluene exhibited an entangled three-dimensional (3D) network composed of thin solid fibers, widths of 10–50 nm, and lengths of several micrometers (Figure 3b). These fibers intertwined together so as to assemble into a dense 3D network, which is responsible for the gelation. The morphologies were further confirmed by SEM (Figure S9, SI). Similar fibrillar networks were also found in other solvents (Figure S4 and S5, SI).

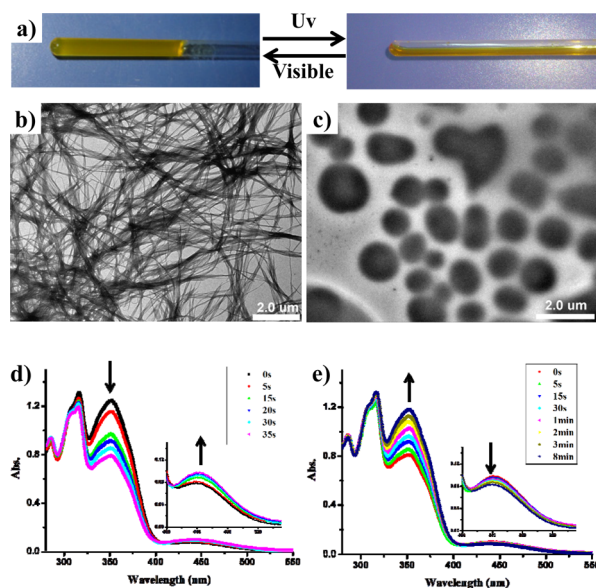


Figure 3. (a) Photographs of the Azo-G3 gel in toluene (0.67 wt %) before and after UV irradiation (365 nm) for 20 min. (b) SEM image of the xerogel after drying from the gel state. (c) SEM image of the aggregates from sol state. (d) Absorption spectra of the Azo-G3 (2.86×10^{-4} M in toluene; 1 mm path length) under UV light irradiation (365 nm) for different time. (e) Absorption spectra of the UV irradiated sample upon visible light irradiation (>460 nm) for different time. The insets show absorption spectral variation in the 400–550 nm range.

Driving Force Analysis. The excellent gelation properties of Azo-G3 promoted us to study the driving forces toward gelation. According to our previous study,^{12a,b} temperature dependent (TD) ^1H NMR, UV–vis spectroscopy, and powder X-ray diffraction (PXRD) were applied to investigate the π – π stacking interactions between the individual component. In the TD- ^1H NMR experiments, the resonance signals for the aromatic protons on the peripheral DMIP, the internal benzyl rings, and the azobenzene were found to be strikingly shifted downfield upon increasing the temperature from 278 to 323 K. In contrast, the signals of the benzyl ring at the focal point remained constant (Figure S6, SI). The above observation reflected the increasing π – π stacking interaction upon cooling. Moreover, the interactions between the azobenzene chromophores were observed by UV–vis spectroscopy (Figure S7, SI). The sol state in toluene showed a π – π^* absorption maximum of azobenzenes at 350 nm, which was blue-shifted by about 20 nm from the absorption maximum in the gel state. This phenomenon indicated that azo groups adopted the “H-aggregates” π – π interaction mode in the gel state. In addition, the π – π interactions were also evidenced by PXRD study. As shown in Figure S8 in the SI, a prominent reflection characteristic of a typical π – π stacking distance was observed in the wide-angle region at 3.5 Å of the PXRD patterns.^{12a,17} On the basis of all these results, the strong intermolecular multiple π – π stacking might be the key factor guiding the self-assembly processes and responsible for the gel formation.

Sol–Gel Transformations of Dendritic Gels by Light Stimuli. In addition to temperature and sonication, as designed, the gel–sol phase transition could be triggered by light. Upon UV irradiation, the stable orange gels were found to collapse gradually and finally turned into solution. Also, gel regeneration was achieved by the subsequent irradiation of visible light. As an example (Figure 3a), when the dendritic gel formed with 0.5 mL toluene (0.67 wt %) in an NMR tube was irradiated with UV light (365 nm) for 20 min, it collapsed gradually and transformed into a clear solution. This solution could be reverted to an orange-yellow gel upon visible light ($\lambda > 460$ nm) irradiation for approximately half an hour. The UV irradiation time for the gel–sol phase transition was dependent on the gelator concentration and the amount of the gel under investigation. Such gel–sol phase transition for the organogels with Azo-G3 triggered by UV and visible light irradiation was reversible and could be repeated many times.

In addition, the UV irradiation also caused the morphology change of the gel system (Figure 3b,c, and Figure S9, SI). Compared to the entangled 3D network of the xerogel in toluene, TEM and SEM images of the dried sol after UV irradiation showed no sign of fibers. The recovered gel by the irradiation of visible light showed similar fibrillar morphology again. Thus, UV irradiation disrupted the molecular packing of dendritic gelator Azo-G3, followed by dissociation of the fibers and their three-dimensional networks of the gel.

The configurable changes of azobenzene chromophores upon light irradiation were further studied by UV–vis spectroscopy and thin-layer chromatography (TLC). Under UV irradiation at 365 nm, the photoisomerization of the azobenzene groups from trans- to cis-isomer in toluene solution occurred as evidenced by the spectral changes. As shown in Figure 3d, along with the elongate of the irradiation time, a gradual decrease of the intensity of the absorption at 348 nm band and the concomitant increase of the intensity of the peak at 440 nm band (n – π^* transition) were observed, indicating

the progress of the photoisomerization. Subsequent visible light irradiation (>460 nm) showed an opposite tendency of spectra variation (Figure 3e). These spectral changes were well related to the change of the macroscopic state of the sample observed.

The photoreversible isomerization of azobenzene, which might be responsible for the observed gel-to-sol transitions, was further confirmed by TLC (Figure S10, SI).^{10g,h} Considering both azobenzene chromophores in dendron Azo-G3 are capable of E/Z isomerization, the dendron could exist in three discrete states (i.e. EE, EZ and ZZ isomers), which could be easily detected by TLC due to the difference in polarity. As shown in Figure S10 in the SI, the gel state in toluene showed the only existence of EE isomer. When the gel was turned into sol under UV irradiation (365 nm), the other two isomers (EZ, ZZ) were also observed. These results from both UV-vis spectroscopy and thin-layer chromatography indicated that the E to Z isomerization of azobenzene moieties gave rise to the gel-to-sol transition upon UV irradiation.

Sol–Gel Transformations of Dendritic Gels by Mechanical Stimuli, A Rheological Study. Unexpectedly, these dendritic gels from most tested organic solvents (Table S1, SI) were found to be thixotropic. As shown in Figure 4a, for example, the transparent gel of Azo-G3 in toluene was changed into a clear sol by vigorous shaking. Upon resting, the gel could be regenerated rapidly. This reversible gel–sol phase transition could be repeated many times (Figure 4a). Although the thixotropic organogels have been known for a while,^{7b,d,18} there is only one reported example of thixotropic dendritic organogel system developed by Percec and co-workers in 2008.¹⁹ The mechano-responsive behavior of the dendritic organogels reported here had been investigated in detail by rheological techniques.

As shown in Figure 4b, the linear regime of the Azo-G3/toluene (1.7 wt %) gel system was determined first, as a representative. The storage modulus G' , associated with energy storage, and the loss modulus G'' , associated with loss of energy, were monitored as functions of shear strain. It had been clearly exhibited that at low strain values, the value of G' (about 7500 Pa) was more than 1 order of magnitude greater than G'' (about 300 Pa), indicating dominant elastic characters of the sample. Both moduli remained roughly constant below a critical strain value of 1.0%, known as the upper limit of the linear viscoelastic regime. Above the value, a sharp decrease of G' and G'' was observed, representing a partial breakup of the gel.

The recovery property of the dendritic gel was also investigated. By monitoring the time evolution of G' and G'' (Figure 4c), an extremely rapid recovery of the gel was observed. Just when the external stress was removed, the sample recovered its elastic property immediately and behaved as a gel-like material ($G' > G''$). After 40 min, G' reached its initial value of the gel (about 7500 Pa before shearing). Clearly, the gel exhibited an unusual and smart thixotropic property.

To further verify the reproducibility of this thixotropic organogel, another more serious test was carried out. With reference to Figure 4d, once a high strain was applied (100%), the gel was completely broken as indicated by the larger value of G'' than G' . The elasticity immediately recovered ($G' > G''$) once the high strain was canceled, though the G' parameter of the recovered gel (within 30 s) was only about 40% of the initial value. However, with prolonged time of more than one hour, the system could successfully recover to its initial state, which was confirmed by the similar storage modulus G' as its

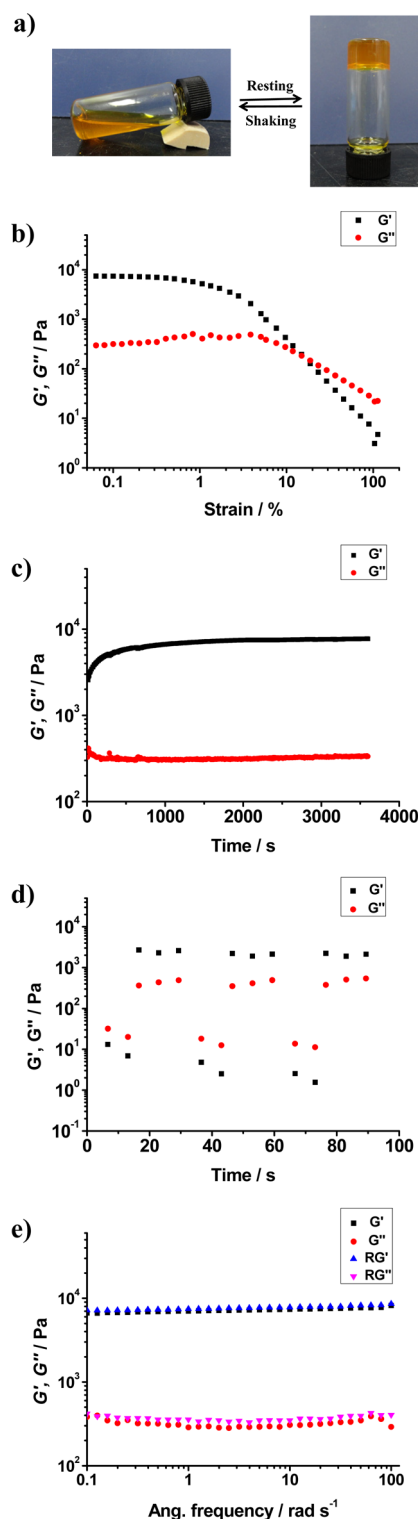


Figure 4. (a) Reversible sol–gel phase transition of the gel of Azo-G3 in toluene triggered by shear-stress. Storage modulus G' and loss modulus G'' values of a Azo-G3 organogel (toluene, 1.7 wt %) on rheological experiments of (b) strain sweep; (c) time sweep; (d) three cycles of deformation and recovery processes; (e) frequency sweep.

original value (Figure S11A–B, SI). Furthermore, this thixotropic process could be repeated several times.

To detect the tolerance performance of the original gel of Azo-G3 in toluene and its recovered gel system RG as mentioned above, frequency sweeps were conducted. The

result depicted in Figure 4e showed that both gel samples had close G' and G'' values, suggesting similar elastic properties of the original and the recovered gels. Furthermore, the G' and G'' of both gels exhibited slight frequency dependence in the frequency range of 0.1–100 rad/s, demonstrating that both gels have good tolerance to external forces. The thixotropic properties of the dendritic organogels in other solvents (e.g., anisole, ethyl acetate) had also been investigated by rheological experiments (Figure S11C–J, SI), affording conformable conclusions.

CONCLUSION

In summary, we have designed and synthesized a highly efficient and versatile dendritic organogelator Azo-G3 based on an azobenzene-containing poly(aryl ether) dendron. It was found that Azo-G3 could form stable organogels toward various apolar and polar organic solvents with CGCs approaching 0.05 wt %. These organogels exhibited multistimuli responsive behaviors upon exposure to external stimuli including temperature, sonication, light, and shear stress. These prominent features of the Azo-G3 dendritic organogels make them excellent intelligent soft materials with promising potential applications, and also imply that the incorporation of stimuli-sensitive functional groups into the dendritic backbone is one efficient way to develop multistimuli-responsive organogels.

EXPERIMENTAL SECTION

General. All starting materials were obtained from commercial suppliers and used as received. All solvents were distilled with suitable drying agents. Moisture-sensitive reactions were performed under an atmosphere of dry argon. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer (^1H : 300 MHz; ^{13}C : 75 MHz) or a Bruker AMX-600 spectrometer (^1H : 600 MHz; ^{13}C : 150 MHz) at 298 K. Chemical shifts were reported in parts per million (ppm) relative to the internal standards, partially deuterated solvents or tetramethylsilane (TMS). Matrix-assisted laser desorption-ionization (time-of-flight) mass spectrometry (MALDI-TOF) was performed on a Bruker Biflex III MALDI-TOF spectrometer with α -cyano-4-hydroxycinnamic acid (CCA) as the matrix. HR-ESI mass spectra were obtained on a Bruker APEX IV instrument. Elemental analyses were performed on a Carlo-Erba-1106 instrument. Powder wide-angle X-ray diffraction (WAXD) patterns of xerogels were obtained using a Japan Rigaku D/MAX-2500/PC diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$).

Field Emission Scanning Electron Microscope (FE-SEM). The morphologies and sizes of the dendritic xerogels were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an accelerating voltage of 15 kV. Samples were prepared by dropping the diluted gels on silicon slices and dried by air for 2 days. To minimize sample charging, a thin layer of Au was deposited onto the samples before SEM examination.

Transmission Electron Microscopy (TEM). TEM was performed on a JEOL JEM-1011 microscope. Samples were prepared by dropping the diluted gels on carbon coated copper grids, and the TEM pictures were obtained without staining.

Photoresponsive Measurements. Photo irradiation was carried out with a 300-W Xe lamp (CEL-HXF 300) through a light guide and an appropriate color filter ($330 < \lambda < 390 \text{ nm}$ for UV light and $\lambda > 460 \text{ nm}$ for visible light). UV–vis absorption spectra were recorded on a Varian Cary 100 UV–visible spectrophotometer with temperature controller. Analytical thin-layer chromatography (TLC) was performed on HSGF-254 precoated TLC plates.

Rheological Measurements. Rheological measurements were carried out with a stress-controlled rheometer (TA Instruments, AR-G2) equipped with steel parallel-plate geometry (40 mm diameter). The gap distance was fixed at $750 \mu\text{m}$. A solvent-trapping device was

placed above the plate to avoid evaporation. All measurements were made at 10°C . Strain sweep at a constant frequency (6.28 rad/s) was performed in the 0.05–200% range to determine the linear viscoelastic region (LVER) of the gel sample. The frequency sweep was obtained from 0.1 rad/s to 100 rad/s at a constant strain of 0.1%, well within the linear regime determined by the strain sweep. A thixotropic study was conducted to examine the recovery behavior of a dendritic organogel after the strain sweep. The recovery of the storage modulus of the destroyed gel was monitored at a constant frequency (6.28 rad/s) under a low strain (0.1%) just after the strain sweep progress. The storage modulus G' and the loss modulus G'' were recorded as functions of time in the recovery processes.

The cycle of deformation and recovery included two steps. (1) Deformation: A constant oscillatory strain (100%) that was enough to destroy the gel was applied to the fresh gel in the sample holder for 10 s. The frequency of the measurement was 6.28 rad/s. (2) Modulus recovery in a time sweep: The recovery of the storage modulus was monitored at a constant frequency (6.28 rad/s) under a low strain (0.1%) within 20 s. The storage modulus G' and the loss modulus G'' were recorded as functions of time in both processes.

Gelation Test. A weighed sample of dendritic gelator was mixed with a solvent (0.5 mL) in a septum-capped vial and heated in an oil bath until the solid was dissolved. Then, the sample vial was cooled to room temperature, a T-Gel was obtained when the prepared sample was left for a period of time in a certain solvent at ambient conditions. An S-Gel was obtained when the prepared sample was treated with ultrasound (0.40 W/cm^2 , 40 kHz) for 1–5 min at the beginning of the cooling process. The aggregation state was then assessed. If no flow was observed when inverting the vial, a stable gel was formed and noted as gelation (G). If part of the mixture formed a gel but flow was still observed, the phenomenon was recorded as partial gelation (PG). If precipitation occurred, P was noted, and if the clear solution ($>60 \text{ mg/mL}$) was retained, it was marked as soluble (S). Repeated heating and cooling confirmed the thermo-reversibility of the gelation process. The critical gelation concentration (CGC) of the organogelator was determined by measuring the minimum amount of gelator required for the formation of a stable gel at room temperature.

The thermally reversible gel–sol transition temperature (T_{gel}) was determined by using a tube-inversion methodology. A sealed vial containing the gel was immersed upside-down in a thermostatted water bath. The temperature of the bath was raised at a rate of approximately 2°C/min . T_{gel} was defined as the temperature at which the gel moved on tilting of the vial. The experimental error of T_{gel} in repeated independent measurements was less than 1°C .

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures and characterization data for new compounds, the thermal behaviors and morphologies of the xerogels in different solvents, additional experiments for studying the driving forces, and SEM, TEM, thin-layer chromatography, and rheological experiments supporting the stimuli-responsive behavior. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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