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# Solvent-dependent Self-assembly and Morphological Transition of Low-Molecular-Weight Azobenzene Organogel

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## ABSTRACT

A novel low molecular weight organogelator (LMOG) containing an azobenzene group has been designed and synthesized. Stable gels could be formed in various organic solvents. UV-Vis spectroscopy indicated that the sol-gel transition of the organogels could be reversibly tuned by UV/visible light irradiations. Importantly, scanning electron microscopy (SEM) revealed that the characteristic gelation morphologies would vary from solvents of different polarities. FT-IR, XRD and rheological measurements demonstrated that the different nanostructures in polar and non-polar solvents might result from the differences in the intermolecular hydrogen bonding,  $\pi$ - $\pi$  stacking driving forces as well as the different stacking models for the formation of the gels. Moreover, as an efficient phase-selective gelator, this photo-switchable gel could perform as an efficient absorbent and water cleaner to remove pollutants (e.g. rhodamine B).

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#### 1. Introduction

Supramolecular gels, generated from self-assembly of small gelators, have attract considerable attentions in the past decades, due to their wide applications including tissue engineering, biomaterials, sensors, optoelectronic devices, nanomaterials, pollutants removal, control of crystal, and so on.<sup>1-9</sup> During the formation of the gels, the noncovalent interactions, such as hydrogen-bonding,  $\pi$ - $\pi$  stacking, host-guest interactions, chargetransfer (CT) interactions, metal ion to ligand coordination and electrostatic interactions,<sup>10-17</sup> play a significant role in driving the small gelators to form the one-dimensional (1D) aggregate to further 3D network. As a typical supramolecular gelator, lowmolecular-weight organogelators (LMOGs) take advantages of accurate molecular weight, easy modification, multifarious nanostructures, and stimuli-responsive properties.9 Compared with traditional gels, it is easier for these supramolecular gels to form and dissociate because of the weak interactions between the gelator molecules, giving an access to possess stimulateresponsive sol-gel phase transition performances. The stimulus could be heat,<sup>18</sup> light,<sup>2,19-21</sup> sound,<sup>22</sup> pH,<sup>23</sup> host-guest interaction,<sup>24-25</sup> complexation,<sup>26</sup> and oxidative/reductive reactions,<sup>27</sup> etc., and the combination of several independent/synergetic stimuli creates multifunctional smart gels.<sup>28-34</sup> In these LMOG gels, solvents are the major components gelled by the minor gelators. Not only the gelator-gelators but also the gelator-solvents interactions play important roles in the formation of gels. Meanwhile, different degrees of the noncovalent interactions of gelator-gelators and gelator-solvents would have a significant effect on the selfassembly, resulting in different morphologies and properties of the organogels.<sup>35-38</sup> For instance, Duan et al. showed that the supramolecular chirality of an azobenzene LMOG based organogel could be modulated via solvent polarity.<sup>39</sup> Recently, Zhang et al. reported a Fmoc-amino acid gelator based supramolecular gel, whose morphology could also be tuned by changing the solvent polarity.<sup>40</sup> Therefore, it is essential to investigate how solvents can influence the self-assembly and gelation of the LMOGs, which could help understand the gelation mechanism and further facilitate their potential applications.



#### azo-BDAD

#### Scheme 1. The structure of azo-BDAD.

Herein, we constructed a novel photoresponsive LMOG (azo-BDAD) based on an azobenzene derivative (Scheme 1) and investigated its solvent-dependent self-assembly behavior in various solvents. In non-polar solvents, the gelators selfassembled to nanorod structure with the model of an interdigitated bilayer, whereas the gelators stacked with a oneabove-the-other bilayer model to form lamellar structures in polar solvents. All the assembled organogels would undergo reversible sol-gel transitions tuned by UV/visible light irradiations for several cycles. Moreover, the gelators show selective gelation from aromatic solvents-water at room temperature, and the selfassembled organogels can be capable of adsorbing cationic dyes, such as rhodamine B, which implies a potential application in pollutants removal from water.

#### 2. Results and Discussion

#### 2.1. Gelation Properties

The gelation ability of azo-BDAD in various organic solvents was investigated by inverting the vials upside down.<sup>41</sup> The gelator and solvent were first mixed in a screw-capped sample tube, and the resulted mixture was then heated until the solid was dissolved completely. After cooling down to the room temperature, the corresponding gels were formed as the sample stayed intact even the vial was inversed upside down. The gelation testing results and the critical gelation concentration (CGC, mg/mL) data were summarized in Table 1.

Table 1. Results of Gelation Testing in Various Organic Solvents and Water at Room Temperature<sup>a</sup>

Solvent	Phase(CGC)	Solvent	Phase(CGC)
<i>n</i> -hexane	Ι	ethyl acetate	S
cyclohexane	TG (2.5)	<i>i</i> -propanol	S
$CCl_4$	TG (1.7)	chloroform	S
toluene	TG (5.0)	1,4-dioxane	S
diethyl ether	Р	acetone	G (10)
<i>i</i> -butanol	PG (13)	ethanol	Р
DCM	S	acetonitrile	G (7)
<i>n</i> -butanol	PG	DMF	S
THF	S	methanol	Р
dichloroethane	Р	DMSO	S

<sup>a</sup>G = turbid gel; TG = transparent gel; PG = partial gelation; P = precipitate; I = insoluble upon heating.

As shown in Table 1, azo-BDAD presented a good gelation ability in a wide range of organic solvents. Transparent gels were formed in several non-polar solvents, such as cyclohexane, CCl<sub>4</sub> and toluene, whereas turbid gels were obtained in polar solvents, such as acetone, acetonitrile, *i*-butanol. The different appearances may be resulted from the different microstructures and refractive indexes between the organolges.42 In addition, the CGC of the organogels in non-polar solvents is lower than that in polar solvents, which shows that the gelator has a better gelling ability in non-polar solvents (CCl<sub>4</sub> has a lowest CGC of 1.7 mg/mL of all the tested solvents). All these organogels are very stable and can endure more than half a month without obvious phase separation at room temperature. Similar with organogels previously reported,<sup>38-39</sup> the azo-BDAD based organogels can undergo thermoreversible gelation cycles, which the organogels were melted upon heating and turned into gels upon cooling (Fig. S1).

#### 2.2. Photoisomerization investigation in solution and gel states

As a typical photochromic molecule, azobenzenes can transform between *trans* and *cis* isomers when irradiated by alternate UV/Vis light.<sup>43-46</sup> Thus, photochromic performances of Azo-gels were first investigated in both solvents and gel states, as shown in Fig. 1.

Photochromism of azo-BDAD was first examined in toluene  $(1.0 \times 10^{-4} \text{ M})$ . Upon irradiation with light of 365 nm for 10 min,

the decrease of  $\pi$ - $\pi$ \* absorbance band at 328 nm and the blueshift of n- $\pi^*$  absorbance band from 450 nm to 441 nm suggested that the transformation from *trans* form to *cis* form. The *cis* form returned to the trans form after visible light irradiation for 3 min (Fig. 1A). The isomerization ratio for trans-cis and cis-trans are over 60% and 80%, respectively (Fig. S2). Besides, the photoswitching cycles between trans and cis isomers can be operated several times without obvious degradation, showing a good fatigue resistance for azo-BDAD (Fig. 1C). Similar results were also observed in the organogel state (Fig. 1B). The photoswitchable sol-gel transition was then conducted in a quartz cell. After UV light ( $\lambda = 365$  nm) irradiation for 20 min at room temperature, the organogel in toluene gradually collapsed and transformed into a viscous solution (Fig. 1D), demonstrating the dissociation of the gel into solution phase. The transparent gel formed again after visible light irradiation for 5 minutes ( $\lambda > 400$ nm). Similar phenomena were obtained when *i*-butanol was used as the solvent (Fig. S3). Surprisingly, compared to the photoswitchable organogel in toluene, the backward sol-gel transition didn't occur under visible irradiation in *i*-butanol. The relatively stiff structure of gels in *i*-butanol may attribute to the failure in sol-gel transition reversibility under photo-irradiation.



**Fig. 1** A) Absorption spectra of azo-BDAD in toluene under UV light (365 nm) and visible light irradiation for different times. B) Absorption spectra of azo-BDAD gels from toluene under UV (365 nm) and visible light for different times. C) The cycles of absorbance intensity at 328 nm in toluene. D) The reversible gel-sol transition under UV/Vis light irradiation. All the concentration of the solution and gel are  $1.0 \times 10^{-4}$  M, 5 mg/mL, respectively.

#### 2.3. Rheological Measurements

The mechanical properties of the formed gels from toluene, *i*butanol and acetone were then checked by rheological measurements at 25  $\square$ . The storage modulus (G') is an order of magnitude higher than the loss modulus (G") at all the testing frequencies in all solvents, indicating the formation of the organogels (Fig. 2). In toluene and *i*-butanol, G' and G" at high frequencies are always slightly higher than those at low frequencies, possibly resulting from the slow rearrangement of azo-BDAD molecules in gels at high stress.<sup>47</sup> It should be noted that G' and G" values of azo-BDAD gels in *i*-butanol and acetone become larger than those in toluene. For example, at  $\omega = 10$  Hz, the G' and G" in *i*-butanol and acetone reach  $1.56 \times 10^5$ ,  $6.38 \times$  $10^4$  Pa and  $1.90 \times 10^5$ ,  $3.19 \times 10^4$  Pa respectively, whereas those in toluene only attain  $9.85 \times 10^4$  and  $2.30 \times 10^4$  Pa, respectively. The results indicated that the gel formed from *i*-butanol and acetone were more rigid than toluene, which might result from the different self-assembly of these azo-gels in different solutions. Also, as mentioned above, the azo-BDAD gives access to transparent and turbid organogels in non-polar and polar solvents, respectively. The different appearance of the gels together with the different gel rigidities prompted us to shed light on the possible intrinsic interactions and self-assembly models of the resultant gels from different solvents.



**Fig. 2** Viscoelastic behaviors of organogels at 75 mg/mL from A) toluene, B) *i*-butanol, C) acetone.

#### 2.4. Aggregation Morphology Studies

In order to explore the intrinsic factors for different gel appearances, the micromorphologies were first examined by monitoring the corresponding air-dried xerogels via SEM in Fig. 3. The microstructure of the organogels obtained from toluene was stubbly rod-like structure of more than 4 micrometers in the length and about 1 micrometer in the width (Fig. 3A). In ibutanol, azo-BDAD self-assembled orderly into lamellar structures with about 5-10 micrometers in length and 2-4 micrometers in the width (Fig. 3B). In acetone, the aggregates of the turbid organogels indicated that nanofibers were formed of about 10-20 nanometers in the width and up to several micrometers in the length and seemed to stack on top of each other at intersections to yield an entangled structure (Fig. 3C). Similar rod-like nanostructures and nanofibers were observed in the CCl<sub>4</sub> and acetonitrile, respectively (Fig. S4). The different micromorphologies present the different assembly of the gelator, which is determined by the gelator-gelators/gelator-solvents interactions.35 From toluene/CCl4 to i-butanol and then to acetone/acetonitrile, the microstructures gradually changed from three-dimensional rod-like structures to lamellar structure and then to nanofibers, demonstrating a solvent polarity-induced regulation of the microstructures of the gel 3D networks.



**Fig. 3** SEM images of the organogels in various solvents at their CGCs: A) toluene, B) *i*-butanol C) acetone.

#### 2.5. Determination of the Driving Forces in Self-Assembly

In order to investigate the driving forces in self-assembly, we monitored the FT-IR spectroscopies of azo-BDAD in solvent and xerogel states. As shown in Fig. 4A, the  $\nu_{N\text{-}H}$  signals of azo-BDAD in DMF solution appeared at about 3459 cm<sup>-1</sup>, and amide carbonyl stretching (N-C=O, amide I) and N-H bending (amide II) bands appeared at around 1667 and 1497 cm<sup>-1</sup>, respectively, indicating a non-hydrogen bonding state.<sup>41</sup> In the gel state, the peaks of N-H stretching and N-C=O stretching vibrations redshifted to 3312-3318 cm<sup>-1</sup> and 1629-1630 cm<sup>-1</sup>, respectively. Also, the peak at 1522-1524 cm<sup>-1</sup> appeared, which was ascribed to the amide II stretching frequency. Furthermore, the carboxylate (O-C=O) band at 1731-1735 cm<sup>-1</sup> was shown in xerogels. All these results indicated that all the N-H and N-C=O are hydrogen bonded in the gel state.<sup>41</sup> On the other hand, comparing with DMF solution, N-H stretching of the xerogel from toluene redshifted more wavenumbers than that from *i*-butanol, indicating a more strengthened hydrogen bonding interactions in toluene gel

than that in *i*-butanol gel. In other words, hydrogen bonding is probably the more preferred driving force in gels from non-polar solvents. Similar trend can be observed in gels generated from other solvents as shown in Table 2. Taking the molecular structure of the gelator into considering, besides the hydrogen bonding proved by FT-IR spectra,  $\pi$ - $\pi$  interaction is also expected to be one of the major driving forces for self-assembly. To explore the  $\pi$ - $\pi$  stacking interactions between azobenzene chromophores, we investigated UV-Vis spectra of azo-BDAD in gradual increasing concentrations (Fig. S5). The absorption band in *i*-butanol showed a red-shift of about 2 nm, whereas no changes were seen in toluene, indicating a more preferred  $\pi$ - $\pi$ stacking interaction in gels from polar solvents.48 Combined with these results above, it could be summarized that the hydrogen bonding and  $\pi$ - $\pi$  stacking interactions are expected to be the two major driving forces for gel formation. In non-polar solvents, intermolecular hydrogen bonding via amide groups is the more preferred driving force form gelation, while gelation counts more on  $\pi$ - $\pi$  stacking when polar solvents are used.



Fig. 4 A) FT-IR spectra of azo-BDAD in DMF solution and gel states from toluene and *i*-butanol. B) XRD patterns of the xerogels obtained from toluene gels (5 mg/mL) and *i*-butanol gels (13 mg/mL). C) Staking models for the gelator arrangements in the toluene gel. D) Stacking models for the gelator arrangements in *i*-butanol gel.

<b>Table 2.</b> Characteristic Vibrations (cm <sup>-1</sup> ) of the azo-BDAI	)
Obtained in Solvent (s) and Xerogel (x) States.	

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States	υ(N-H)	υ(C=O)	δ(N-H)
DMF (s)	3459	1667	1497
toluene (x)	3366,3312	1734,1685,1629	1522
$CCl_4(x)$	3363,3313	1735,1685,1629	1522
<i>i</i> -butanol (x)	3363,3316	1731,1686,1630	1524
acetone (x)	3365,3318	1735,1686,1630	1523

#### 2.6. XRD Studies and DFT analysis

To further understand the molecular arrangements and the orientation of azo-BDADs in the gel state from different solvents, the xerogels from toluene and *i*-butanol were examined by XRD. In Fig. 4B, two broad diffraction peaks corresponding to the d spacing of 3.13, 1.54 nm in the low angle region were observed in toluene. The approximate d spacing ratio of 1:1/2 was consistent with a lamellar structure.<sup>39</sup> Taking the intermolecular strong hydrogen bonding interaction into consideration, it could be speculated that an interdigitated bilayer structure was obtained in toluene, which was proved by computational method of density functional theory (DFT) in Fig. 4C. The azo-BDADs packed into interdigitated bilayer structures mainly through the

hydrogen-bonds of the N–H…N type binding (Fig. S7A), M which agreed with our previous experimental conclusion. Whereas, the length of 3.13 nm corresponded neither with the extended molecular length of azo-BDAD (3.0 nm) nor with twice the length (6.0 nm), which was the results of the interdigitation of the alkyl chains in the aggregates.<sup>35</sup> With the aliphatic alkyl chain interdigitated together, the amide moieties organized into a welldefined array which leads to the strong hydrogen bonding interaction between gelator molecules. Similar results were also observed in the xerogels from CCl<sub>4</sub> (Fig. S6A).

Nevertheless, as for the xerogels from *i*-butanol, three pronounced peaks corresponding to the d spacing of 4.90, 2.49, and 1.67 nm appeared in the low-angle region. The approximate d spacing ratio of 1:1/2:1/3 was also indicative of the formation of a lamellar structure.<sup>41</sup> According to the preceding results, we suspected gelators formed gels in one-above-the-other assembly model in *i*-butanol, which was also verified by computational method of density functional theory (DFT) in Fig. 4D. In hydrogen bond breaking polar solvents (e.g. i-butanol), the formation of intermolecular hydrogen bonds are weakened. As a result, intermolecular  $\pi$ - $\pi$  stacking interaction becomes the dominant driving forces, which prefer the one-above-the-other assembly model (Fig. S7B). It should be noted that the width of the column as calculated from the energy minimized orientations was longer (5.3 nm) than the distance (4.9 nm) obtained from the low-angle diffraction peaks presented in *i*-butanol xerogel, which could be explained by some degree of tilt for the stacking planes.<sup>39</sup> Similar results were also observed in the xerogel from acetone (Fig. S6B).

#### 2.7. Pollutants removal study

Water purification with gel-like materials is one of the most popular water treatment methods nowadays.<sup>7</sup> Phase-selective gelation, which is used for removing aromatic pollutants (which is always highly carcinogenic and toxic) from waters, is urgently required but challenging.<sup>27</sup> To check the phase-selective gelation performances of azo-BDAD for potential application in the water purification, the commonly used RhB dye was selected as the "pollutant" due to its good solubility in water while relatively lower solubility in common organic solvents. To a 2 mL of RhB aqueous solution (0.03 mM), 1.0 mL of toluene was added. Then 10 mg of the gelator was added to the mixture and heated until the gelator was dissolved in the toluene layer. Cooling to the room temperature gave the azo-BDAD gel in the above toluene layer. After 36 hours, the original purple red aqueous layer with RhB gradually turned colorless, indicating that almost all of the RhB was removed from aqueous layer to the gel. As a control experiment, the color of RhB solution without organogels had almost no change in the same condition (in Fig. S8B). The dye was adsorbed in the toluene gel and purified water could be collected by simple filtration. The purification efficiency was determined using UV-Vis adsorption spectroscopy and calculated as high as 97% (Fig. S8A). Thus, though the azobenzene gelator itself is toxic, it could be used for absorbing water-soluble organic dyes from water, providing a feasible and efficient proofof-concept approach for removing the toxic dyes from water.

#### 3. Conclusion

We successfully designed and synthesized an efficient photoresponsive organogel based on an azobenzene derivative, which can achieve the sol-gel transition reversibly by heat/cool process or UV/visible light irradiation. The gelator shows a good gelation ability in organic solvents ranging from non-polar solvents to polar solvents due to hydrogen bonding and  $\pi$ - $\pi$  stacking. Interestingly, two different kinds of packing models

were discovered in non-polar and polar solvents, respectively. In non-polar solvents, an interdigitated stacking model was preferred in the self-assembled 3D micromorphology of the gels, due to the inversed strong hydrogen bonding interactions and weak  $\pi$ - $\pi$  stacking interactions; Whereas in polar solvents, the gelator self-assembled into 3D nanostructure via a one-abovethe-other stacking model due to strong  $\pi$ - $\pi$  stacking and weak hydrogen bonding interactions. More importantly, as an efficient room-temperature phase-selective gelator, it could offer a simple and feasible approach for removing the RhB dye from water with purification efficiency as high as 97%.

#### 4. Experimental Section

#### 4.1. Materials

All starting reagents were commercially available and of analytical purity and used without further purification. Solvents used were analytical grade without further treatment, except the dimethylformamide for amidation reaction and those for optical tests, which were purified according to standard laboratory methods. Thin layer chromatography (TLC) analysis was performed on silica-gel plates. Column chromatography was operated using silica-gel purchased from Qingdao Haiyang Chemical (China).

#### 4.2. Instruments

NMR spectra were recorded on Bruker AM-400 spectrometers, and high resolution mass (HRMS) spectra were recorded on a Waters LCT Premier XE spectrometer. UV/Vis spectra were recorded on Varian Cary 500 (1 cm quartz cell) at 25 °C. Fourier transform-infrared (FT-IR) spectra of samples were recorded on IR Trace-100 (Shimadzu) spectrometer, and the samples were ground with anhydrous KBr and pressed into thin wafers and scanned between the wavelengths of 4000 and 400  $\text{cm}^{-1}$ . Scanning electron microscope (SEM) images were obtained on a JEOL JSM-6360LV, and the samples were prepared by the airdrying method and then coated with gold. Oscillatory rheology measurements were performed using a Physica MCR501 (Anton Paar GmbH, Austria) rheometer equipped with 25 mm parallel plate geometry. All the gels were tested at a 0.1% of strain. X-ray diffraction (XRD) was achieved on a Rigaku D/Max-2550 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å), which was operated at 40 kV, 100 mA. Irradiation at 365 nm was carried out using a hand-held UV lamp (the power density is ca.  $2.0 \text{ W/m}^2$ ), and visible irradiation using a flashlight (the power density is ca.  $150 \text{ W/m}^2$ ) with a broad band interference filters (Shenyang HB optical Technology) for  $\lambda$  irr > 400 nm).

#### 4.3. Synthesis

The target compound azo-BDAD was prepared from the amidation reaction of p-(Phenylazo)benzoic acid (1) and N-Boc-1, 12-diaminododecanein (2) in the presence of BOP/TEA. The detailed synthetic approach and methods are provided in Supporting Information, Scheme S1.

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