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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, π-π 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).

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.[1−9] During the formation of the gels, the noncovalent interactions, such as hydrogen-bonding, π−π stacking, host-guest interactions, charge-transfer (CT) interactions, metal ion to ligand coordination and electrostatic interactions,[10−17] 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, low-molecular-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 stimulate-responsive sol-gel phase transition performances. The stimulus could be heat,[18] light,[2,19−21] sound,[22] pH,[23] host-guest interaction,[24,25] complexation,[26] and oxidative/reductive reactions,[27] etc., and the combination of several independent/synergetic stimuli creates multifunctional smart gels.[28−34] 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 self-assembly, resulting in different morphologies and properties of the organogels.[35−38] For instance, Duan et al. showed that the supramolecular chirality of an azobenzene LMOG based organogel could be modulated via solvent polarity.[39] Recently, Zhang et al. reported a Fmoc-amino acid gelator based supramolecular gel, whose morphology could also be tuned by changing the solvent polarity.[40] 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.

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 self-assembled to nanorod structure with the model of an interdigitated bilayer,

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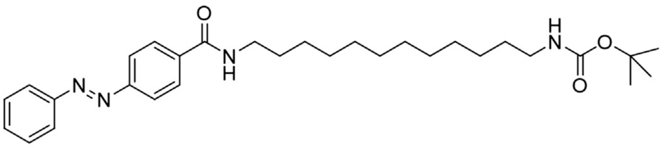

azo-BDAD

Scheme 1. The structure of azo-BDAD.

whereas the gelators stacked with a one-above-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 self-assembled 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.[41] 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.

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_4 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_4 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,[38,39] 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).

Table 1
Results of gelation testing in various organic solvents and water at room temperature.[a]

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

[a] G = turbid gel; TG = transparent gel; PG = partial gelation; P = precipitate; I = insoluble upon heating.

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.[43–46] 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 (1.0×10^{-4} M). Upon irradiation with light of 365 nm for 10 min, the decrease of π-π^* absorbance band at 328 nm and the blue-shift of n-π^* 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 photo-switchable sol-gel transition was then conducted in a quartz cell. After UV light (λ = 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 min ($\lambda > 400$ nm). Similar phenomena were obtained when *i*-butanol was used as the solvent (Fig. S3). Surprisingly, compared to the photo-switchable 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.

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 °C. 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

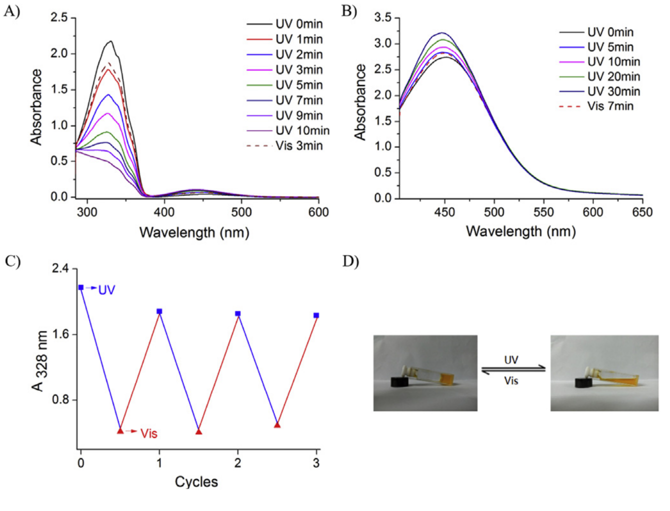

Fig. 1. A) Absorption spectra of azo-BDAD in toluene under UV light (365 nm) and visible light irradiation for different times. B) Absorption spectra of azo-BDAD gels from toluene under UV (365 nm) and visible light for different times. C) The cycles of absorbance intensity at 328 nm in toluene. D) The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