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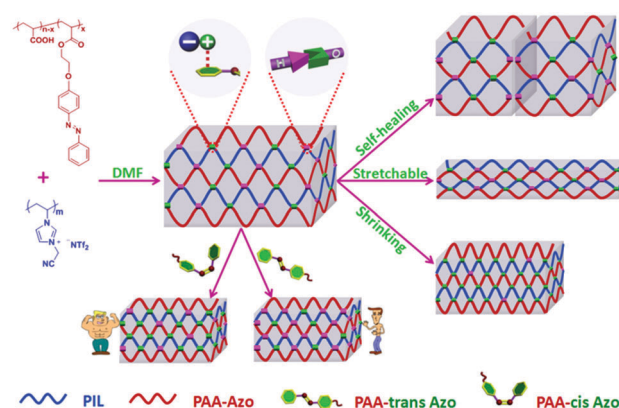
# An autonomic self-healing organogel with a photo-mediated modulus†

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**A new method is described for fabricating autonomic, self-healing, deformable organogels. We combined imidazolium-based poly(ionic liquid) (PIL) and azobenzene-grafted poly(carboxylic acid) (PAA-Azo) in *N,N*-dimethyl formamide. Further, complexing PIL with unirradiated (*trans*) or irradiated (*cis*) PAA-Azo tuned the elastic modulus of the organogel.**

Polymeric networks mediated by non-covalent interactions are more sensitive to their external environment and return more easily to their original state compared to covalently-cross-linked networks.<sup>1</sup> As a result, they have attracted significant attention in materials and chemical science.<sup>2</sup> Owing to the unique features of the weak interactions, these polymer networks can respond to external stimuli while maintaining stability and functionality similar to covalently bonded systems.<sup>3</sup> Although significant progress has been made in organogels, exploring novel materials with intrinsic self-healing properties *via* non-covalent interactions,<sup>4</sup> such as the ubiquitous cation- $\pi$  interaction, is of outstanding importance in determining the structure and function of supramolecular assemblies in chemistry, materials science, and biology.<sup>5</sup>

Poly(ionic liquid)s (PILs), derived from the polymerization of ionic liquid (IL)-based monomers, can combine some unique features of ILs with the mechanical properties of polymers.<sup>6</sup> Thus, PILs are of interest for solid ion conductors, CO<sub>2</sub> conversion, porous materials, and carbon precursors.<sup>7</sup> However, there are few reports on the fabrication of PIL-based supramolecular gels through non-covalent interactions. Herein, we report a novel supramolecular organogel which is prepared by combining imidazolium (Im)-based PIL, poly(3-cyanomethyl-1-vinyl imidazolium bis(trifluoromethane sulfonyl)imide) (PCMVImTf<sub>2</sub>N),



**Scheme 1** Schematic illustration of preparation of a PIL@PAA-Azo organogel and its versatile performances.

and azobenzene (Azo)-grafted poly(acrylic acid) (PAA-Azo). PIL@PAA-Azo organogels are both self-healable and stretchable (Scheme 1). Yet, they shrink in the presence of guanidine hydrochloride (Gdn-HCl). Additionally, azobenzene groups show reversible *cis-trans* photoisomerization and PIL@PAA-Azo organogels have a higher modulus when PIL is complexed with PAA-*cis*-Azo than with PAA-*trans*-Azo. These versatile properties of PIL@PAA-Azo organogels were understood in terms of the synergistic interactions of cation- $\pi$  and H-bonding.

PCMVImTf<sub>2</sub>N with a molecular weight of  $1.12 \times 10^6$  g mol<sup>-1</sup> was prepared by free radical polymerization (Scheme S1, Fig. S1 and S2, ESI†). PAA-Azo was prepared by grafting azobenzene groups onto PAA ( $M_w = 2.5 \times 10^5$  g mol<sup>-1</sup>) (Scheme S2, ESI†).<sup>8</sup> The grafting density measured using <sup>1</sup>H NMR spectroscopy was 11.3 mol%. PIL@PAA-Azo organogels were prepared by mixing DMF solutions of PCMVImTf<sub>2</sub>N and PAA-Azo. Although the solvent for both polymer solutions was DMF, the two polymer solutions initially separated after combining the PAA-Azo and PIL solutions (Fig. S3, ESI†). After agitating and standing for several minutes, a semitransparent organogel was obtained, which was confirmed *via* vial inversion. When the mass ratio of

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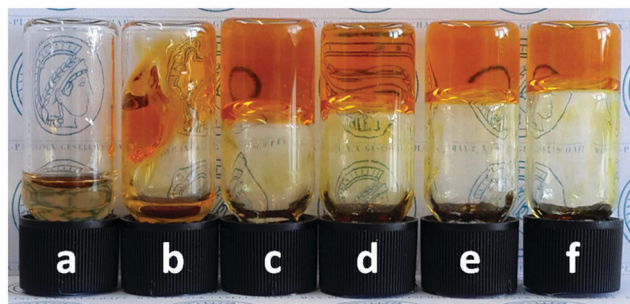


Fig. 1 Photographs of PIL@PAA-Azo organogels (10.0 wt%) with different compositions: (a) PIL@PAA, 2 : 1; (b) 4 : 1; (c) 2 : 1; (d) 2 : 1 after UV irradiation; (e) 1 : 1; (f) 2 : 3, mass ratio of PIL to PAA/PAA-Azo.

PIL to PAA-Azo was 4 to 1, only a high-viscosity solution was obtained rather than an organogel (Fig. 1). However, all the solutions were gelled when the mass ratio was less than 2 : 1. For comparison, PIL solution was also mixed with pure PAA under identical conditions (PIL : PAA = 2 : 1, w/w) and no gelation occurred. These results confirmed that the introduction of azobenzene groups was critical for the formation of the organogels.

PIL@PAA-Azo organogels exhibit some interesting features. Firstly, the organogel could autonomically self-heal after it was damaged. When two pieces of gel were kept in contact with each other without applying pressure (Video 1, ESI<sup>†</sup>), the two gels joined together quickly. The combined pieces did not separate even by pulling from two different ends. To demonstrate the self-healing ability of PIL@PAA-Azo organogels more practically, a PIL@PAA-Azo organogel was prepared in a vial and cut with a notch (Fig. 2). Without any external stimuli, the notch became smaller and disappeared completely within 6 h. These results demonstrated that the PIL@PAA-Azo organogel can self-heal autonomically after damage. Additionally, the PIL@PAA-Azo organogel is highly stretchable (Video 2, ESI<sup>†</sup>). The organogel can withstand the tensile stress of elongation to 5 times its original length.

A PIL@PAA-Azo organogel with a PIL to PAA-Azo ratio of 2 : 1 (w/w) was studied using dynamic rheology (Fig. S4, ESI<sup>†</sup>). PIL@PAA-Azo presented a higher storage modulus ( $G'$ ) than loss modulus ( $G''$ ) within the frequency range investigated. This indicated quasi-solid-state behavior, confirming the formation of an organogel. *Trans-cis* isomerization of Azo has been widely utilized to fabricate gel-sol transitions and association/dissociation systems.<sup>10</sup> To that end, the photoresponse of PIL@PAA-Azo

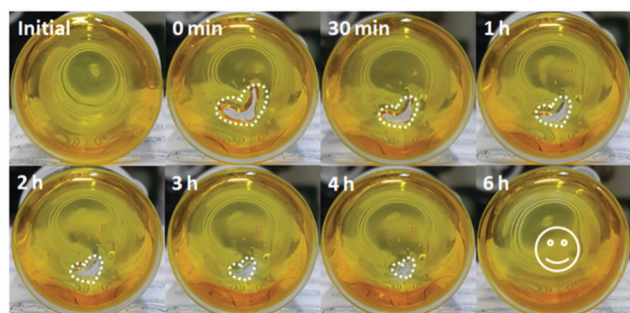


Fig. 2 Self-healing process of the PIL@PAA-Azo organogel.

organogels was studied using UV-vis spectroscopy. As depicted in Fig. S5 (ESI<sup>†</sup>), PAA-Azo exhibited  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition absorption bands at 352 nm and 446 nm, respectively. Approximately 65% *trans*-isomer in PAA-Azo transformed into a *cis*-isomer under UV irradiation ( $0.45 \text{ mW cm}^{-2}$ ) for 90 s. After subsequent green light irradiation ( $0.9 \text{ mW cm}^{-2}$ ) for 90 s, the *cis*-isomer completely transformed back into the *trans*-isomer. These results demonstrate that the reversible isomerization of PAA-Azo can be mediated by alternative UV and visible light irradiation. The photocontrol of the PIL@PAA-Azo organogel can alternatively be applied in solution, before the formation of the organogel. By irradiating the PAA-Azo solution with UV light before the complexation, complete isomerization of Azo units was achieved. Then, the PAA-*cis*-Azo solution was immediately combined with PIL and the resultant organogel was studied using dynamic rheology. Both  $G'$  and  $G''$  of the PIL@PAA-*cis*-Azo organogel were much higher than those of the PIL@PAA-*trans*-Azo organogel (prepared using PAA-Azo without UV light, Fig. 3). This performance indicates that the interaction of PIL with PAA-*cis*-Azo was stronger than that with PAA-*trans*-Azo. Thus, photo-control of the bulk modulus of the PIL@PAA-Azo organogel was achieved. The mechanism of the photo-controlled modulus is presented below.

The different binding abilities of PAA-*trans*-Azo and PAA-*cis*-Azo with PIL were estimated using isothermal titration calorimetry (ITC). The enthalpy changes ( $\Delta H$ ) in the process of mixing PIL solution ( $5 \text{ mM}^{-1}$ ) with PAA-Azo solution ( $1 \text{ mM}^{-1}$ ) before and after UV irradiation were  $3.61 \text{ kcal mol}^{-1}$  and  $2.75 \text{ kcal mol}^{-1}$  (Fig. 4). Fig. 4 also illustrates that the binding affinity ( $K_B$ ) for PIL and PAA-Azo was  $5.1 \times 10^4 \text{ M}^{-1}$  before and  $1.19 \times 10^5 \text{ M}^{-1}$  after UV light irradiation. Thus, PIL was more inclined to bind PAA-*cis*-Azo rather than PAA-*trans*-Azo, consistent with the rheology results. The binding affinity of PIL with PAA-*cis*-Azo is also much higher than alpha cyclodextrin compounds with *trans*-Azo.<sup>10</sup> As a result, a much stronger organogel can be obtained by complexing PIL with PAA-*cis*-Azo compared to previous work (Scheme 2). And, in addition, the modulus of the PIL@PAA-Azo organogel can be tuned through photo-induced isomerization of PAA-Azo.

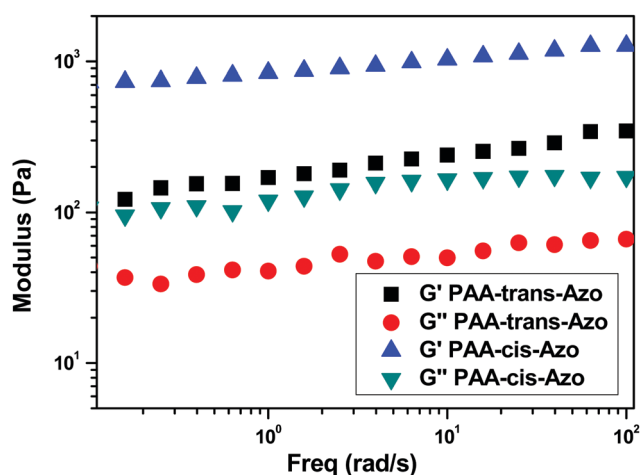


Fig. 3 Rheological properties of the 10 wt% PIL@PAA-Azo organogel (PIL : PAA-Azo = 1 : 1, w/w) at 25 °C (storage modulus  $G'$  and loss modulus  $G''$  as a function of frequency).



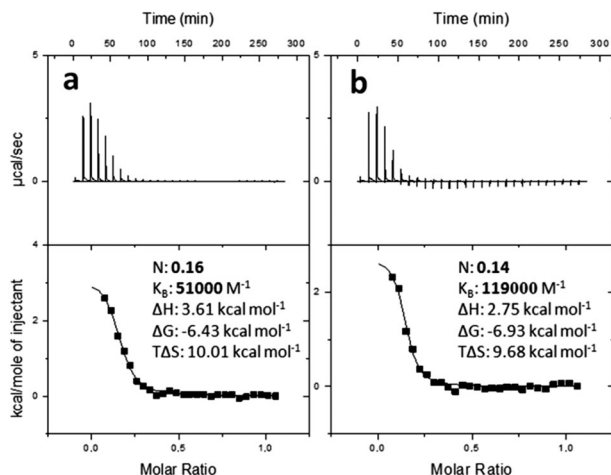
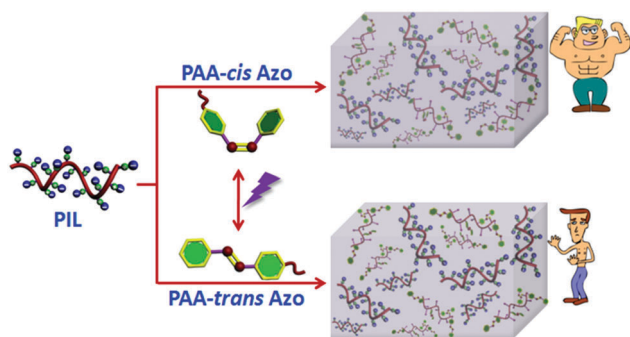


Fig. 4 Heat effects measured using ITC in the titration of PAA-Azo by PIL in traditional mode: (a) PAA-Azo solution before UV irradiation; (b) PAA-Azo solution after UV irradiation ( $N$ , stoichiometric ratio;  $K_B$ , binding affinity;  $\Delta H$ , enthalpy;  $\Delta G$ , free energy;  $T\Delta S$ , entropy).



Scheme 2 Illustration of the photo-tunable modulus of the PIL@PAA-Azo organogel.

Im-IL has been found to form H-bonding interactions with polar molecules.<sup>11</sup> Thus, H-bonding between carboxyl groups and Im-IL is likely one of the driving forces for the formation of the PIL@PAA-Azo organogel. Since it is unlikely that an organogel can be produced only by H-bonds, there must be some other interactions between the Azo groups and PIL. Based on the structures of PIL and PAA-Azo, we suggest that cation- $\pi$  interactions between PIL and PAA-Azo lead to the formation of a gel. To verify our hypothesis, <sup>1</sup>H NMR spectroscopy was utilized to investigate the interactions between PIL and PAA-Azo. Curves a and b in Fig. S6 (ESI<sup>†</sup>) depict the resonance absorption signal of PAA-Azo and PIL, respectively. All the characteristic signals ascribed to azobenzene and Im units were recognized, such as *trans*-Azo (7.16, 7.54, 7.85 ppm), Im (9.22, 7.82 ppm) and N-CH<sub>2</sub>-CN (5.49 ppm). Additionally, the proton signal ascribed to free -COOH disappeared, which was probably due to deuterium-hydrogen exchange in the presence of trace water. However, the proton signal ascribed to -COOH emerged when some PIL was added into PAA-Azo solution. This is probably because that H-bonding between PIL and PAA-Azo can prevent the deuterium-hydrogen exchange. Moreover, a new signal (6.84 ppm) emerges after the

addition of PIL. Simultaneously, the signal ascribed to the Im unit (9.22 ppm) shifted to a low field, which probably points to an interaction between Im and Azo units. When more PIL was added, the new signal also enhanced a little. Subsequently, the sample was irradiated by UV light. It can be found that the new signal enhanced greatly and the *trans*-Azo signal attenuated. After green light irradiation, the new signal also attenuated. The results demonstrated that the new signal is ascribed to *cis*-Azo, and the formation of *cis*-Azo is possible because of the presence of PIL.

Additionally, shrinking of the PIL@PAA-Azo organogel was observed when it was treated with Gdn-HCl (Fig. 5). The treated organogel became much stronger than the one before Gdn-HCl treatment (Video 3, ESI<sup>†</sup>). Since Gdn-HCl is known to break H-bonds between biomacromolecules, this toughening likely stems from an increase in cation- $\pi$  interactions (see below), which are stronger and thus toughen the gel.<sup>9</sup> Thus H-bonding is one of the forces driving the formation of the organogel and determining its properties of deformation.

According to the above results, a plausible mechanism for the versatile performance of a PIL@PAA-Azo organogel was postulated. Cation- $\pi$  and H-bonding interactions were taken as the main driving forces for the formation of the organogel. When the gels are damaged by an external force, new cation- $\pi$  and H-bonding interactions can take place on the interface between two pieces of organogel. Therefore, the broken organogel can reform intermolecular bonds to self-heal. Compared with cation- $\pi$  interactions, the H-bonding interaction is relatively weaker.<sup>12</sup> Thus, H-bonds between PIL and PAA-Azo are more easily destroyed during stretching, whereas cation- $\pi$  interactions more likely remain intact. However, in the presence of Gdn-HCl, most H-bonds will break while leaving the cation- $\pi$  interactions unaffected. Simultaneously, due to the cleavage of H-bonds, some new binding sites for cation- $\pi$  interactions will become available. Thus, the solvent is extruded due to the cleavage of the H-bonding network and formation of new cation- $\pi$  interaction which causes the PIL@PAA-Azo organogel to shrink.

In summary, a novel autonomic, self-healing, and deformable organogel was prepared by complexing PIL and PAA-Azo in

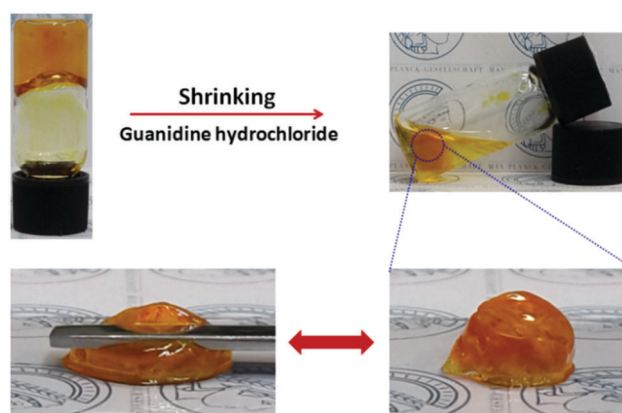


Fig. 5 Shrinking behavior of the PIL@PAA-Azo organogel in the presence of Gdn-HCl.





DMF. The formation of the PIL@PAA-Azo organogel was due to H-bonding and cation- $\pi$  interactions. The modulus of the PIL@PAA-Azo organogel was photo-tuned by combining PIL with different Azo isomers. Our findings thus provide an alternative tactic for fabricating self-healing materials with a photo-tunable modulus. These organogels may be used as solid electrolytes, which can find extensive application in the fields of supercapacitors, batteries, and flexible electronics.

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