



# A fluorescent non-conventional organogelator with gelation-assisted piezochromic and fluoride-sensing properties



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## ABSTRACT

A fluorescent non-conventional organogelator, 2-(anthracen-9-yl)-4,5-diphenyl-1*H*-imidazole, was found to be an integrated platform with multiple functionality. Balanced supramolecular interactions, based on  $\pi$ - $\pi$  stacking between aromatic rings and intermolecular hydrogen bonding between neighboring imidazole rings, promote solvent gelation with a critical gelation concentration of 1.2 mg/mL ( $3.03 \times 10^{-3}$  mol/L) in cyclohexane. The intermolecular interactions can be modified by mechanical force, giving it piezochromic properties, and the xerogel has a much higher specific surface area, conferring higher sensitivity to pressure compared to the crystalline powder. The presence of imidazole in the gelator enables a selective response to fluoride anion. Addition of 0.3 equivalents of fluoride anion destroyed the gel (1.2 mg/mL), resulting in precipitation of a red solid that was isolated and identified by <sup>1</sup>H NMR and X-ray single crystal analysis. The red solid can be converted to the starting gelator molecule by addition of water to provide a recyclable chemosensor. This system represents a unique example of a simple organogelator with multiple functionality.

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## 1. Introduction

Integration of multifunctional systems with stimuli-responsive behaviour has proven to be an effective strategy for practical applications in many research fields [1–3]. Supramolecular gels are suitable carriers for combining different physical properties [4–8] and a variety of functionality has been introduced into gel systems, including visual-size molecular recognition [4,5] and stimulus-responsive molecular switching [6–8].

Gel formation is usually promoted by multiple non-covalent interactions, such as hydrogen bonding, van der Waals interactions,  $\pi$ - $\pi$  stacking, and solvophobic forces. Recently,  $\pi$ -conjugated low-molecular-weight gelators (LMWGs) have attracted considerable interest because of their unique optical and optoelectronic properties, such as multicolour emission, enhanced fluorescence, and sensing capabilities [9–12]. Most of the  $\pi$ -conjugated LMWGs reported so far bear alkyl chains to balance their

solubility and crystallinity, but these groups do not contribute to their photoelectric properties. Rational design of LMWGs containing only rigid  $\pi$ -conjugated structures is a significant challenge. The self-assembly in LMWGs must balance parameters influencing solubility with the driving forces for solvent gelation. However, a few such rigid LMWGs without alkyl chains have been reported, in which the balanced  $\pi$ - $\pi$  interactions between various aromatic rings play an important role in gel formation [13–17]. Some xerogels of supramolecular gelators containing small substituents are mechanochromic, but no mechanochromic examples of gelators containing only aromatic rings as substituents have been reported [18–22].

In addition to  $\pi$ - $\pi$  interactions between aromatic rings, non-conventional hydrogen bonding between aromatic rings can also promote organogel formation, and imidazole has been widely used for this purpose [23–28]. There are only a limited number of aromatic rings that have an active proton that can participate in intermolecular hydrogen bonding. The active proton of the imidazole unit could also respond to external stimuli, enabling construction of multi-stimuli-responsive materials, and fluoride detection has been widely investigated [29–36]. The small ionic radius, high charge density and hard Lewis basic nature of fluoride

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may permit removal of the imidazole active proton and/or participation in supramolecular interactions (halogen bonding), resulting in significant structural and photophysical changes. Fluoride detection in the gel state is very popular because fluoride usually induces selective gel collapse, making the detection more visual and facilitating gelator recycling [37–43].

Anthracene is a highly planar aromatic system and usually exhibits strong  $\pi$ – $\pi$  interactions in organic solvent, which is a vital driving force for gelation of solvents. Recently, we described a piezochromic anthracene-based molecule with a rigid structure (**ADPI**) [44]. Single crystal X-ray analysis of **ADPI** indicated that  $\pi$ – $\pi$  interactions between anthracene planes and hydrogen bonding between imidazoles varied in different environments. Considering that hydrogen bonding and intermolecular  $\pi$ – $\pi$  stacking are potential driving forces for gelation, we postulated that **ADPI** would gelate organic solvents and combine multiple functionality. Indeed, we found that **ADPI** could gelate a non-polar organic solvent, and that the gel could sensitively and selectively detect fluoride. Further, the xerogel has a large specific area, making it more sensitive to pressure compared to the crystalline solid. Herein, we report that this simple molecule can act as a platform to integrate multiple functions, *via* construction of variable supramolecular forces.

## 2. Experimental

All starting materials were obtained from commercial supplies and used as received. Anhydrous THF was obtained by distillation of commercial analytical-grade THF after treated with sodium.  $^1\text{H}$  NMR spectrum was recorded on Bruker instruments, using  $\text{CD}_3\text{CN}$  or cyclohexane- $d_{12}$  as solvent. XRD diagrams were tested on a D8 ADVANCE (Bruker). SEM images of the xerogels were obtained by using SSX-550 (Shimadzu) and FE-SEM S-4800 (Hitachi) instruments. TEM was performed on a JEOL JEM2011 apparatus operating at 200 kV. Uv–vis and fluorescent measurements were carried out on Shimadzu UV-2600 and Hitachi F-4600, respectively. Single-crystal X-ray diffraction data were collected on a Bruker APEX II CCD diffractometer with graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature, and the CCDC number is 1031198.

## 3. Results and discussion

**ADPI** is found to be able to gelate cyclohexane and solvent mixtures containing cyclohexane (e.g., dichloromethane, chloroform, ethyl acetate) to form a semi-transparent gel. The critical gelation concentration is 1.2 mg/mL ( $3.03 \times 10^{-3} \text{ mol/L}$ ) in cyclohexane, and the gel-sol transition temperature was measured to be 45 °C. To investigate the morphology of the gel, a xerogel sample prepared by freeze-drying was subjected to scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From the SEM and TEM images (Fig. 1), the gel was found to be composed of intricately intertwined retiform structures, formed by bundles of long and thin fibres (approximately 30 nm in diameter). X-ray diffraction of the xerogel showed only a broad peak around 20° (Fig. S1A, corresponding to a  $d$ -spacing of 4.40 Å), probably related to the weak  $\pi$ – $\pi$  interaction [44]. However, there were two moderate diffractions in the small angle range with  $d$ -spacings of 16.63 Å (100) and 12.38 Å (010), indicating long range regular packing of gelator molecules in the gel (Fig. S1B).

The absorption band of **ADPI** gel was centred at 380 nm, matching the absorption in dilute cyclohexane solution, but accompanied by disappearance of the fine structure and broadening of the spectra (Fig. 2). Fluorescence of the cyclohexane gel was at 490 nm (blue-green fluorescence), also consistent with that of the solution in cyclohexane. However, both the fluorescence and absorption bands in the gel state were broader than those in solution. Temperature-dependent fluorescence spectra indicated that the emission centre remained almost invariable as the temperature was increased, but the starting point of the emission band displayed a red-shift (Fig. S3). These data suggest very weak intermolecular  $\pi$ – $\pi$  stacking between the anthracene and phenyl rings in the gel state.

Considering that potential intermolecular hydrogen bonding between imidazole rings might play an important role in gelation, temperature-dependent  $^1\text{H}$  NMR analysis was conducted. Fig. 3 shows the  $^1\text{H}$  NMR spectra of **ADPI** gel in cyclohexane- $d_{12}$ . In the gel state, the active proton on imidazole appeared at 9.60 ppm as a broad peak. As the temperature was increased, this peak clearly shifted up-field. At 60 °C, the imidazole proton signal was located at 8.98 ppm. The significant up-field shift (0.62 ppm) at higher

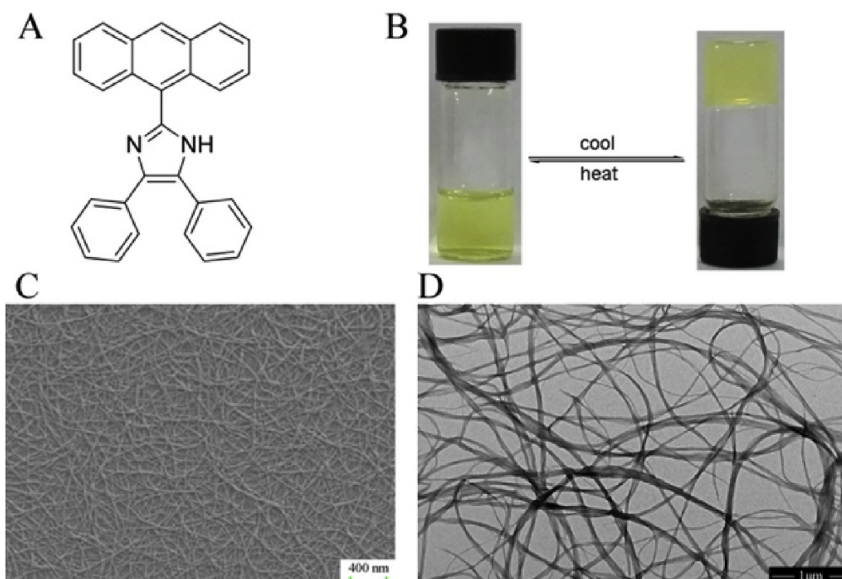


Fig. 1. (A) Chemical structure of **ADPI** and (B) its sol-gel transition in cyclohexane; (C) SEM and (D) TEM images of cyclohexane xerogel.

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