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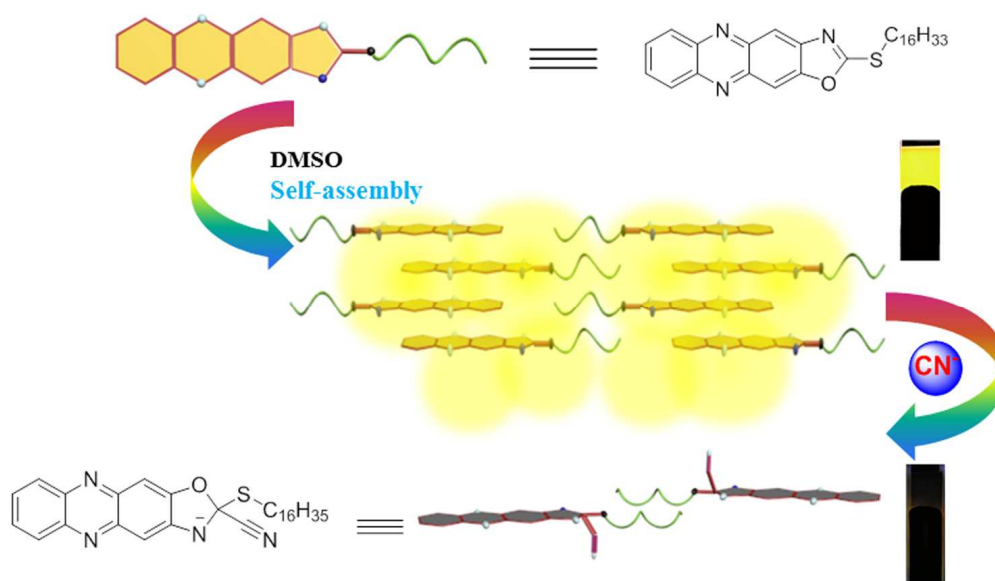
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Graphical Abstract:

A supramolecular gel (**PN-G**) was constructed, which could ultrasensitively detect cyanide.

A Self-Assembled Supramolecular Gel Constructed by Phenazine Derivative and Its Application in Ultrasensitive Detection of Cyanide

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Abstract:

In this work, we constructed a supramolecular gel (**PN-G**) by phenazine derivative, which can ultrasensitive detect cyanide (detection limit equals to 4.18×10^{-10} M). The decrease of fluorescent intensity displayed a linear relationship in the range of 0-0.4 equivalents of cyanide. And no significant fluorescence quenching was observed for all used interfering ions. The cyanide recognition mechanism of **PN-G** was verified by XRD, NMR, MS and SEM. With addition of cyanide to the supramolecular gel (**PN-G**), cyanide broken π - π stacking of **PN-G**, and then **PN-G** undergoes a nucleophilic addition reaction with CN^- , resulting in fluorescence quenched.

Keywords: supramolecular gel, phenazine derivative, cyanide, assemble, nucleophilic addition

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1. Introduction

Noncovalent interactions (NCI), such as hydrogen bonds [1-2], hydrophobic interaction [3], π - π stacking [4-5], C-H- π [6-7], exo-wall π - π interactions [8], cation- π [9-10] and anion- π [11-12] interactions et al, arise from the balance between attractive and repulsive effects and are usually classified into multipole-multipole interactions are ubiquitous in nature [13-14]. They play significant roles in broad areas, for instance: supramolecular chemistry, structural biology, and material science [15-16]. As we all know, the DNA/RNA double-helix is a life-matter example in which stabilization arises from both π -stacking and hydrogen-bonds between the base pairs [17-18].

In recent years, benefiting from the dynamic and reversible nature of noncovalent interactions (NCI), supramolecular gels have attracted increasing attention in diverse fields including, sensors, biomedicine, environmental monitoring, and materials synthesis [19-22]. In particular, reversible nature in the supramolecular gels and the physical properties of these gels in response to a specific signal input are thus pivotal for the creation of smart materials [23-25]. The integration of selective molecular recognition units into the gelator molecules is advantageous to create specific responses or develop multistimuli-responsive gels. The recognition process of these units inevitably affects the structure of the supramolecular gels, resulting in changes in macroscopic properties. In particular, anions and metal ions also play a crucial structural and regulatory role in supramolecular gels [26-28].

Cyanide (CN^-) is known for their high toxic effects [29-31]. Therefore, the

sensitive and selective detection of this extremely toxic anion is highly necessary. In recent years, various analytical and spectroscopic methods have been developed to detect metal ions and anions in various chemical and biological systems, but problems associated with high cost and low sensitivity limit their use [32-45]. Recently, our group has devoted to comprehensive investigations of the phenazine derivative assembly mechanism and supramolecular gel, in which the close π - π stacking of phenazine derivatives is the driving factor of the final structures [46-48]. In this work, 2-(hexadecylthio)oxazolo[4,5-b]phenazine (**PN**) was successfully synthesized (Scheme 1). **PN** was capable of forming supramolecular gel in DMSO solution by van der Waals interaction and π - π stacking. We surveyed the response of **PN** gel (**PN-G**) to various anions in water. The result displayed that when added cyanide anion at room temperature, the fluorescence of **PN-G** didn't show any change. Nevertheless, after heating from the gel to the sol and gelling again, the fluorescence was dramatically quenched from bright yellow.

2. Experimental section

2.1. Materials and Characterizations

All reagents were commercially available and used as supplied without further purification. The fluorescence spectra were recorded on a Shimadzu RF-5301PC fluorescence spectrophotometer. ^1H NMR (400 MHz and 600 MHz) and ^{13}C NMR spectra (151 MHz) were carried out with a Mercury-600 BB spectrometer. High-resolution mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. Melting points were measured on an X-4 digital melting-point

apparatus. The X-ray diffraction (XRD) pattern was generated using a Rigaku RINT2000 diffract meter equipped (copper target; $\lambda = 0.154073$ nm). Scanning electron microscopy (SEM) images of the xerogels were investigated using JSM-6701F instrument.

2.2. Synthesis of receptor molecule PN Compound

A mixture of oxazolo[4,5-b]phenazine-2-thiol (0.253 g, 1 mmol), K_2CO_3 (0.138 g, 1 mmol), KI (1.992 g, 1.2 mmol), 1-bromohexadecane (0.365 g, 1.2 mmol) and acetonitrile (50 mL) were added to a 100 mL round-bottom flask under nitrogen atmosphere. The reaction mixture was stirred at $80^\circ C$ for 72h. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 20:1) as the eluent, compound **PN** as yellow solid (0.393 g, yield 80%) was isolated, (Fig. S1, Fig. S2 and Fig. S3). m.p. $>300^\circ C$, 1H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.24 (d, $J = 2.8$ Hz, 2H), 8.13 (s, 1H), 7.83 (dd, $J = 3.5, 1.3$ Hz, 2H), 3.43 (s, 2H), 1.90 (s, 2H), 1.52 – 1.51 (m, 2H), 1.37 (d, $J = 7.8$ Hz, 4H), 1.24 (s, 22H), 0.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.45, 153.76, 146.53, 142.66, 142.58, 141.62, 141.27, 130.19, 130.15, 129.29, 129.11, 114.92, 105.76, 32.64, 31.89, 29.67, 29.66, 29.64, 29.62, 29.60, 29.53, 29.42, 29.33, 29.04, 29.03, 28.65, 22.66, 14.09. ESI-MS m/z: Calcd for $C_{22}H_{13}N_4O_2$ [**PN** + H] $^+$: 478.2892; Found 478.2881.

2.3. General Experimental Procedures

2.3.1. General procedure for fluorescence spectra experiments.

All the fluorescence spectroscopy was carried out in DMSO solution on a Shimadzu RF-5301 spectrometer. Any changes in the fluorescence spectra of

compound were recorded on addition of sodium salt, while gelation concentration of the sensor was 5% in all experiments. Sodium salt (1 M) of anions (F^- , Cl^- , Br^- , I^- , AcO^- , PO_4^{3-} , SO_4^{2-} , CO_3^{2-} , NO_3^{2-} , S^{2-} , HS^- , ATP , SO_3^{2-} , SCN^- and CN^-) were used for the fluorescence experiments.

3. Result and Discuss

Due to the excellent self-assemble properties of phenazine [49-52], and the introduced of alkyl group in **PN**, we explored whether this receptor can formed as gel in various solvents. Firstly, we configured **PN** in 10 different solvents into the proportion of 5% and heated it completely. As shown in Table S1, when cooled to room temperature, we found that **PN** could form as gel only in DMSO and DMF. The lowest critical gelation concentration (CGC) was 2% (w/v, 10 mg/mL = 1%), while the gel-sol transition temperature (T_{gel}) was 25-97°C. As shown in Fig. 1, **PN-G** didn't have any fluorescence in DMSO ($T > T_{gel}$). After the temperature cooling down to the T_{gel} ($T < T_{gel}$) gradually, the emission dramatically enhanced at 523 nm and reached a steady state within 1 min. At the same time, **PN-G** showed a bright yellow fluorescence, which indicated that **PN** assembled as supramolecular gel in DMSO (Fig. S6). To further confirm the stability of **PN-G**, fluorescence decay experiments were conducted. The decay curve of **PN-G** was fitted, which showed the fluorescence lifetimes of $\tau_1 = 0.3670$ ns, $\tau_2 = 2.3650$ ns and $\tau_3 = 7.3668$ ns (Fig. S7). And time-dependent experiments showed that the fluorescence intensity of **PN-G** remained unchanged (Fig. S8). Moreover, it was interesting to find that **PN-G** showed reversible transition (gel-sol) in response to temperature and performed many times

with small fluorescence efficiency loss (Fig. S9).

As is well-known, selectivity and sensitivity are important properties for sensors. Therefore, we carefully investigated the specific selectivity of **PN-G** toward various anions. Firstly, a series of anions (F^- , Cl^- , Br^- , I^- , AcO^- , PO_4^{3-} , SO_4^{2-} , S^{2-} , HS^- , ATP, SO_3^{2-} , SCN^- , CO_3^{2-} , NO_3^{2-} and CN^- , 1 equivalent) were diffused into **PN-G** in DMSO ($T > T_{gel}$). After the temperature cooling down to the T_{gel} ($T < T_{gel}$) gradually, the results showed that basic ions (F^- , AcO^- , PO_4^{3-} , CO_3^{2-} , CN^- , SO_3^{2-} , S^{2-} , HS^-) caused a small amount of red shift in the fluorescence spectrum of **PN-G**, but only CN^- could lead to complete fluorescence quenching. However, other miscellaneous anions including (Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^{2-} , ATP, SCN^-) did not lead to any significant change in the **PN-G** sensing process as shown in Fig. 2. And make bar graph to comparison them with error bar. As shown in Fig. S10, No significant fluorescence quenching was observed for all used interfering ions.

To further explore the optimized condition about the sensing behavior of **PN-G** toward CN^- , The sensitivity and lowest fluorescence detection concentrations of **PN-G** for CN^- was determined by fluorescent titrations (Fig. 3). The incremental addition of cyanide (0–0.55 equivalents) to **PN-G** (5%) at room temperature reveals a gradual decrease of the strong fluorescence emission at 523 nm with a significant red shift. At the same time, a visible fluorescence quenched from yellow could be observed by naked eyes (Fig. 3). This should be attributed to destruction of phenazine π - π stacking. However, no further change was observed in the fluorescence spectra beyond the addition of 0.55 equivalents of CN^- (Fig. S11). On the basis of the $3\delta/S$

method, the LODs of **PN-G** for CN^- was 4.18×10^{-10} M (Fig. S12). The most noteworthy was that the lowest detection limit of supramolecular gel **PN-G** for CN^- was much better than most reported fluorescent gel sensors for CN^- (Table 1) [29, 39, 53-55]. This result indicates that **PN-G** could be used as good fluorescence material for detecting CN^- in water.

What we predicted that the self-assembly behavior of **PN-G** could be demonstrated by XRD through monitoring the molecular spacing (Scheme 2). The XRD patterns of xerogel **PN-G** suggested that there was a distances of 3.46 Å at $2\theta = 25.74^\circ$ which confirmed the π - π stacking consisted of phenazine groups in **PN-G** (Fig. S13). The result proved that the orderly arrangement characteristics of **PN** molecules induce their assembly into stable supramolecular gel of **PN-G**. There results were further confirmed by ^1H NMR spectra. As shown in Fig. S14 and Fig. S15, as the **PN** concentration increases, all proton peaks on the phenazine aromatic ring shifted upfield, which suggested that the self-assembled system was formed by π - π stacking in the solution. Interestingly, Partial peak shift to downfield on the **PN** alkyl chain, which shows that Van der Waals interactions also participated in the **PN** self-assembly process.

The possible mechanism of **PN-G** interacted with CN^- was further investigated by ^1H NMR, MS and SEM (Scheme 2). Because **PN** had poor solubility in DMSO solution, **PNM**, a compound with similar structure to **PN** was synthesized for ^1H NMR titration experiments (Fig. S4, Fig. S5 and Fig. 4.). Upon addition of CN^- in **PNM** solution, the signals of protons H^a , H^b and H^c on **PNM** aromatic hydrocarbon

shifted downfield. Meanwhile, the signals of protons H^d on **PNM** alkyl group shifted upfield. These results confirmed that the ubiquitous intermolecular interaction would occur between CN⁻ and phenazine rings of **PNM**. Firstly, CN⁻ destroyed the π - π assembly in **PNM**. To further verify rationality of sensing mechanism, we tested the reaction mixture of **PN** and CN⁻ by mass spectrometer. To our delight, Fig. S16 manifests an increased molecular weight of 27, which was equal to the molecular weight of HCN. CN⁻ destroys the π - π stacking of **PN**, and then **PN** undergoes a nucleophilic addition reaction with CN⁻, resulting in fluorescence quenched.

Finally, the morphologies of **PN**, **PN-G** and **PN-G** with CN⁻ were investigated by scanning electron microscope (SEM). As shown in Fig. 5, **PN** powder showed fragment structure (Fig. 5a), and **PN-G** showed regular large pieces of layered structure (Fig. 5b), the images demonstrated the idea that **PN** could self-assemble into supramolecular gel by π - π stacking interactions and van der waals interaction. However, after adding CN⁻ in **PN-G**, the xerogel showed thin strips are inlaid in blocks structure (Fig. 5c). The above experiments further support the correctness of our proposed sensing mechanism.

4. Conclusion

In summary, we efficiently synthesized a simple organic molecule with 16 alkyl group 2-(hexadecylthio)oxazolo[4,5-b]phenazine (**PN**) and investigated its self-assembly behavior by ¹H NMR and XRD. The aggregation formation was found to be dependent on the π - π stacking interactions and van der waals interaction between **PN** molecules. We surveyed the response of **PN** gel (**PN-G**) to various

anions in water, whereas with the addition of CN^- and heated from gel to sol, after gelation again, the ability to selected recognize CN^- unfolding. The yellow fluorescence quenching of **PN-G** could be observed by naked eyes. The detection limit of **PN-G** to CN^- was as low as 4.18×10^{-10} M. Detailed analyses reveal that CN^- destroyed the π - π assembly in **PN-G**, and **PN-G** undergoes a nucleophilic addition reaction with CN^- .

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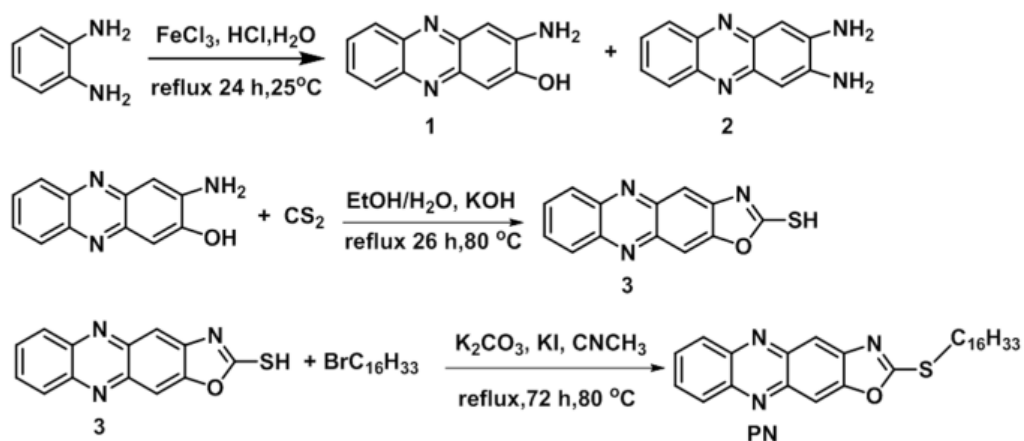
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Scheme 1 Structure and synthesis of the sensor PN.

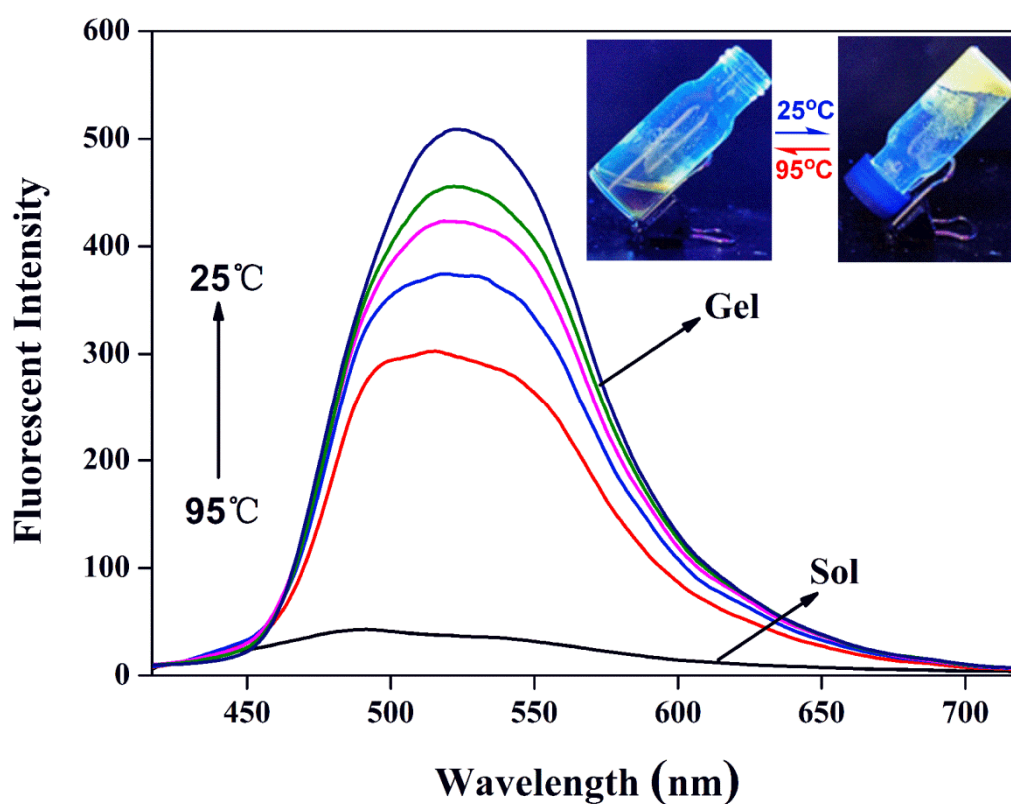


Fig. 1 Fluorescence spectra and photograph of supramolecular gel PN-G and sol.

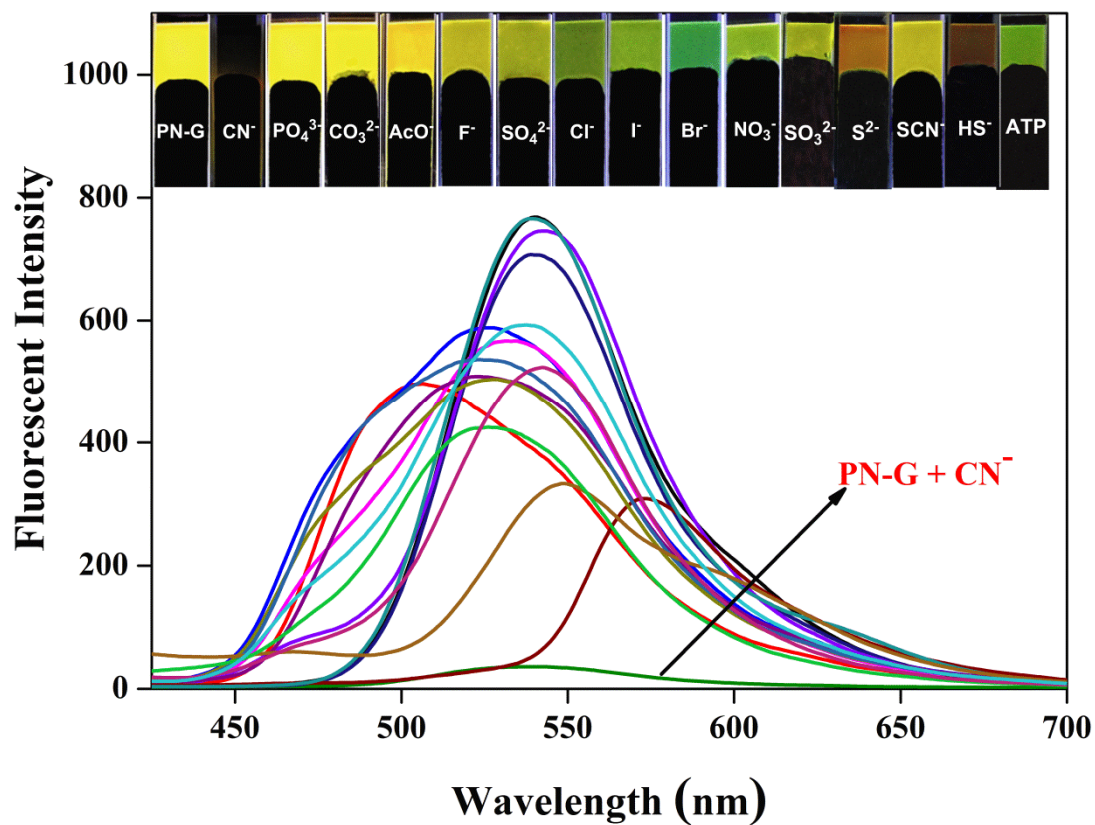


Fig. 2 Fluorescent spectra of target supramolecular gel **PN-G** in the presence of CN^- ion and other anions (1 equiv.). Inset: photograph showing the change in color of the supramolecular gel of **PN-G** after addition of CN^- ion and other anions using UV-lamp (365 nm) at room temperature.

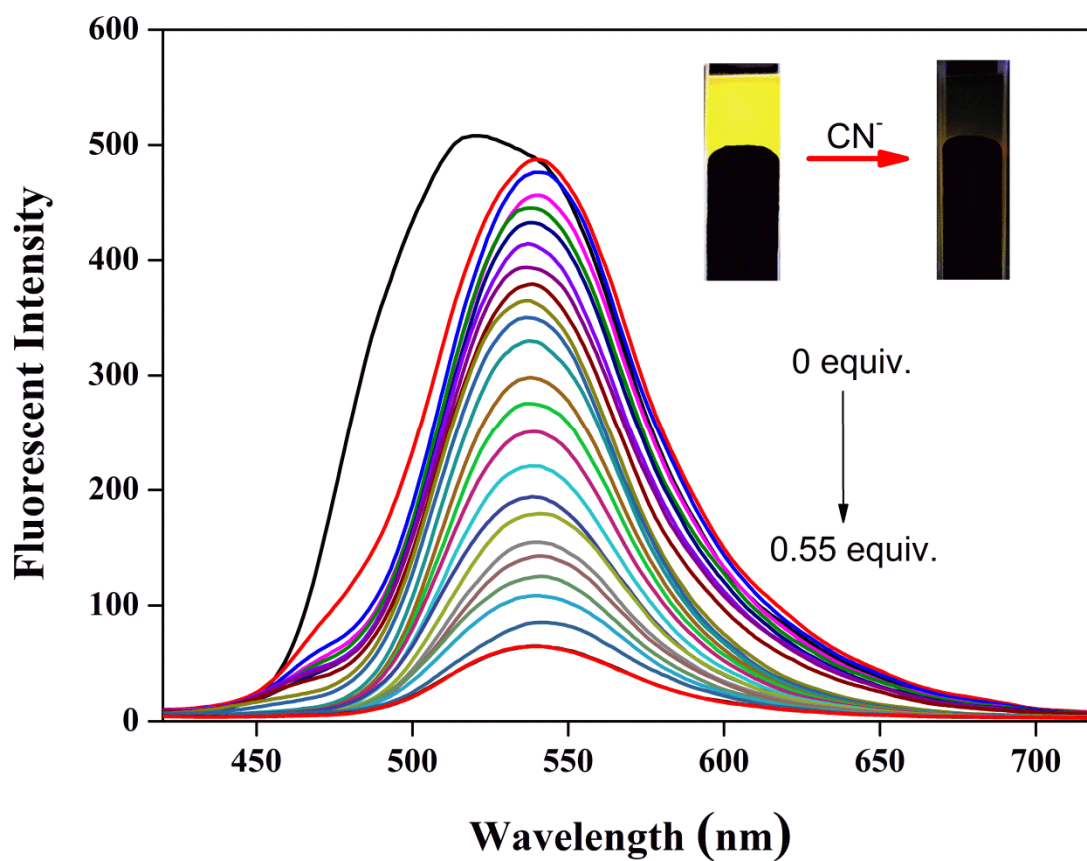
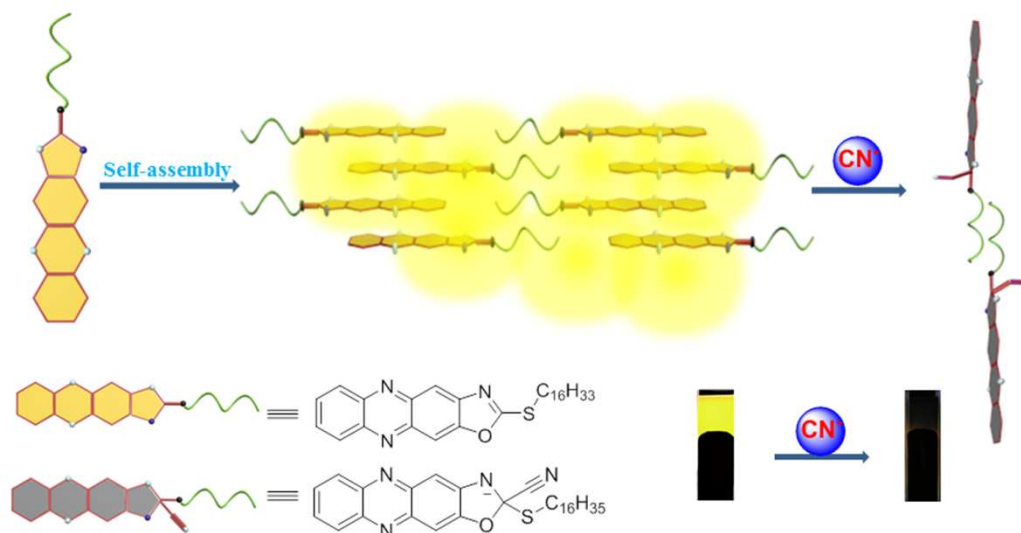


Fig. 3 Fluorescence titration spectra of **PN-G** (5%) in DMSO solution upon added different concentrations of CN^- anions; Inset: fluorescent photograph of **PN-G** and after added CN^- anions in it. ($\lambda_{\text{ex}} = 390 \text{ nm}$).

Table 1 Comparison of the Analytical Performance of the Sensor Molecules for CN^- .

Ref.	State	Mechanism	LOD
53	solution	nucleophilic addition	$4.97 \times 10^{-7} \text{ M}$
54	solution	deprotonation	$1.48 \times 10^{-7} \text{ M}$
55	solution	nucleophilic addition	$1.60 \times 10^{-7} \text{ M}$
29	solution	Complexation approach	$5.77 \times 10^{-7} \text{ M}$
39	polymer	Complexation approach	\
This work	gel	nucleophilic addition	$4.18 \times 10^{-10} \text{ M}$



Scheme 2 Chemical structures and cartoon representations of **PN** and **CN⁻** and the reaction mechanism in this system.

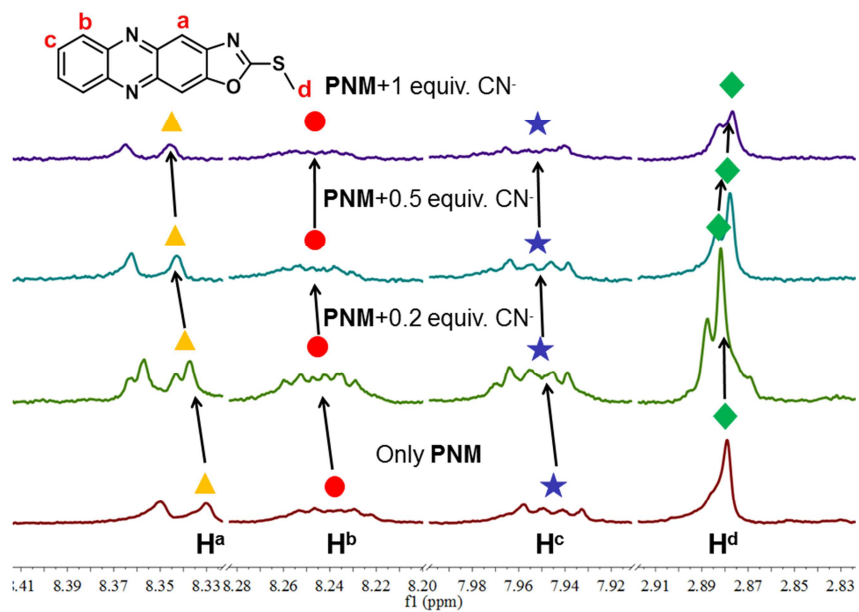


Fig. 4 Partial ^1H NMR spectra of PNM ($\text{DMSO}-d_6$) and in the presence of varying amounts of CN^- (1M, D_2O).

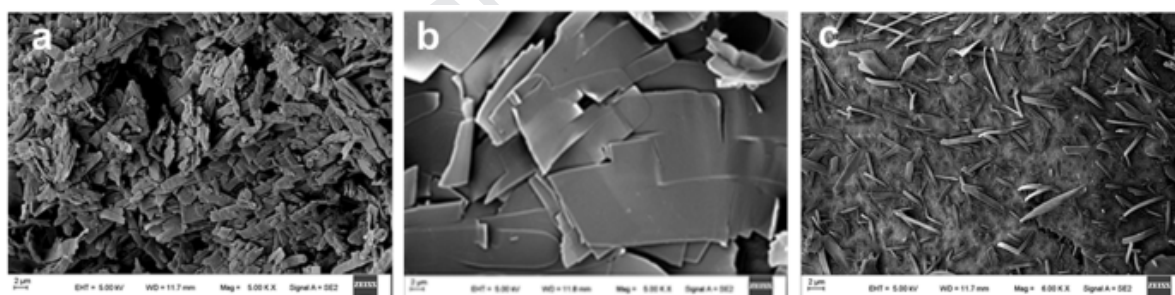


Fig. 5 SEM images of (a) PN powder, (b) the large pieces of layered self-assembled from PN-G, (c) the thin strips are inlaid in blocks structure after adding CN^- in PN-G.

Highlights

1. Constructed a supramolecular gel by self-assembly.
2. A novel supramolecular gel for highly selective and sensitive detection of cyanide.
3. Taking advantage of a simple mechanism of nucleophilic addition reaction.

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Author Statement

Hu Fang: Investigation, Software, Writing- Original draft preparation.

Wen-Juan Qu: Data curation, Writing- Reviewing and Editing, Project administration.

Hao-Hang Yang: Visualization, Investigation.

Jun-Xia He: Supervision.

Hong Yao: Validation, Resources.

Qi Lin: Formal analysis, Funding acquisition.

Tai-Bao Wei: Methodology, Funding acquisition.

You-Ming Zhang: Conceptualization, Funding acquisition.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: