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Novel conductive metallo-supramolecular polymer AIE gel for multi-channel highly sensitive detection of hydrazine hydrate

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ABSTRACT

Hydrazine hydrate (DH) is an important fine chemical intermediate and as fuel for rockets, however, it also has serious toxic for humans and environment. Developing novel materials and methods for sensitive detection of DH in water and air is an important task. In order to effectively detect DH, a novel conductive supramolecular polymer metallogel (PQ-Ag) has been constructed by the coordination of bis-5-hydroxyquinoline functionalized pillar[5]arene (PQ5) with Ag^+. The metallogel PQ-Ag could realize the multi-channel sensitive detection of DH through naked-eye, fluorescence, and electrochemical methods. The lowest limit of detection (LOD) is 0.1 mg/m^3 in air and 2.68×10^{-8} mol/L in water, which is lower than the standard of the US Environmental Protection Agency (EPA) for DH of maximum allowable concentration in drinking water. More importantly, an electronic device for DH detection based on the metallogel PQ-Ag was designed and prepared, which can realize conveniently and efficiently multi-channel detection and alert of DH through sound and light alarms not only in water but also in air.

Stimuli-responsive conducive smart metallo-supramolecular polymer attracted more and more attentions due to its promising prospect [1]. The metallo-supramolecular polymer possesses two merits to act as smart conductive materials. Firstly, metallo-supramolecular polymer inherits the abundant optical, electronic or magnetic properties of metal ions [2], which will supply various functions for this kind of materials. Secondly, the supramolecular assembly nature of the metallo-supramolecular polymer endows them special reversible stimuli-response properties [3–5]. Therefore, combined these two merits and conductivity together, metallo-supramolecular polymer shows excellent prospect in the field of smart electronic device and act as sensor, electronic nose or skin and so on [6,7]. Although conductivity metallo-supramolecular polymer shows fantastic prospect in smart materials, there are still many challenges in the development of this kind of materials, for example, how to realize high sensitivity and specific selectivity for target stimuli is very difficult.

In addition, there is a huge demand for effective materials, methods and devices for sensitive detection of poisonous gas [8,9]. For example, hydrazine hydrate (DH) is widely used in the synthesis of pesticides and medicines, fuel for satellites and rockets and preservative in nuclear and power plants [10]. However, DH is highly toxic and easily absorbed through human body orally and skin, it not only causes serious damage to organs and central nervous system of human and animals, but also has mutagenesis and carcinogenic effects [11]. Therefore, efficient detection of DH is crucial. The US Environmental Protection Agency (EPA) classified hydrazine as a potential carcinogen and set its threshold limit value (TLV) at 3.1×10^{-7} mol/L [12]. Thus, it is very important to develop new materials and methods for detection of DH through convenient, quick and sensitive approaches. While, the common instrument detection methods are expensive and inconvenient to operate [13,14]. Moreover, many materials have been developed for detection DH, while, most of them only could detect DH in solution [15,16]. Therefore, there is urgent need for novel materials which could simultaneously detect DH in multiple ways. Interestingly, the conductive metallo-supramolecular polymer also provides a good way to develop novel materials and methods for efficient detection of DH.

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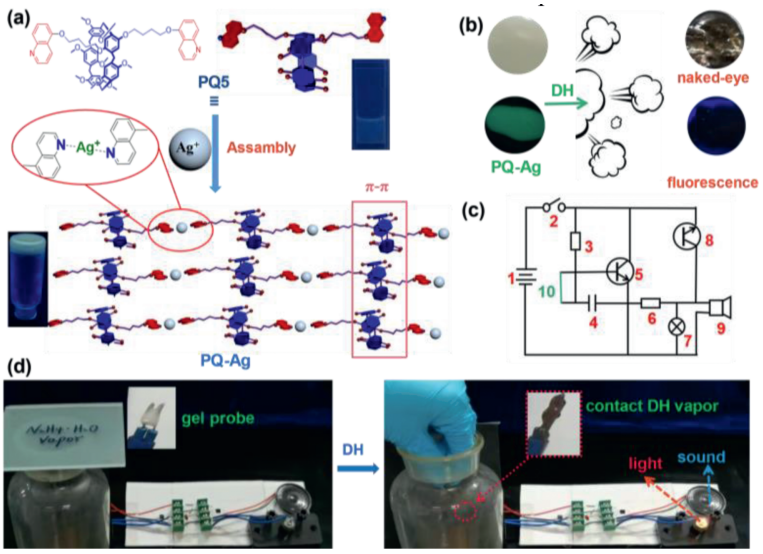

Scheme 1. (a) Cartoon illustration of the assembly mechanism on the metallo-supramolecular polymer gel PQ-Ag. (b) The multi-channel DH detection of the PQ-Ag. (c) Schematic diagram of DH alarm circuit (1: electric source; 2: switch; 3: resistance; 4: electric capacity; 5: NPN triode; 6: resistance; 7: bulb: 8: PNP triode; 9: buzzer; 10: gel probe), and (d) presentation of the DH detection electronic device.

In light of this, and as part of our interests on supramolecular polymer materials [17–22], host-guest recognition [23–31], and detection methods [32–34], herein, in order to develop novel and efficient material and method for DH detection, a conductive metallo-supramolecular polymer aggregation induced emission (AIE) gel (PQ-Ag) was developed through coordination-linking based on a quinoline functionalized pillar[5]arene. The PQ-Ag could achieve multi-channel ultrasensitive detection DH and its vapor by naked-eye, fluorescence, and electrochemistry. The design ideas of the PQ-Ag are as follows, as shown in Scheme 1, the 5-hydroxyquinoline was employed to functionalize the pillar[5]arene-based host and obtained bis-5-hydroxyquinoline functionalized pillar[5]arene (PQ5). Firstly, the introduction of pillar[5]arene group cannot only provide $\pi\cdots\pi$ interaction for the self-assembly process but also offer AIE effect [35–39], which could endow fluorescence response properties for PQ-Ag. Secondly, quinoline units are not only a kind of fluorophores but also coordination groups which could provide metal coordination sites and contribute to the formation of metallo-supramolecular polymer gel. Based on the coordination properties of quinoline units with Ag^+, the metallo-supramolecular polymer AIE gel (PQ-Ag) was successfully constructed. As expected, the PQ-Ag possesses AIE and conductive properties and shows nice naked-eye, fluorescent and electrochemistry response to DH, which could realize the selective ultrasensitive detection of DH. The detection limit (LOD) of PQ-Ag for DH is 2.68×10^{-8} mol/L, which is lower than the standard of the EPA for DH maximum allowable concentration in drinking water.

The synthesis details of PQ5 were presented in supplementary information (Scheme S1 in Supporting information). At the beginning of the work, we carefully investigated the self-assemble properties of the PQ5, as shown in Table S2 (Supporting information), the PQ5 couldnot self-assemble into supramolecular polymer in common solvents. While, based on the good coordination between Ag^+ and quinoline groups of PQ5, the PQ5 could form stable metallo-supramolecular polymer gel PQ-Ag with Ag^+ in DMSO/H_2O binary solution (water volume fractions fw = 20%) (Fig. S3 in Supporting information). The lowest critical gelation concentration (CGC) is 8% (w/v, 10 mg/mL = 1%) while the gel-sol transition temperature (T_{gel}) is 62–63 °C. Interestingly, as shown in Fig. 1a, the hot ($T > T_{gel}$) DMSO/H_2O binary solution of metallo-supramolecular polymer gel (sol state) showed negligible fluorescence emission. However, with the temperature of the solution dropping below the T_{gel} ($T < T_{gel}$), the PQ-Ag solution changed into a stable metallogel and showed blue fluorescence under the UV lamp (365 nm). This result indicated that the metallo-supramolecular polymer gel PQ-Ag has AIE effect.

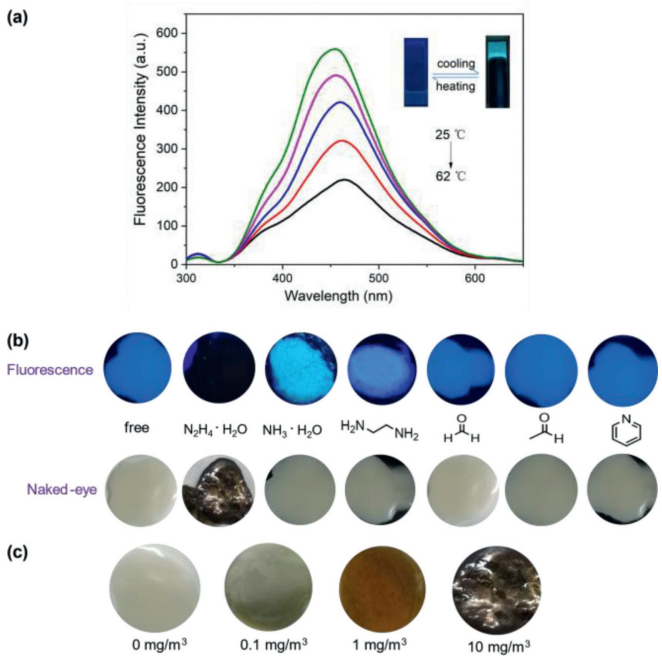

Fig. 1. (a) Temperature-dependent fluorescence spectra of PQ-Ag during gelation process (λ_{ex} = 310 nm). (b) Photograph of PQ-Ag fumigated by VOCs; (c) Photograph of PQ-Ag detecting different concentrations of DH vapor under naked eye condition.

Then, the performance of the PQ-Ag to detect volatile organic compounds (VOCs) was studied. As shown in Fig. 1, the PQ-Ag was placed in a sealed bottle containing DH at room temperature and pressure, and its color changed from white to black rapidly upon contact with DH vapor, at the same time, the blue fluorescence of PQ-Ag quenched when the PQ-Ag contacted with DH, these results indicating that the PQ-Ag could achieve a rapid

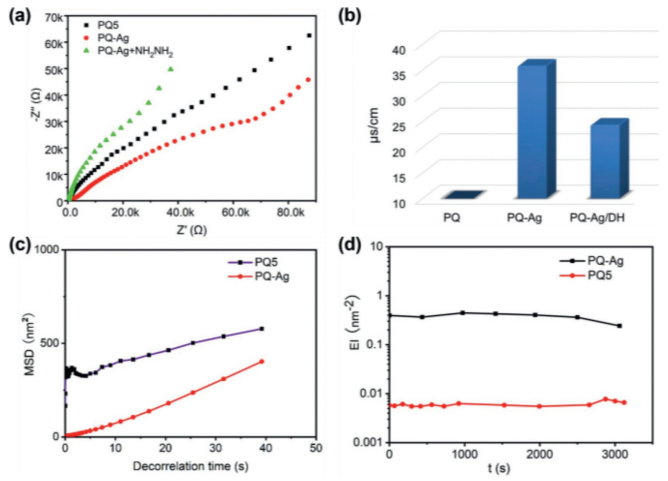

Fig. 2. (a) Nyquist impedance plots, (b) conductivity of PQ5, PQAg and PQ-Ag/DH, (c) graph of mean squared displacement (MSD) against decorrelation time curves, (d) EI *versus* time of PQ5, PQ-Ag.

response to DH vapor through naked-eye visible color and fluorescent changes. While, other VOCs including ammonia, 1,2-ethylenediamine, formaldehyde, acetaldehyde and pyridine could not induce similar response for PQ-Ag, which indicated that metallogel PQ-Ag could selectively detect DH vapor (Figs. 1b and c). In addition, the LOD of the PQ-Ag to DH vapor could reach 0.1 mg/m^3 through colorimetric monitoring. Furthermore, as shown in Fig. S4 (Supporting information), the LOD of PQ-Ag for DH was also calculated according to fluorescence titration experiments. Based on the 3 δ/S method [40], the LOD of metallogel PQ-Ag for DH is about 2.68×10^{-8} mol/L (Fig. S5 in Supporting information), which is lower than the standard of the EPA for DH maximum allowable concentration in drinking water.

Since metallo-supramolecular polymer gels are generally inherited the electrical conductivity of metal, the DH detection performance of the metallogel PQ-Ag was studied from an electrochemical perspective. The oxidation and reduction peaks of PQ5, PQ-Ag and PQ-Ag/DH were compared according to the cyclic voltammetry curves, the results showed that the electrode reactions were irreversible (Fig. S6 in Supporting information). The Nyquist impedance diagram shown in Fig. 2a presents an approximate semicircle in the high frequency region and a linear evolution in the low frequency region. Meanwhile, the conductivity of the PQ5, PQ-Ag and PQ-Ag/DH was measured by conductivity meter (Fig. 2b). The conductivity of PQ5, PQ-Ag and PQ-Ag/DH were 0.62, 35.8 and 24.5 μs/cm, respectively. These results indicated that the PQ-Ag possess considerable conductivity, while, after reacted with DH, the conductivity of PQ-Ag underwent a distinct decrease.

For convenient application of this DH responsive and conductive metallogel PQ-Ag, as shown in Scheme 1c, an electronic device-based on PQ-Ag for DH detection was designed by employing a circuit breaker [41]. In this device, the metallo-supramolecular polymer gel PQ-Ag was employed as DH detection probe. When the PQ-Ag remained intact, the probe based on the PQ-Ag was in good conductivity and equivalent to a wire, and the buzzer and bulb did not work because the metallogel PQ-Ag short-circuits the buzzer and bulb. However, when the metallogel PQ-Ag contacted with DH vapor, the PQ-Ag reacted with the DH, the electric circuit of buzzer and bulb switches on and gives off light and sound alarms (Scheme 1d). Thus, the PQ-Ag-based electrochemical device for the detection of DH is successfully realized and the alarm trigger time of this device is in 3∼5 s. As shown in the Fig. S11 (Supporting information), the electrochemical device could conveniently and quickly detect and alarm DH.

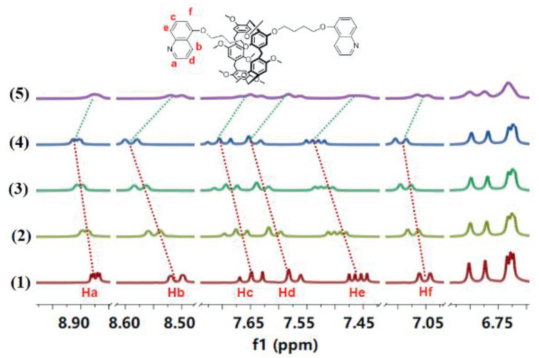

Fig. 3. Partial ^{1}H NMR spectra (400 MHz, 298 K) in DMSO-d_6: (1) free PQ5, (2∼4) PQ5 + 1.0, 2.0, 3.0 equiv. Ag^+, respectively. (5) PQ5 + 2.0 equiv. Ag^+ + 2.0 equiv. DH.

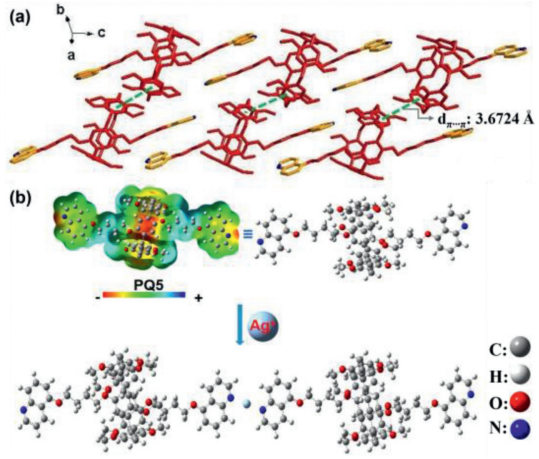

Fig. 4. (a) The crystal structure (omit hydrogen atoms) of PQ5; (b) ESP maps of the PQ5 and structural optimization are calculated of PQ-Ag at the B3LYP/6-311G level of theory.

In order to investigate assembly mechanism of the metallo-supramolecular polymer gel PQ-Ag, a series of experiments and theoretical calculations have been carried out. Firstly, to verify the binding mode between PQ5 and Ag^+, ^{1}H NMR titration experiment was performed. As shown in Fig. 3, with the addition of different equivalents Ag^+ to the PQ5 solution, proton signals of H_a∼H_f showed downfield shifts, which could be attributed to the coordination between Ag^+ and the N from quinoline groups of PQ5. In addition, IR and ESI-MS spectra also provided evidence for the assembly process. As shown in Fig. S7 (Supporting information), after complexed with Ag^+ and formed PQ-Ag, the vibration absorption peak of -C=N- of PQ5 was moved from 1400 cm^{-1} to 1384 cm^{-1}, which indicated the coordination of the Ag^+ with the N on quinoline groups of PQ5. Meanwhile, in the ESI-MS spectrum (Figs. S8 and S9 in Supporting information), signal peaks at 667.16 and 1227.14 shown good agreement with $[PQ5 + 2Ag]^{2+}$ and $[PQ5 + Ag]^+$, these results indicated 1:2 and 1:1 binding stoichiometry of PQ5 to Ag^+ in PQ-Ag. Moreover, a single crystal of PQ5 was obtained on the condition of slow evaporation of PQ5's acetonitrile solution at room temperature. As shown in Fig. 4a, according to the crystal structure of PQ5, $\pi\cdots\pi$ interactions exist between pillar[5]arene groups of adjacent PQ5. Therefore, based on these evidences, the proposed assembly mechanism of PQ-Ag is as illustrated in Scheme 1, the PQ5 coordinated with Ag^+ through the N on quinoline groups and formed one dimensional coordination polymer, meanwhile, the adjacent coordination polymer connected each other through $\pi\cdots\pi$ interaction between pillar[5]arene groups, which promoted the formation of metallogel PQ-Ag.

For deeply understanding the assembly model of the PQ-Ag, the density functional theory (DFT) was carried out based on quantum chemical calculations at the B3LYP-D3/6-311G level of theory using Gaussian-09 program [42,43]. As shown in Fig. 4b, the electrostatic potential maps (ESP) revealed that the nitrogen of quinoline on PQ5 possess negative charge distribution, which indicated that PQ5 has potential to coordinate with Ag^+. Furthermore, the proposed binding mechanism is verified by calculating the optimized structure of PQ-Ag complex.

The rheological properties of the metallo-supramolecular polymer gel PQ-Ag also support the proposed assembly mechanism, which was investigated on a Rheolaser Lab Diffusing, Wave Spectroscopy [44,45]. For a gel system, the lower the plateaus of the mean squared displacement (MSD) indicate the higher the elasticity of the gel. Therefore, according to Fig. 2c, the MSD of PQ-Ag is lower than PQ5, which indicated the addition of Ag^+ enhanced the elasticity of PQ-Ag gel. Meanwhile, in order to assess the viscoelastic change, the elasticity index (EI) was plotted according to time. From Fig. 2d, the addition of Ag^+ induced the EI platform height of PQ-Ag became higher than PQ5, which indicated that the formation of metallogel enhanced viscoelastic the system. All these results could be attributed to the coordination between PQ5 and Ag^+ effectively improved the cross-linking strength and strengthen the network structure of metallogel.

In order to understand the DH response mechanism of the PQ-Ag, a series experiments were carried out. Firstly, as shown in Fig. 3, according to ^1H NMR titration experiments, with the addition of the DH to the PQ-Ag solution, proton signals of $H_a \sim H_f$ showed upfield shifts, which indicated that DH destroyed the coordination of Ag^+ and PQ5 through reducing the Ag^+. This result caused the metallogel PQ-Ag collapsing and fluorescence quenching. Meanwhile, the DH reducing the Ag^+ induced the formation of amorphous Ag, which induced the color of PQ-Ag gel changed from white to black. Secondly, SEM experiments also supported the proposed DH sensing mechanism. As shown in Fig. S11 (Supporting information), under SEM, the micro-morphology of PQ5 shows lamellar structure. After adding Ag^+ into the PQ5, the obtained metallogel PQ-Ag changed to folded film structure, which could be attributed to the coordination linking of the Ag^+ and PQ5. While, after the metallogel PQ-Ag was exposed into the DH vapor, the folded film structure changed to micro-spherical morphology, this phenomenon indicating the Ag^+ coordination linking had been destroyed and the PQ5 forming micro-spherical morphology based on the hydrophobic effect.

In conclusion, through Ag^+ coordination linking method, the conductive metallo-supramolecular polymer gel PQ-Ag was successfully prepared from bis-5-hydroxyquinoline functionalized pillar[5]arene and Ag^+. The PQ-Ag successfully achieved the sensitive detection of DH by naked eye, fluorescence and electrochemical methods. Moreover, the PQ-Ag-based DH detection device could conveniently and efficiently detect and alarm of DH. This study not only provides a feasible multi-channel detection method for DH with conductive metallo-supramolecular polymer gel, but also provided theoretical experience for the design of novel conductive materials as well as electronic device for detection poisonous gas by using metallo-supramolecular polymer.

Declaration of competing interest

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.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.108082.

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