Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: http://www.elsevier.com/locate/dyepig

Stimuli-responsive supramolecular hydrogel with white AIE effect for ultrasensitive detection of Fe^{3+} and as rewritable fluorescent materials

Qi Zhao, Xin-Yu Dai, Hong Yao, You-Ming Zhang, Wen-Juan Qu, Qi Lin^{**}, Tai-Bao Wei

Key Laboratory of Eco-functional Polymer Materials of the Ministry of Education. Key Laboratory of Eco-environmental Polymer Materials of Gansu Province. College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, PR China

ARTICLE INFO

Keywords: Ultrasensitive Aggregation-induced emission Supramolecular polymer hydrogel White light emission Fluorescent material

ABSTRACT

The development of fluorescent smart materials by introducing white light emission into supramolecular polymer hydrogels, and tuning their aggregation-induced emission (AIE) effect are essential for the manufacture of advanced functional materials. Herein, a novel bi-component supramolecular polymer hydrogel (NDG) was successfully constructed via a simple host-guest assembly process based on two easy-to-synthesize tripodal gelators (NTS and DTB). Strikingly, the NDG exhibits strong white aggregation-induced emission (WAIE), and can act as an AIE-based sensor for ultrasensitive detect Fe^{3+} and F^- . The lowest limits of detection (LODs) are 5.33×10^{-9} M and 1.61×10^{-8} M, respectively. The xerogel of NDG exhibits nice adsorption and separation capacity for Fe^{3+} , the adsorption rate reaches to 99.26%. In addition, the prepared NDG-based thin films can be used as rewritable fluorescent display material for the continuity detection of Fe^{3+} and F^- . Due to the outstanding optical behavior of the NDG, it also be used as an "IMPLICATION" logic gate at the molecular level. The AIE hydrogel-guided enriches the self-assembly strategy of new supramolecular polymers, which also makes it become a good candidate for flexible optical materials.

1. Introduction

White light-emitting devices have become a research hotspot in the past decades because they have great potential in the field of solid-state lighting, display systems and fluorescent biomedicine [1–3]. Nowadays, the majority of white-light-emissive systems have been obtained by combining phosphor color conversion materials or by doping specific rare earth ions, but sometimes these systems likely suffer from low luminous efficiency, low thermal stability and high manufacturing cost [4–7]. It is especially worth mentioned that the supramolecular organic fluorescent materials have attracted attention due to their special properties (such as low cost, low toxicity, and ease of fine-tuning) [8-12]. In this case, it's valuable to develop organic white light-emitting materials with special performances (for example, good thermal stability, high efficiency and flexibility).

Supramolecular polymers, which combine the advantages of supramolecular chemistry and polymeric materials, they possess better processability and recycling properties [13,14]. Tang and colleagues observed the phenomenon of aggregation-induced emission (AIE) in 2001, which is the exact opposite of the ACQ effect [15]. This discovery

materials science. Importantly, supramolecular polymers have been proved to be an ideal platform for constructing AIE functional materials [16–18]. As an important part of supramolecular polymers, stimuli-responsive supramolecular polymer gels with AIE effect not only demonstrate dynamic features originating from the noncovalent bonds [19-22], but also exhibit fluorescence responses to various external stimuli [23-28]. ${\rm Fe}^{3+}$ is one of the essential metal ions in the human body system, it

has brought new opportunities and challenges to the development of

overloading or deficiency causes numerous biological complications such as endotoxemia and hepatic cirrhosis [29-32]. Likewise, iron homeostasis is an important factor involved in neuroinammation and the progression of Alzheimer's disease [33]. In addition, fluoride ion (F⁻) has received an ever-growing attention because of its beneficial effects in dental health [34], and potential use in the treatment of osteoporosis [35]. However, chronic exposure to high levels of F⁻ can cause acute gastric and kidney problems, and even skeletal fluorosis [36]. Hence, ultrasensitive detect and efficient separate Fe³⁺ and F⁻ in the environment have attracted increased attention. Among various detection strategies, fluorescence sensor-based methods become a fascinating

* Corresponding author.

https://doi.org/10.1016/j.dyepig.2020.108875

Received 5 July 2020; Received in revised form 15 September 2020; Accepted 16 September 2020 Available online 19 September 2020





PIGMENTS

^{**} Corresponding author.

E-mail addresses: lingi2004@126.com (Q. Lin), weitaibao@126.com (T.-B. Wei).

^{0143-7208/© 2020} Elsevier Ltd. All rights reserved.



Fig. 1. Possible mechanisms about the assembly of NDG and ultrasensitive sensing of Fe^{3+} .

subject because of their as time effective, simple, low cost, selective, and sensitive for the detection [37,38]. Up to now, many methods have been reported about ultrasensitive detection and separation of important analytes [39,40]. Despite great effort, the preparation of novel smart fluorescence sensors, which can be used for both ultrasensitive detection and separation of specific ions remains challenging.

Inspired by these facts and as a part of our research efforts [41,42], we report a novel bi-component AIE hydrogel (NDG), which was constructed via a simple host-guest interactions of a 1-naphthaleneacetic hydrazide functionalized tripodal hydrazide as host (NTS) and a tri-(pyridine-4-yl)-functionalized trimesoyl amide as guest (DTB) (Fig. 1). In the design, methyl 1-naphthaleneacetate derivative and 4-amino pyridine were introduced into the NTS and DTB as the π - π interaction site and fluorophore, respectively, as well as providing self-assembly driving forces. The tripodal structure provide a stronger binding site for the guest by cooperation of its three arms. As we expected, the gelators NTS and DTB assemble into a stable supramolecular polymer hydrogel (NDG) in DMSO-H₂O (3.3:6.7, v/v) binary solution, and exhibits strong white aggregation-induced emission. It is worth noting that the NDG exhibits the characteristics of ultrasensitive detection and separation of Fe³⁺, and act as fluorescent display material. Moreover, the fluorescence changes of NDG upon the addition of Fe^{3+} and F^- be used at the molecular level to design "IMPLICATION" logic gate. The precise design of small molecules assemble into polymer hydrogels by weak interaction forces to prepare white AIE gels provide a new idea for the developing of white light materials.

2. Experimental

2.1. Materials

All commercially available reagents were used as received. All ions were purchased from Alfa Aesar and used as received. Fresh doubly distilled water was used throughout the experiment. The sources of various ions (Tables S1 and S2) and the experimental details are provided in the supporting information.

2.2. Instruments

¹H NMR (600 MHz) and ¹³C NMR spectra (151 MHz) were carried out with a Mercury-600 BB spectrometer. High-resolution mass spectra were performed on Bruker Esquire 3000 plus mass spectrometer equipped with ESI interface and ion trap analyzer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Infrared spectra were recorded using a FT-IR spectrometer with KBr discs in the 4000-500 cm⁻¹ region. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The morphologies and sizes of xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. The X-ray diffraction analysis (XRD) is a desktop X-ray diffractometer model Miniflex 600.

2.3. Synthesis of compound NTH

Methyl 1-naphthaleneacetate (1.0 g, 5.0 mmol) and hydrazine hydrate (\geq 85%, 0.8 g, 20.0 mmol) were dissolved in ethanol (100 mL). The mixture was stirred at 85 °C for 24 h. After the reaction finished, the solvent was removed under reduced pressure and the residue was recrystallized in alcohol. Washed by alcohol and water afforded **NTH** (0.98 g, 98%) as a white needle-like solid: m.p. 181–182 °C; ¹H NMR (Fig. S1) (600 MHz, CDCl₃) δ (ppm): 7.92-7.91 (d, J = 6 Hz, 1 H, ArH), 7.88-7.87 (d, J = 6 Hz, 1 H, ArH), 7.83-7.82 (d, J = 6 Hz, 1 H, ArH), 7.56-7.50 (d, J = 30 Hz, 2 H, ArH), 7.45-7.42 (t, J = 18 Hz, 1 H, ArH), 7.39-7.38 (d, J = 6 Hz, 1 H, ArH), 6,56 (s, 1H, NH), 4.03 (s, 2H, NH₂), 3.75-3.74 (d, J = 6 Hz, 2H, CH₂); ¹³C NMR (Fig. S2) (151 MHz, CDCl₃) δ (ppm):171.38, 133.96, 131.89, 130.02, 128.86, 128.65, 128.35, 126.90, 126.24, 125.56, 123.53, 39.91; HR-MS calculated for (C₁₂H₁₃N₂O⁺) [NTH + H]⁺ (*m*/z): 201.1028. Found: 201.1022 (Fig. S3).

2.4. Synthesis of compound NTS

A mixture solution of trimesoyl chloride (0.237 g, 1.0 mmol) and triethylamine (1-2 d) were slowly added into the solution of NTH (0.66 g, 3.3 mmol) in DCM (150 mL), and then the mixture was stirred at room temperature for 24 h, getting a white solid. The solid was vacuumed suction, and the resulting mixture was filtered and washed with cold



Scheme 1. The synthesis of NTH and NTS.



Fig. 2. a) Temperature-dependent fluorescence spectra of "Gel-Sol" (NDG) transition in DMSO-H₂O binary solution (fw = 67%). b) Fluorescent "Gel-Sol" cycles of NDG, controlled by cooling and heating ($\lambda_{ex} = 300$ nm).



Fig. 3. Partial ¹H NMR spectra of **NTS** in DMSO- d_6 with increasing amounts of **DTB**: a) Free **NTS** (0.01 M); b) Free **DTB** (0.01 M); c) **NTS** (0.0098 M) and **DTB** (0.0032 M); d) **NTS** (0.0095 M) and **DTB** (0.0095 M); e) **NTS** (0.0098 M) and **DTB** (0.0095 M) and **DTB** (0.0095 M).



Fig. 4. SEM images of a) NTS; b) DTB; c) NDG; d) NDG + Fe^{3+} ; e) NDG + Fe^{3+} + F^- .

ethanol solution. Finally, the product solid was dried in a vacuum oven at 40 °C for 24 h gave pure **NTS** (0.64 g, 85%): m.p. > 300 °C; ¹H NMR (Fig. S4) (600 MHz, DMSO-*d*₆) δ (ppm): 10.71 (s, 3 H, NH), 10.48 (s, 3 H, NH), 8.52 (s, 3 H, ArH), 8.19-8.17 (d, *J* = 12 Hz, 3 H, ArH), 7.94-7.92 (d, *J* = 12 Hz, 3 H, ArH), 7.85-7.83 (d, *J* = 12 Hz, 3H, ArH), 7.58-7.45 (m, 12H, ArH), 4.05 (s, 6H, CH₂); ¹³C NMR (Fig. S5) (151 MHz, DMSO-*d*₆) δ (ppm):169.80, 164.91, 133.74, 133.65, 132.46, 132.32, 130.06, 128.78, 128.21, 127.67, 126.46, 126.11, 125.92, 124.74, 38.13; HR-MS calculated for (C₄₅H₃₇N₆O₆⁺) [**NTS** + H]⁺ (*m*/*z*): 757.2769. Found: 757.2775 (Fig. S6).

3. Results and discussion

Based on the original design, a new host compound 1-naphthaleneacetic hydrazide functionalized tripodal hydrazide **NTS** was synthesized (Scheme 1), and the guest compound tri-(pyridine-4-yl)functionalized trimesoyl amide **DTB** was synthesized according to the reported method (Scheme S1) [43]. Additionally, the **NTH**, **NTS** and **DTB** were characterized using ¹H NMR, ¹³C NMR and HR-MS (Figs. S1–S9).

As shown in Fig. S10, in a binary solution, the NTS $(2 \times 10^{-2} \text{ M})$ exhibits weak fluorescence emission at 470 nm, and did not assemble into a stable supramolecular polymer hydrogel. The gel DTB (CGC, 3.0%, 10 mg/mL = 1%, w/v) exhibits fluorescence emission at 470 nm. However, when the DTB was added to the binary solution of DMSO-H₂O (3.3:6.7, v/v) of the NTS, the fluorescence emission of NDG exhibits a significant enhancement at 470 nm. The assembly ability and gelation properties of NTS and DTB were tested in various solutions via a "stabilized reverse tube" method (Tables S3 and S4). The host NTS (0.0063 g, 8.35 mmol) and guest DTB (0.0037 g, 8.35 mmol) were completely dissolved in DMSO (110 µL)-H₂O (220 µL) binary solution by heating, and then cooled to room temperature. As a result, a stable bi-component supramolecular polymer hydrogel NDG formed. The NDG exhibits the lowest critical gelation concentration (CGC, 3.0%, 10 mg/mL = 1%, w/ v) and the highest phase transition temperature ($T_{gel} = 96$ °C) in this binary solution. As shown in Fig. 2a, with the transformation from solgel, the NDG exhibits a strong white AIE phenomenon [44,45]. The fluorescence quantum yields of NTS, DTB and NDG are approximately 0.47, 0.53, 0.64 according to the corresponding formula, respectively (Fig. S10) [46]. Additionally, the NDG exhibits a reversible transition in response to temperature, which repeated multiple times with little

fluorescence efficiency loss (Fig. 2b).

The possible assembly mechanism of the NDG was investigated by HRMS, ¹H NMR, 2D NOESY NMR, FT-IR, SEM and XRD. First, the HRMS (Fig. S11) spectrum of NDG exhibits a parent peak at m/z 1195.4196 (calcd $C_{69}H_{55}N_{12}O_9^+$ 1195.4215) corresponding to the [NTS + DTB + H]⁺ fragment, which could be attributed to the formation of a 1 : 1 stoichiometry for the host and guest complexation. It is remarkable that the NTS and DTB displayed very strong binding affinities with binding constant K_a was up to 2.17×10^7 M⁻¹ (Fig. S12). Second, in the ¹H NMR titration spectra of NTS and DTB (Fig. 3), the signals of protons H_b and H_c on NTS exhibited distinct downfield shifted. Meanwhile, the signals of protons H₂, H₃ and H₄ on DTB also exhibited distinct downfield shifted, which indicated that hydrogen bond interactions existed between NTS and DTB. The signals of protons $H_{e, h}$, H_{g-k} of NTS underwent obvious upshifted, which indicated that ð-ð interactions existed between naphthalenes of NTS [47]. Meanwhile, zoom in to show the data with a vertical reference line were also provided for clear comparison (Fig. S13). In the concentration-dependent ¹H NMR spectra (Fig. S14), as the concentration increased of NTS and DTB, the proton peaks exhibited corresponding shifted. In the 2D NOESY NMR of NDG (Fig. S15), two correlations were observed for H_b, H_c and H_2 of the $\ensuremath{\textbf{NDG}}.$ Meanwhile, in the FT-IR spectra (Fig. S16a), upon addition of DTB into the NTS, the C=C signals of NTS and DTB shifted from 1527 cm^{-1} and 1521 cm^{-1} to 1534 cm⁻¹, supporting the **DTB** and **NTS** assembled via π - π stacking interactions. The –N–H signals of NTS and DTB shifted from 3216 cm⁻¹ and 3301 cm⁻¹ to 3195 cm⁻¹, the -C=O signals of NTS and DTB shifted from 1713 cm^{-1} and 1719 cm^{-1} to 1708 cm^{-1} , respectively. These results indicated that intermolecular hydrogen bonds (-N-H···O=C-) formed between NTS and adjacent DTB molecules. The SEM images of NTS and DTB exhibited amorphous powder structures (Fig. 4), while the xerogel of NDG exhibited a rod structure, which indicated that NTS and DTB assembled into a regular rodlike supramolecular polymer. Additionally, in the small-angle X-ray diffraction experiment of NDG (Fig. S17a), the d-spacing of 3.41 Å at $2\theta = 26.08$ also supported the above mentioned ð-ð stacking interactions [48]. According to the above results, we speculated that the possible self-assembly mechanism of the NDG being based on multiple supramolecular interactions (hydrogen bonding, ð-ð stacking and Van der-Waals interactions, e.g.). These aggregates have different aggregation-induced luminescence phenomena due to the different degree of polymerization and assembly methods. Under the irradiation of ultraviolet light, these different aggregates emit



Fig. 5. After the addition of 0.5 equiv. of various cations to **NDG**. Changes in a) fluorescence color (under UV-lamp, 365 nm) and b) fluorescence spectra ($\lambda_{ex} = 300$ nm). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

different wavelengths of fluorescence. Therefore, it is observed that the NDG with white light emission [49].

The photophysical properties of **NDG** in the presence of various ions were investigated. In order to evaluate the selective detection and separation properties of the **NDG** to different cations, we carefully studied the cation-response properties by adding and diffusing various metal ions aqueous solution (Hg²⁺, Ca²⁺, Mg²⁺, Ni²⁺, Cu²⁺, Cr³⁺, Cd²⁺, Pb²⁺, Ag⁺, Zn²⁺, Fe³⁺, Ba²⁺, Co²⁺, La³⁺, Eu³⁺, Tb³⁺, and Al³⁺, c = 0.1 M) into **NDG**. As shown in Fig. 5, after 0.5 equiv. of various cations were added into **NDG** only Fe³⁺ make the fluorescence of **NDG** quenched, indicating **NDG** can carry out selective fluorescent detection of Fe³⁺. In order to examine the sensing efficiency of **NDG** for Fe³⁺, the fluorescence titration experiment was monitored. As shown in Fig. 6a, with the increased of the amount of Fe³⁺ (0–0.45 equiv.), the fluorescence emission bands at 470 nm decreased and the fluorescence titration curve of **NDG** towards Fe³⁺ exhibited a good linear trend. Meanwhile, the detection limit of **NDG** towards Fe³⁺ was calculated to be 5.33×10^{-9} M (Fig. 6b) on the basis of the $3\delta/s$ method [50]. The results indicated that the detection of Fe³⁺ by **NDG** reached the ultrasensitive level. In order to further investigate the selectivity of the **NDG** for Fe³⁺, we implemented antiinterference experiments separately (Fig. S18), coexisting competition cations did not induce any interference in the sensing of the **NDG** for Fe³⁺.

It is worth noting that the host-guest interactions, a typical noncovalent interaction. Due to the responsiveness of non-covalent interaction, stimuli-responsive soft materials can be fabricated via the orthogonal combination of non-covalent interaction and metal-ligand interactions, extending the applications of supramolecular polymers in fluorescence materials [51]. In the above experiments, the **NDG** exhibited excellent response and binding property for Fe^{3+} , we rationally introduced competitive coordination properties by adding Fe^{3+} into **NDG** to prepare Fe^{3+} coordinated metallogel, and named as **NDG-Fe**. Interestingly, by competitive coordination interactions, the metallogel **NDG-Fe** exhibited specific anion-response properties.

To further investigate the anions response properties of **NDG-Fe**, a series of anions aqueous solution (AcO⁻, HSO₄, H₂PO₄, F⁻, Cl⁻, Br⁻, I⁻, ClO₄, SCN⁻, CN⁻, S²⁻, and N₃, c = 0.1 M) were separately added and permeated into the **NDG-Fe**. As shown in Fig. 5a, the fluorescence of



Fig. 6. The fluorescent titrations of a) NDG for Fe³⁺ and c) NDG-Fe for F⁻; Data fitting of the fluorescent titrations with b) Fe³⁺ and d) F⁻ ($\lambda_{ex} = 300$ nm).



Fig. 7. a) Writing and erasing of a natural light invisible image on the NDG film; b) schematic for patterning fluorescent hydrogel by photolithography.

NDG-Fe enhanced when F⁻ was added. In addition, the fluorescence titration experiments was carried out (Fig. 6c), the LOD of **NDG-Fe** for F⁻ was 1.61×10^{-8} M (Fig. 6d). Meanwhile, the addition of other anions did not cause a significant change on the fluorescence intensity of the **NDG-Fe** (Fig. S19). Thus, the **NDG-Fe** was able to selectively detect F⁻ in aqueous solution.

Supramolecular polymer hydrogel NDG was constructed by hostguest interactions. Nowadays, the host-guest interactions have been employed to hold two or more ions or molecules together in certain structures. The combination of host-guest interactions with metal-ligand coordination is an efficient approach for the hierarchical self-assembly of functional complex architectures [52]. We all know that Fe^{3+} is an ion of a single electron and has high ionic strength [53], which is easy to induce the π electrons on naphthalene group transfer to Fe³⁺ and form cation- π interactions, so that Fe³⁺ can be identified by cation- π interactions. Based on this, the continuity detection mechanism of Fe³⁺ and F⁻ by NDG was researched via FT-IR, XRD, SEM and HRMS analyses. First, the HRMS (Fig. S20) spectrum of NDG exhibits a parent peak at m/z 523.6006 corresponding to the [NTS + DTB + 3Fe + 6Cl]³⁺ fragment. In the corresponding IR spectra (Fig. S16b), the stretching vibration absorption peaks of = C-H, C=C, -C=O and -N-H groups appeared at 3046, 1534, 1708 and 3195 cm⁻¹, respectively. With the addition of Fe^{3+} into NDG and formed NDG-Fe, the vibration absorption peak of = C-H, C=C, -C=O and -N-H red shifted (the vibration absorption peak shifted to 2930, 1512, 1697 and 3188 cm⁻¹), which demonstrated that the NDG combined with Fe^{3+} via cation- π interactions [54]. The electrons transferred from NDG to Fe^{3+} due to the existence of cation- π and metal coordination interactions. The electron cloud density of NDG decreases, causing the proton peaks move to low wavenumbers, which induced the fluorescence quenching of NDG. As we expected, after the addition of F⁻ into the NDG-Fe, the -C=O, =C-H and -N-H absorption peaks recovered to their initial positions. These results attributed to the strong coordination ability of Fe³⁺ with F⁻, and the competitive binding of F^- with Fe^{3+} [55].

In the XRD patterns (Fig. S17), the xerogel of NDG exhibited a peak of 3.41 Å at $2\theta = 26.08$, which indicated the existence of π - π stacking interactions in NDG [48]. However, the peak disappeared when Fe³⁺ was added to NDG, and formed metallogel NDG-Fe. A new peak at $2\theta =$ 31.36 (d = 2.85 Å) appeared, indicating that the NDG combined with Fe³⁺ via cation- π interactions [54,56,57]. After addition of F⁻ into NDG-Fe, the signal peak of 3.47 Å at $2\theta = 25.62$ appeared again. These results indicated that F⁻ competitively bound with Fe³⁺, and the π - π stacking interactions formed again [58]. As shown in SEM images, the graceful rod structure of NDG (Fig. 4c) became fibrous structure of NDG-Fe (Fig. 4d), and after adding F⁻ to NDG-Fe, the fibrous structure was approximately restored to rod structure (Fig. 4e). Indicating F⁻ competitively bound with Fe³⁺ induce the change of morphology. Therefore, the results support the possible **NDG** continuity recognition mechanism proposed in Fig. 1 [59]. In addition, the chelator EDTA (ethylenediaminetetraacetic acid) has strong affinity with Fe³⁺. In order to confirm the binding competition mechanism, we use EDTA instead of F⁻. As a result, the EDTA made the fluorescence of **NDG-Fe** recovery, which indicated that F⁻ competitively bound with Fe³⁺ (Fig. S21).

For application purposes, the ingestion capacity of the **NDG** for Fe³⁺ in aqueous solution was assessed by inductively coupled plasma (ICP) analysis. The xerogel of **NDG** (1 mg, 6×10^{-7} mol) was suspended in aqueous solution of Fe³⁺ (1×10^{-5} M, 5.0 mL) and stirred for 12 h. Then the suspension removed by centrifuging at 10,000 rpm for 10 min. Finally, the ICP was used to assess the ingestion capacity of **NDG** for Fe³⁺. As shown in Table S5 and Table S6, after the adsorption Fe³⁺ by the xerogel of **NDG** in aqueous solution, the residual concentration of Fe³⁺ less than 1×10^{-7} M. The absorption rate of **NDG** for Fe³⁺ was approximately 99.26%, and the absorption capacity was about 23 mg/g. Experimental analysis results indicated that the **NDG** efficiently removed Fe³⁺ even in extremely dilute solutions. Compared with other adsorbent materials, supramolecular hydrogel **NDG** not only can carry out ultrasensitive and selective fluorescence detects Fe³⁺, but also efficiently adsorbs Fe³⁺ in extremely dilute solutions.

The conformation, packing and intermolecular interactions of supramolecular organic fluorophores play an important role in the fluorescence emission of molecules. Supramolecular organic fluorescent materials are easy to prepare, low cost, and environmentally friendly. Therefore, fluorescent materials with good stability can be developed to produce an erasable fluorescent anti-counterfeit label, and supramolecular organic fluorescent materials can be used as ion-controlled fluorescent switch excellent candidates. The NDG-based film was prepared by pouring heated DMSO-H2O solution of NDG onto a clean glass surface, and then drying in air. As shown in Fig. 7a, the NDG film exhibited white fluorescence emission under UV (365 nm) light. When writing on the film with a writing brush dipped in Fe³⁺ aqueous solution, a clear dark writing image was observed under irradiation at 365 nm using a UV lamp, which was invisible under natural light. In addition, when aqueous solution of F⁻ was added, the fluorescence effectively restored. Thus, we can control the fluorescence by Fe³⁺ and F⁻ competitive coordination to realize the patterning of hydrogels for protected information display. As shown in Fig. 7b, more complex patterns be facilely obtained by designing the photomask based on ions sensing.

The time-dependency on the Fe³⁺-induced change in fluorescence of the **NDG** was then studied. Generally, reaction-based chemosensors suffer from a long response time, however, the transient response property of **NDG** to Fe³⁺ and **NDG-Fe** to F⁻ was found in this work. The prepared films based on **NDG** and **NDG-Fe** could instantaneous detection of Fe³⁺ and F⁻. The **NDG** film was prepared by pouring heated



Fig. 8. a) Fluorescence intensity of NDG at 470 nm in the presence of different inputs. b) The sequential logic circuit of the memorymachine. c) Truth table for the "IMPLICATION" logic gate. d) Feedback loop showing the reversible logic operations for the memory element with "Reading-Erasing-Reading-Writing" functions.

DMSO-H₂O binary solution of **NDG** onto a clean glass surface and then drying in air. As shown in Fig. S22, the **NDG** exhibits white fluorescence emission under UV (365 nm) light). When Fe³⁺ aqueous solution was added to **NDG**, the fluorescence of **NDG** instantly disappeared. In addition, when aqueous solution of F⁻ was added to Fe³⁺ coordinated metallogel, the fluorescence of **NDG-Fe** instantly restored. These results suggested that the coordination of Fe³⁺ with **NDG** was completed nearly instantaneously. Likewise, the competitive coordination of F⁻ and **NDG-Fe** was almost immediately completed. Therefore, the **NDG** can act as transient response fluorescence switch.

In view of the above, the NDG-Fe was able to effectively sense F^- with specific selectivity, but after addition of Fe^{3+} into F^- containing NDG-Fe, the fluorescence intensity decreased again. Therefore, the NDG could act as an Fe^{3+} and F^- controlled "ON-OFF-ON" fluorescence response switch (Fig. S23), and the switching behavior work repeatedly for at least four successive cycles with a small loss of fluorescence efficiency. Therefore, the NDG film not only can be used as an erasable secure fluorescent display material, but as a convenient reversible Fe^{3+} and F^- test kit. It is worth noting that the reaction-based chemosensors suffer from a long response time. In this text, the prepared films based on NDG and NDG-Fe were able to instantaneous detection of Fe^{3+} and F^- , respectively.

This proposed NDG-based luminescent material, with implementation, instant response and straightforward readout. Moreover, this labelfree assay be successfully applied in the real environmental water sample analysis, which inspired us to apply it as a strategy of logic gate for the detection of ions. Herein, the sensitization of NDG luminescence enabled the design of an "IMPLICATION" logic gate. In this logic gate (Fig. 8), the two input signals are input Fe^{3+} and input F^- , the presence of Fe^{3+} or F^- was defined as the "1" state and their absence as the "0". The output was the fluorescence intensity change of the NDG at 470 nm, and strong fluorescence intensity and weak fluorescence intensity were defined "1" and "0", respectively. For input, with no input (0, 0), the output was "1". With Fe^{3+} (1, 0) input alone causes an extremely weak fluorescence intensity and the output was "0". Similarly, with $F^-(0, 1)$ input alone, the fluorescence intensity was extremely strong and the output was "1". When the system was subjected to the two inputs together (1, 1), the luminescence intensity sharply increased, giving an output signal of "1". The corresponding luminescence signals were presented in Fig. 8. Therefore, this simple supramolecular hydrogel was potential candidate for the development of new generation of digital devices.

4. Conclusion

In summary, we designed and synthesized 1-naphthaleneacetic hydrazide functionalized tripodal hydrazide (NTS) and tri-(pyridine-4-yl)functionalized trimesoyl amide (DTB) successfully. Intriguingly, the NTS and DTB formed a supramolecular polymer hydrogel (NDG) in DMSO-H₂O (3.3 : 6.7, v/v) binary solution by hydrogen bonds and π - π stacking interactions, and the NDG exhibits strong white aggregationinduced emission. Significantly, the NDG exhibits ultrasensitive stimuli-responsiveness to Fe³⁺. Meanwhile, Fe³⁺ was effectively adsorbed and separated by NDG from aqueous solution. After addition of Fe³⁺ into NDG, metallogel NDG-Fe formed, and NDG-Fe can high sensitively detect F^- by the competition between π - π interactions and cation- π interactions. In addition, the NDG-based thin films were prepared, which be used as rewritable fluorescent material and fluorescent switch. Most remarkably, the fluorescence changes of NDG upon the addition of Fe^{3+} and F⁻ were utilized as an "IMPLICATION" logic gate at the molecular level. The new strategy of prepared hydrogel with white AIE effect is now being actively pursued in our laboratory. We hope the outcomes of our study will inspire people to investigate the syntheses and physicochemical properties of smart supramolecular polymer materials.

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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21662031 and 21661028), the Program for Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (IRT 15R56).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108875.

Author statement

Qi Zhao: Software, Formal analysis, Investigation, Data curation, Writing - original draft. Xin-Yu Dai: Data curation. Hong Yao: Conceptualization, Supervision, Project administration. You-Ming Zhang: Conceptualization, Funding acquisition, Validation. Wen-Juan Qu: Conceptualization, Supervision, Project administration. Qi Lin: Funding acquisition, Investigation, Writing - review & editing. Tai-Bao Wei: Funding acquisition, Investigation, Writing - review & editing, Visualization.

References

- [1] Sun P, Wang Z, Sun D, Bai H, Zhu Z, Bi Y, et al. pH-guided self-assembly of silver nanoclusters with aggregation-induced emission for rewritable fluorescent platform and white light emitting diode application. J Colloid Interface Sci 2020; 567:235–42.
- [2] Soriano-Romero O, Lozada-Morales R, Meza-Rocha AN, Carmona-Téllez S, Caldino U, Flores-Desirena B, et al. Cold bluish white and blue emissions in Cu⁺doped zinc phosphate glasses. J Lumin 2020;217:116791.
- [3] Reineke S, Lindner F, Schwartz G, Seidler N, Walzer K, Lussem B, et al. White organic light-emitting diodes with fluorescent tube efficiency. Nature 2009;459: 234–8.
- [4] Reineke S, Thomschke M, Lüssem B, Leo K. White organic light-emitting diodes: status and perspective. Rev Mod Phys 2013;85(3):1245–93.
- [5] Shao B, Huo J, You H. Prevailing strategies to tune emission color of lanthanideactivated phosphors for WLED applications. Adv Opt Mater 2019;7(13): 1900319.
- [6] Zhao M, Liao H, Molokeev MS, Zhou Y, Zhang Q, Liu Q, et al. Emerging ultranarrow-band cyan-emitting phosphor for white LEDs with enhanced color rendition. Light Sci Appl 2019;8:38–47.
- [7] Dai W, Lei Y, Xu M, Zhao P, Zhang Z, Zhou J. Rare-earth free self-activated graphene quantum dots and copper-cysteamine phosphors for enhanced white light-emitting diodes under single excitation. Sci Rep 2017;7:12872–82.
 [8] White MS, Kaltenbrunner M, Głowacki ED, Gutnichenko K, Kettlgruber G, Graz I,
- et al. Ultrathin, highly flexible and stretchable PLEDs. Nat Photo 2013;7:81–6.
- [9] Li X, Li Z, Yang YW. Tetraphenylethylene-interweaving conjugated macrocycle polymer materials as two-photon fluorescence sensors for metal ions and organic molecules. Adv Mater 2018;30:1800177.
- [10] Podder D, Nandi SK, Sasmal S, Haldar D. Synergistic tricolor emission-based white light from supramolecular organic-inorganic hybrid gel. Langmuir 2019;35(19): 6453–9.
- [11] Wang LY, Cui MM, Tang H, Cao DR. Fluorescent nanoaggregates of quinoxaline derivatives for highly efficient and selective sensing of trace picric acid. Dyes Pigments 2018;155:107–13.
- [12] Huang A, Yang Z, Yu C, Chai Z, Qiu J, Song Z. Tunable and white light emission of a single-phased Ba₂Y(BO₃)₂Cl:Bi³⁺, Eu³⁺ phosphor by energy transfer for ultraviolet converted white LEDs. J Phys Chem C 2017;121(9):5267–76.
- [13] Adelizzi B, Van Zee NJ, Windt LNJ, Palmans ARA, Meijer EW. Future of supramolecular copolymers unveiled by reflecting on covalent copolymerization. J Am Chem Soc 2019;141(15):6110–21.
- [14] Dong S, Luo Y, Yan X, Zheng B, Ding X, Yu Y, et al. A dual-responsive supramolecular polymer gel formed by crown ether based molecular recognition. Angew Chem 2011;50(8):1905–9.
- [15] Luo J, Xie Z, Lam JW, Cheng L, Chen H, Qiu C, et al. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. Chem Commun 2001;18:1740–1.
- [16] Dai J, Wu X, Ding S, Lou Y, Xia F, Wang S, Hong Y. Aggregation-induced emission photosensitizers: from molecular design to photodynamic therapy. J Med Chem 2020;63(5):1996–2012.
- [17] Cheng HB, Li Z, Huang YD, Liu L, Wu HC. Pillararene-based aggregation-inducedemission-active supramolecular system for simultaneous detection and removal of mercury(II) in water. ACS Appl Mater Interfaces 2017;9(13):11889–94.
- [18] Li J, Wang J, Li H, Song N, Wang D, Tang BZ. Supramolecular materials based on AIE luminogens (AIEgens): construction and applications. Chem Soc Rev 2020;49 (4):1144–72.
- [19] Zhou J, Yu GC, Huang FH. Supramolecular chemotherapy based on host-guest molecular recognition: a novel strategy in the battle against cancer with a bright future. Chem Soc Rev 2017;46(22):7021–53.
- [20] Freeman R, Han M, Álvarez Z, Lewis JA, Wester JR, Stephanopoulos N, et al. Reversible self-assembly of superstructured networks. Science 2018;362(6416): 808–13.
- [21] Mao L, Pan W, Fu Y, Chen L, Xu M, Ren Y, et al. Reversibly tunable lower critical solution temperature behavior induced by H-bonded aromatic amide macrocycle and imidazolium host–guest complexation. Org Lett 2017;19(1):18–21.
- [22] Tu T, Fang W, Bao X, Li X, Dotz KH. Visual chiral recognition through enantioselective metallogel collapsing: synthesis, characterization, and application

of platinum-steroid low molecular-mass gelators. Angew Chem Int Ed 2011;50(29): 6601–5.

- [23] Fu HG, Chen Y, Liu Y. Multistimuli-responsive and photocontrolled supramolecular luminescent gels constructed by anthracene-bridged bis(dibenzo-24-crown-8) with secondary ammonium salt polymer. ACS Appl Mater Interfaces 2019;11(17): 16117–22.
- [24] Li ZY, Zhang Y, Zhang CW, Chen LJ, Wang C, Tan H, et al. Cross-linked supramolecular polymer gels constructed from discrete multi-pillar[5]arene metallacycles and their multiple stimuli-responsive behavior. J Am Chem Soc 2014;136(24):8577–89.
- [25] Tan LL, Li H, Qiu YC, Chen DX, Wang X, Pan RY, et al. Stimuli-responsive metalorganic frameworks gated by pillar[5]arene supramolecular switches. Chem Sci 2015;6(3):1640–4.
- [26] Yang HL, Zhang QP, Zhang YM, Gong GF, Chen YY, Zhou Q, et al. A novel strong AIE bi-component hydrogel as a multi-functional supramolecular fluorescent material. Dyes Pigments 2019;171:107745.
- [27] Xiong W, Wang LY, Tang H, Cao DR. A multistimuli-responsive fluorescent switch in the solution and solid states based on spiro[fluorene-9,9'- xanthene]-spiropyran. J Mater Chem C 2019;7(29):9102–11.
- [28] Zhang CW, Ou B, Jiang ST, Yin GQ, Chen LJ, Xu L, Li X, Yang HB. Cross-linked AIE supramolecular polymer gels with multiple stimuli-responsive behaviours constructed by hierarchical self-assembly. Polym Chem 2018;9(15):2021–30.
- [29] Girelli D, Nemeth E, Swinkels DW. Hepcidin in the diagnosis of iron disorders. Blood 2016;127(23):2809–13.
- [30] Ward RJ, Zucca FA, Duyn JH, Crichton RR, Zecca L. The role of iron in brain ageing and neurodegenerative disorders. Lancet Neurol 2014;13(10):1045–60.
- [31] Eid R, Arab NT, Greenwood MT. Iron mediated toxicity and programmed cell death: a review and a re-examination of existing paradigms. Biochim Biophys Acta Mol Cell Res 2017;1864(2):399–430.
- [32] Prus E, Fibach E. The labile iron pool in human erythroid cells. Br J Haematol 2008;142(2):301–7.
- [33] Theil E, Goss DJ. Living with iron (and oxygen): questions and answers about iron homeostasis. Chem Rev 2009;109(10):4568–79.
- [34] Carter KP, Young AM, Palmer AE. Fluorescent sensors for measuring metal ions in living systems. Chem Rev 2014;114(8):4564–601.
- [35] Okesola BO, Smith DK. Applying low-molecular weight supramolecular gelators in an environmental setting-self-assembled gels as smart materials for pollutant removal. Chem Soc Rev 2016;45(15):4226–51.
- [36] Wade CR, Broomsgrove AEJ, Aldridge S, Gabbaï FP. Fluoride ion complexation and sensing using organoboron compounds. Chem Rev 2010;110(7):3958–84.
- [37] Ma Q, Wang J, Li Z, Wang D, Hu X, Xua Y, et al. Near-infrared-light-mediated highthroughput information encryption based on the inkjet printing of upconversion nanoparticles. Inorg Chem Front 2017;4(7):1166–72.
- [38] Ouyang XY, Yu R, Jin J, Li J, Yang R, Tan W, et al. New strategy for label-free and time-resolved luminescent assay of protein: conjugate Eu³⁺ complex and aptamerwrapped carbon nanotubes. Anal Chem 2011;83(3):782–9.
- [39] Zeng L, Zeng H, Wang S, Wang S, Hou J, Yoon J. A paper-based chemosensor for highly specific, ultrasensitive, and instantaneous visual detection of toxic phosgen. Chem Commun 2019;55(91):13753–6.
- [40] Das R, Sugimoto H, Fujii M, Giri PK. Quantitative understanding of charge-transfermediated Fe³⁺ sensing and fast photoresponse by N-doped graphene quantum dots decorated on plasmonic Au nanoparticles. ACS Appl Mater Interfaces 2020;12(4): 4755–68.
- [41] Kwon N, Baek G, Swamy KMK, Lee M, Xu Q, Kim Y, et al. Naphthoimidazolium based ratiometric fluorescent probes for F⁻ and CN⁻ and anion-activated CO₂ sensing. Dyes Pigments 2019;171:107679.
- [42] Lin Q, Lu TT, Zhu X, Wei TB, Li H, Zhang YM. Rationally introduce multicompetitive binding interactions in supramolecular gels: a simple and efficient approach to develop multi-analyte sensor array. Chem Sci 2016;7:5341–6.
- [43] Zhao Q, Gong GF, Yang HL, Zhang QP, Yao H, Zhang YM, et al. Pillar[5]arenebased supramolecular AIE hydrogel with white light emission for ultrasensitive detection and effective separation of multianalytes. Polym Chem 2020;11: 5455–62.
- [44] Mei J, Leung NLC, Kwok RTK, Lam JWY, Tang BZ. Aggregation-induced emission: together we shine, united we soar. Chem Rev 2015;115(21):11718–940.
- [45] Xu L, Wang R, Cui W, Wang L, Meier H, Tang H, et al. Stronger host-guest binding does not necessarily give brighter particles: a case study on polymeric AIEE-tunable and size-tunable supraspheres. Chem Commun 2018;54(67):9274–7.
- [46] Kempe D, Schöne A, Fitter J, Gabba M. Accurate fuorescence quantum yield determination by fluorescence correlation spectroscopy. J Phys Chem B 2015;119 (13):4668–72.
- [47] Gopikrishna P, Meher N, Iyer PK. Functional 1, 8-Naphthalimide AIE/AIEEgens: recent advances and prospects. ACS Appl Mater Interfaces 2018;10(15): 12081–111.
- **[48]** Son SY, Kim JH, Song E, Choi K, Lee J, Cho K, et al. Exploiting π - π stacking for stretchable semiconducting polymers. Macromolecules 2018;51(7):2572–9.
- [49] Tian D, Qi F, Ma H, Wang X, Pan Y, Chen R, et al. Domino-like multi-emissions across red and near infrared from solid-state 2-/2,6-aryl substituted BODIPY dyes. Nat Commun 2018;9:2688–97.
- [50] Analytical Methods Committee. Recommendations for the definition, estimation and use of the detection limit. Analyst 1987;112(2):199–204.
- [51] Zheng W, Wang W, Jiang ST, Yang G, Li Z, Wang XQ, et al. Supramolecular transformation of metallacycle-linked star polymers driven by simple phosphine ligand-exchange reaction. J Am Chem Soc 2019;141(1):583–91.

Q. Zhao et al.

Dyes and Pigments 184 (2021) 108875

- [52] Dong S, Zheng B, Wang F, Huang F. Supramolecular polymers constructed from macrocycle-based host-guest molecular recognition motifs. Acc Chem Res 2014;47 (7):1982–94.
- [53] Zhang W, Ning B, Sun C, Song K, Xu X, Fang T, et al. Dynamic nano-Ag colloids cytotoxicity to and accumulation by Escherichia coli: effects of Fe³⁺, ionic strength and humic acid. J Environ Sci 2020;89:180–93.
- [54] Kennedy CR, Lin S, Jacobsen EN. The cation-π interaction in small molecule catalysis. Angew Chem Int Ed 2016;55(41):12596–624.
- [55] Wang L, Fang G, Cao D. Diketopyrrolopyrrole-derived Schiff base as colorimetric and fluorometric probe for sequential detection of HSO₄⁻ and Fe³⁺ with "off-on-off" response. Sens Actuators, B 2015;209(31):536–44.
- [56] Tsuzuki S, Uchimaru T, Mikami M. Is the cation/π interaction in alkaline earthmetal dication/benzene complexes a covalent interaction. J Phys Chem 2003;107: 10414–8.
- [57] Yamada S. Cation-π interactions in organic crystals. Coord Chem Rev 2020;415: 213301.
- [58] Ma Y, Ma H, Yang Z, Ma J, Su Y, Li W, et al. Methyl cinnamate-derived fluorescent rigid organogels based on cooperative π-π stacking and C=O···π interactions instead of H-bonding and alkyl chains. Langmuir 2015;31(17):4916–23.
- [59] Suganya S, Naha S, Velmathi S. A critical review on colorimetric and fluorescent probes for the sensing of analytes via relay recognition from the year. 2012–17. Chemistry 2018;3(25):7231–68.