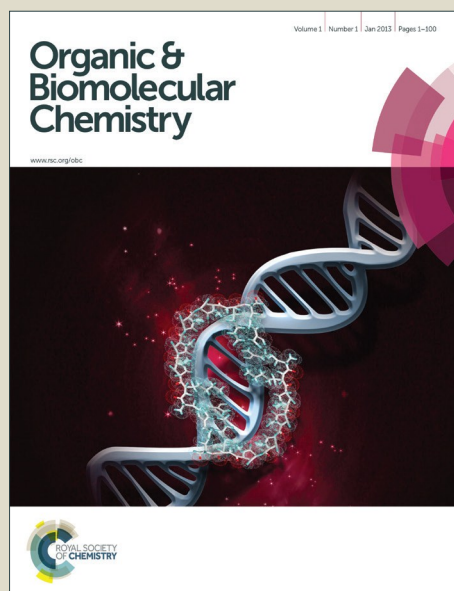


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Ultrasound accelerated organogel: application for visual discrimination of Hg^{2+} from Ag^+

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Abstract: a new kind of naphthalimide based organolator **TN** was designed and synthesized. The intramolecular guanylation of **TN** promoted by Hg^{2+} or Ag^+ in both solution and gel state was studied through several approaches including FL, UV-vis, NMR, FT-IR and SEM experiments. **TN** could selectively sense Hg^{2+} and Ag^+ ions with obvious fluorescence quenching and color changes from yellow to colorless among test ions in the solution state. Interestingly, the S-gel of **TN** could be used to selectively discriminate Hg^{2+} from Ag^+ via phase and morphology changes. Hg^{2+} ions triggered the gel-to-gel transition with morphology changes of **TN** S-gel from nanofibrils to porous sheet structure, together with fluorescence quenching. Whilst, the gel collapsed in the presence of Ag^+ ions, which was comprised of short and disordered fiber structure. To the best of knowledge, this is the first example that gels could selectively sensing Hg^{2+} or Ag^+ via reaction approach.

Introduction

In the past decades, the detection of mercury has received a great deal of attention due to its important role in environment, food chain, and human health.^{1–7} One of the attractive approach for this purpose involves the development of highly selective reactions induced by target analytcs, in which fluorescent signal outputs are usually observed. Some fluorescent chemodosimeters via irreversible mercury-promoted desulfurization approach for mercury ion have been developed.^{8–10} However, very few of them could discriminate Hg^{2+} from Ag^+ because that the Ag^+ could also promote guanylation reaction of ethylamine-thiourea group. Seeking novel system which could selectively discriminate Hg^{2+} from Ag^+ via guanylation approach is still a challenge.

Recently, Design of functional Low Molecular Weight Gelators (LMWGs) to create sensing systems toward analytcs has emerged as a research area of great importance. They often express instant and visual response including fluorescent, color and phase changes to tested analytcs such as gas, chiral compounds, ions, as well as biomolecules.^{11–26} These studies showed that the gel networks might be more efficient for the luminescence and sensing properties of materials such as enhanced fluorescence and energy transfer, high sensitivity, as well as multiple signal outputs compared with that of solution. In previous works, we also reported many kinds of sonogels and their application for analyst sensing.^{27–35} Recently, we

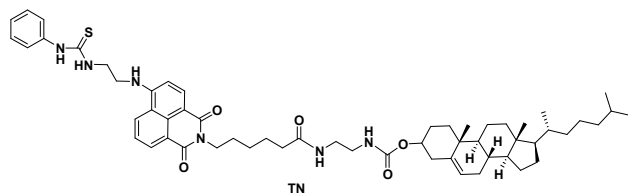
found that the ordered fibrous network could be exploited to discriminate Ca^{2+} from Mg^{2+} via different emission color changes, which was not observed in diluted solution state.³⁴ Therefore, we envisioned that a gel scaffold might be more efficient to discriminate Hg^{2+} from Ag^+ due to their different reaction abilities, sizes, and coordination modes, which played an important role in assembly approach. Inspired by this concept, herein, a novel organogelator (**TN**) containing ethylamine-thiourea segment as the reaction group with Hg^{2+} and Ag^+ and naphthalimide segment as the fluorogenic signal group was designed and characterized (Scheme 1 and 2), which could form stable gels in organic solvents by heating-cooling process or ultrasound. The gel formed by ultrasound at room temperature without heat stimuli was more meaningful for practical application. Considering about the solubility and gel preparation by ultrasound, the solutions and gels in butanol were mainly studied. Fluorescent quenching and discoloration of **TN** solution (10^{-5} M) were observed upon the addition of Hg^{2+} or Ag^+ . Interestingly, gel collapsing happened upon the addition of Ag^+ , while the Hg^{2+} only triggered the fluorescence quenching of the gel without phase changes. Although many chemical sensors for selectively sensing Hg^{2+} and Ag^+ via intramolecular guanylation approach were reported, this is the first report about the sensing properties of this reaction in gel tissue, which could be developed for selectively discriminating Hg^{2+} from Ag^+ by visual changes.

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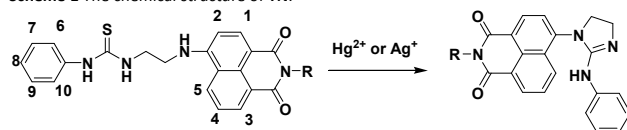
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† Electronic supplementary information (ESI) available. See DOI:



Scheme 1 The chemical structure of TN.

Scheme 2 Intramolecular guanylation of TN promoted by Hg^{2+} or Ag^+ .

Experimental

Materials

All starting materials were obtained from commercial supplies and used without further purification. Cholesteryl chloroformate (99%) was obtained from Sigma-Aldrich. Methyl L-lysinate dihydrochloride, HOBt (NHydroxybenzotriazole, 98%), EDC·HCl (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, 98%), 4-Br-1, 8-naphthalic anhydride, phenyl isothiocyanate and other reagents were supplied from Shanghai Darui fine chemical Co. Ltd.

Techniques

FTIR spectra were recorded by using an IRPRESTIGE-21 spectrometer (Shimadzu). SEM images of the xerogels were obtained by using SSX-550 (Shimadzu) and FE-SEM S-4800 (Hitachi) instruments. Samples were prepared by spinning the gels on glass slides and coating them with Au. NMR spectra were performed on a Bruker Advance DRX 400 spectrometer operating at 500/400 and 125/100 MHz for ^1H NMR and ^{13}C NMR spectroscopy, respectively. The high-resolution mass spectra (HR-MS) were measured on a Bruker Micro TOF II 10257 instrument. Fluorescence spectra were collected on an Edinburgh instrument FLS-920 spectrometer with a Xe lamp as an excitation source. The X-ray diffraction pattern (XRD) was generated by using a Bruker AXS D8 instrument (Cu target; $\lambda = 0.1542$ nm) with a power of 40 kV and 50 mA. UV-Vis absorption and fluorescent spectra were recorded on a UV-vis 2550 spectroscope (Shimadzu). Sonication treatment of a sol was performed in a KQ-500DB ultrasonic cleaner (maximum power, 100 W, 40 KHz, Kunshan Ultrasound Instrument Co, Ltd., China).

Gel preparation

Formation of T-gel: 5 mg TN and 200 μL organic solvents was added in the HPLC tube (2 mL), then heating the close tube to 90 $^\circ\text{C}$ followed by rest for minutes. Formation of S-gel: the suspension of TN (5 mg/200 μL) were subjected to sonication in KQ-500DB ultrasonic cleaner for less than 2 min, a gel formed.

The ion sensing experiments

Nitrite salts of metal ions (Mg^{2+} , Ca^{2+} , Na^+ , Bi^{3+} , Al^{3+} , Hg^{2+} , Ba^{2+} , Ag^+) and chloride salts of metal ions (Sn^{2+}) were used to evaluate the metal ion binding properties by the synthesized compound TN. After staying for 8 hours in dark, the fluorescence and UV-vis spectra of samples were tested.

Results and discussion

The synthesis and characterization of TN could be seen from ESI. From an overall consideration of solubility of ions and gelation solvents of TN, the ion recognition properties were performed in n-butyl alcohol. We tested the fluorogenic and chromogenic sensing activity of TN for nine kinds of colorless ions, e. g. Mg^{2+} , Ca^{2+} , Na^+ , Al^{3+} , Hg^{2+} , Ba^{2+} , Ag^+ , Al^{3+} , and Sn^{2+} . As seen from Fig. 1a and 1b, addition of Hg and Ag would triggered color changes from yellow to colorless and the fluorescence quenching of the TN solution (10^{-5} M), whereas other ions caused no obvious changes. The fluorescence changes were in accordant with fluorescence spectra of TN solution upon the addition of different kinds of ions (Fig. 2a and 2b).

To further evaluate the sensing properties of TN toward Hg^{2+} and Ag^+ , fluorescent titrations were performed. AS seen in Fig. 2c and 2d, upon the addition of Hg^{2+} from 0 to 4 eq., the fluorescence quenched by a factor of 7.6. Ag^+ also triggered similar but weaker changes of TN fluorescent intensity (the fluorescent intensity quenched by 7.1 fold). The gradual addition of Hg^{2+} into TN solution (10^{-5} M) resulted in the regular decrease of the peak at 436 nm, simultaneously, a new peak at 340 nm appeared and enhanced (Fig. 3a), which was attributed to the absorption peak of imidazole based compound produced by guanylation reaction of TN and Hg^{2+} (scheme 2). Ag^+ triggered similar spectral changes of TN in the solution state. The above result indicated the guanylation of TN could also be accelerated by Ag^+ , which might be attributed to the formation of Ag_2S . The measured intensity ($1/(I-I_0)$) as a function of $1/([\text{Hg}^{2+}])$ or $1/([\text{Ag}^+])$ was in a linear relationship, which was the 1:1 stoichiometry of the ion-promoted cycloguanylation of TN (Fig. S1). Therefore, TN was a colorimetric and fluorogenic sensor toward both Hg^{2+} and Ag^+ via intramolecular guanylation in a stoichiometric process in the diluted solution state.



Fig. 1 a) the fluorescence emission response of **TN** (10^{-5} M) on addition of 50 eq. cations in *n*-butanol excited at 254 nm using UV lamp. Left to right: free metal, Mg^{2+} , Ca^{2+} , Na^{+} , Al^{3+} , Hg^{2+} , Ag^{+} , Ba^{2+} , Al^{3+} , and Sn^{2+} .

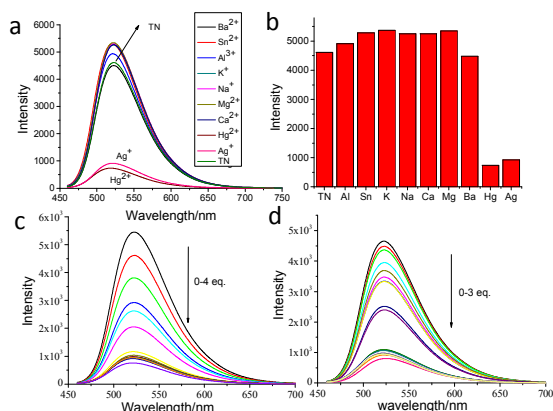


Fig. 2 Fluorescence emission spectrum changes of **TN** (10^{-5} M) upon the addition of different ions (50 eq.); b) the intensity value of **TN** with ions at 523 nm; c) fluorescent titrations of **TN** with Hg^{2+} ; d) fluorescent titrations of **TN** with Ag^{+} .

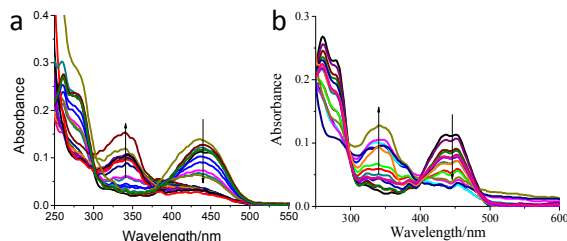


Fig. 3 a) UV-vis titrations of **TN** upon the addition of Hg^{2+} ; b) UV-vis titrations of **TN** upon the addition of Ag^{+} .

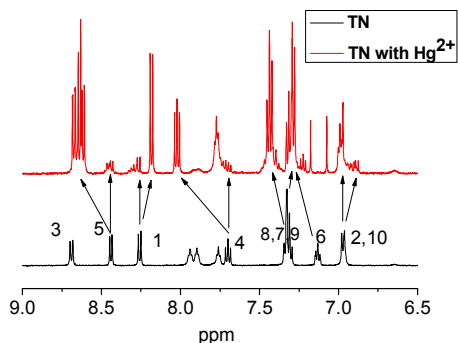


Fig. 4 ^1H NMR titrations of **TN** upon the addition of 5 eq. Hg^{2+} in DMSO solution.

To further confirm the guanylation of **TN** promoted by Hg^{2+} or Ag^{+} , ^1H NMR titrations were carried out. Seen from Fig. 4, upon the addition of 3 equiv. Hg^{2+} , and after aging for 24 hours, significant NMR changes of **TN** were observed on the signals of both naphthalimide and benzyl segments. The peaks of CH(5), CH(4) positioned at 8.44, 7.12 ppm displayed downfield shift to 8.62, 7.32 ppm, and the peak of CH(1) at 8.26 ppm shifted upfield from 8.26 ppm to 8.18 ppm, indicating the weakened ICT process of **TN** after guanylation reaction (Scheme 1). Similar changes were also observed in the CH of benzyl group.

According to the NMR integral studies, 97% product was obtained. MALDITOF mass spectral experiment experiments of **TN** samples after addition of Hg^{2+} or Ag^{+} were also carried out. The intense peak at 925.5922 ($\text{M}+\text{H}^{+}$) or 947.5139 ($\text{M}+\text{Na}^{+}$) was attributed to the product of **TN** after intramolecular guanylation, which strongly certified the above result (Figure S2).

The high selectivity of **TN** toward Hg^{2+} and Ag^{+} make it promising candidate in the application of constructing materials for sensing purpose especially stimulus responsive soft materials. Therefore, we expected that the **TN** could response to Hg^{2+} and Ag^{+} with visually signal outputs. The gelation behavior and sensing properties of **TN** gel in detail was discussed in the following part.

The gelation ability of **TN** in organic solvents were tested by using a test tube method. From table 1 and Fig. S3, compound **TN** (25 mg/mL) could gel in seven kinds of organic solvents such as alcohols, benzene, and ethyl acetate by a heating-cooling process or triggered by sonication. As a typical example, the gel of **TN** in *n*-propanol was studied in detail.

The spectroscopic and microscopy studies of **TN** gels and **TN** gels with Hg^{2+} or Ag^{+} were performed. The UV-vis spectra of **TN** S-gel banded at 437 nm displayed 4 nm blue shift from the solution, and the fluorescent spectra of **TN** redshifted from 520 in the solution to 527 nm, indicating the H aggregates of naphthalimide groups in the gel state (Fig. 5a, 5b). By a heating-cooling process, the precipitate of **TN** assembled to short ribbons seen from the SEM images (Fig. 6a); in the S-gel state triggered by sonication, the gel were comprised of entangled nanofibrils (Fig. 6b), which was the typical structure of gels. The FT-IR spectra (Fig. S4) suggested that there was not obvious change between precipitate and S-xerogel, indicating that the morphological changes was the main factor for the gelation triggered by ultrasound. XRD data revealed one peak at 5.1 nm, which was less than twice the length of molecule **TN**, indicating a dimeric structure (Fig. S5).

Upon the addition of Hg^{2+} on the gel surface (5 eq.), the fluorescence of S-gel quenched by a factor of 8.2, which displayed signal magnification effect compared with that of solution (Fig. 7, Fig. 8); whilst, Ag^{+} triggered the gel-to-precipitate transformation of **TN** gel, together with fluorescence quenching only by 4.1 fold. The results indicated that the **TN** gel could selectively response to Hg^{2+} and Ag^{+} through phase changes. There were no obvious changes upon the addition of other metal salts such as Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} even after two days (Fig. S6), which indicated that the stable gel could selectively response to Hg^{2+} and Ag^{+} among other ions. Moreover, the gel collapsing or complete fluorescence quenching time required could be tuned from hours to days with different amount of Ag^{+} or Hg^{2+} (Table S1 and S2).

Table 1 the gelation properties of **TN** (25 mg/mL)

Solvent	H-C	S
CH ₂ Cl ₂	P	P
n-propanol	P	OG
isopropanol	P	OG
ethanol	P	P
n-butanol	P	OG
ethyl acetate	S	OG
acetone	OG	OG
THF	P	P
benzene	TG	TG
glycol monomethyl ether	TG	TG
Chloroform	P	P

Note: P: precipitate; S: solution; OG: opaque gel; TG: transparent gel. H-C: heating-cooling process; S: ultrasound; G: gel.

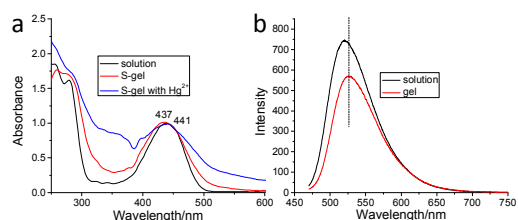


Fig. 5 a) Uv-vis spectra of solution (10^{-5} M), S-gel of **TN** (25mg/mL), and S-gel of **TN** upon the addition of Hg^{2+} ; b) the fluorescence spectra of solution (10^{-5} M) and S-gel of **TN** (25mg/mL).

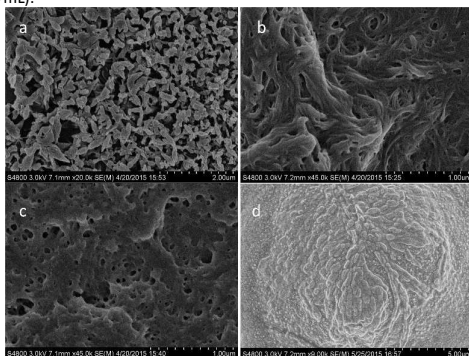


Fig. 6 SEM images of **TN** assembly; a) Precipitate of **TN** assembly from butanol (25 mg/mL); b) S-gel of **TN** assembly (25 mg/mL); c) S-gel of **TN** assembly (25 mg/mL) with

Hg^{2+} (5 eq.); d) S-gel of **TN** assembly (25 mg/mL) with Ag^{+} (5 eq.). Scale bar: 2 μm , 1 μm , 5 μm .

SEM experiments were examined to monitor the gel-to-gel and gel-to-precipitate transitions of **TN** S-gels triggered by Hg^{2+} and Ag^{+} respectively. Seen from Fig. 6c, the gel with Hg gave porous structure originated from entangled fibers. On the contrary, short ribbons and spheres were observed in the precipitate of gel with Ag^{+} (Fig. 6d)

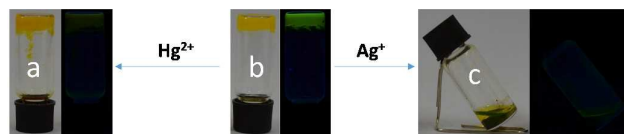


Fig. 7 photos of **TN** gel after coated with Hg^{2+} and Ag^{+} (in light and in dark irradiated by 365 nm).

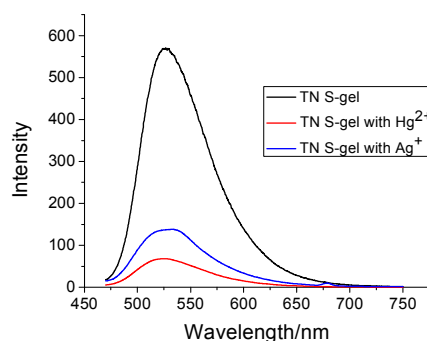


Fig. 8 the *in situ* fluorescent spectra of **TN** S-gel, **TN** S-gel with Hg^{2+} , and **TN** S-gel with Ag^{+} (5 equiv.).

From the above results, the sensing properties of **TN** in both the solution and gel state could be summarized as following: In the solution state, **TN** was able to selectively sense Ag^{+} or Hg^{2+} via guanylation reaction among test ions, accompanied with fluorogenic and chromogenic signal outputs. However, **TN** failed to discriminate Hg^{2+} with Ag^{+} in the solution state. In the gel tissue, the gel undergone gel-to-gel transition in the presence of Hg^{2+} , which was accompanied with fluorescence quenching; while, upon the addition of Ag^{+} , the fiber aggregate assembly of **TN** was destroyed and divided, resulting in the gel collapsing. From macroscopic studies, it was found the assembly of **TN** assembly with Hg^{2+} was denser after guanylation interaction, Hg^{2+} might act as the joint point to connect the gel networks. While, Ag^{+} ions triggered the dissociation of the networks, resulting in the gel collapsing. This converse phenomena might be attributed to the different coordination modes and spaces of Hg^{2+} and Ag^{+} . We also checked the response properties of **TN** organogel toward Hg^{2+} and Ag^{+} in toluene as a kind of apolar solvents. Upon the addition of Hg^{2+} (5 eq.) on the gel surface, the complete quenching for the gel needed more than 28 hours, which was longer than that in the propanol (4 hours), while Ag^{+} could not penetrate into the gel network even after two days (Fig. S7). Therefore, the gel tissue behaved as a highly selective sensor toward Hg^{2+} and Ag^{+} with opposite signal outputs either in butanol or benzene.

Conclusion

In summary, a new kind of naphthalimide based organogel accelerated by sonication or heating-cooling process was designed and characterized. The gelator **TN** was able to selectively sense Hg^{2+} and Ag^+ through test ions in a stoichiometric process in solution state. In gel networks, the gel sensed Hg^{2+} with gel-to-gel transformation, together with fluorescence quenching; whilst the addition of Ag^+ resulted in a collapse of the gel, showing the opposite phase changes compared with that of Hg^{2+} . It was proposed that the morphological transformation triggered by ions was the main factor for the visual phase recognition. To the best of our knowledge, this is the first report of intramolecular guanylation reaction in gel tissue, which provided a novel approach to construct ion sensors with high selectivity.

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