Synthesis of organic nanoparticles of naphthalene–thiourea–thiadiazole-linked molecule as highly selective fluorescent and colorimetric sensor for Ag(I)

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ABSTRACT

A novel fluorescent and colorimetric sensor was synthesized by a reprecipitation to probe Ag^+ ions in water on naphthalene–thiourea–thiadiazole (NTTA) molecular nanocrystals. The fluorescent organic nanoparticles (FONs) allowed a highly sensitive determination of free Ag^+ ions in aqueous media. The possible mechanism was discussed.

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The design and synthesis of fluorescent sensors with high selectivity and sensitivity for heavy and transition metal ions continue to grow at an unabated pace.[1] A number of fluorescent sensors have been reported such as squaraines,[2] cholate foldamers,[3] calixarenes,[4] porphyrins,[5] quinolines,[6] fluorescein,[7] and oligonucleotides.[8] However, most of these systems suffer from applicability in the aqueous medium due to their poor water solubility.[1,5] It is a big challenge to selectively recognize toxic metal ions and subsequent dual-mode[9] signaling of the event in aqueous solutions. Recently, transferring organic compounds to form fluorescent organic nanoparticles (FONs) in aqueous system has afforded a new strategy to employ organic compounds as sensors in water or in a water-rich solvent.

FONs, as a result of their large diversity in molecular structure and optical properties that are of potential use in optoelectronics and biologics, have become the subject of ever increasing attention in recent years.[10–13] Nowadays, the research of FONs is mostly focused on the development of new technology to control their sizes and dispersion. For example, An and co-workers have successfully fabricated 1-cyano-trans-1,2-bis-(4′-methylbiphenyl)ethylene (CN-MBE) FONs by reprecipitation.[14] Jang and Oh have reported the synthesis of shell–core pyrene–polypyrrole FONs by microemulsion.[15] Use of thermal evaporation[16] and laser ablation[17] to prepare FONs have also been reported. In the above methods, the reprecipitation is a simple synthetic approach, which is performed by rapid injection of a solution of the monomer into a solvent in which the monomer is insoluble.[18,19] This can not only make the organic compound to form FONs in water, but also can increase the fluorescent quantum yield (QY).[14]

Naphthalene is known as a highly fluorescent compound, and thiadiazole-linked naphthalene molecules also exhibit interesting optical properties.[20] We reported here a new thiadiazole-linked naphthalene molecule, 5-(3-(2-(naphthalen-3-yloxy)acetyl)thioureido)-1,3,4-thiadiazole-2-carboxylic acid (NTTA), which was synthesized by condensing 5-amino-1,3,4-thiadiazole-2-carboxylic acid $\mathbf{1}$[21] with aroyl isocyanates $\mathbf{2}$ in 70% yield[22] (Scheme 1a). It is reasonable to believe that transferring NTTA to form FONs (Scheme 1b) in aqueous system can be employed to probe metal ions in water, due to the fact that thiourea and thiadiazole groups of NTTA align in parallel, which may effectively make a complex with metal ions.

Herein, we have prepared NTTA FONs by reprecipitation in THF/H_2O solution. They can act as a fluorescent and colorimetric sensor for the determination of silver ions in aqueous system.

The fluorescence (FL) spectra of NTTA FONs in different ratios of THF/H_2O solution was studied in Figure 1. When the THF/H_2O ratio equals 1:1, the fluorescence (FL) intensity reaches maximum. Therefore, the THF/H_2O (v/v = 1:1) is selected for further experiments.

NTTA molecules were found to be readily self-assembled into colloidal nanoparticles as a result of reprecipitation[23] when the THF solution of NTTA was added to water (Scheme 1b). Two monomers of NTTA formed a dimer via hydrogen bonds. These dimers were the actual building blocks for solid state, and were brought together via van der Waals interactions. The NTTA nanoparticles,

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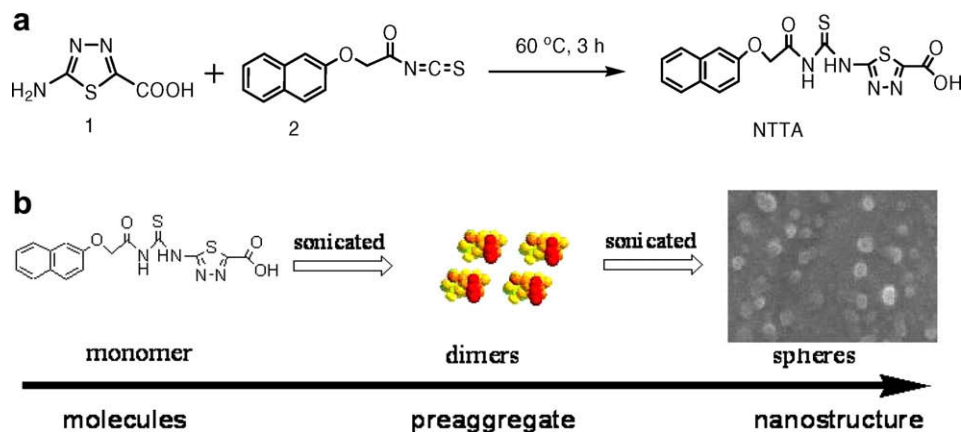
Scheme 1. (a) Synthesis of NTTA and (b) schematic representation for the formation processes of nanoscale materials of NTTA.
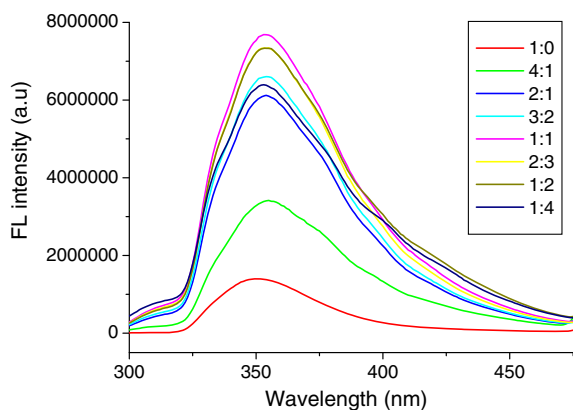

Figure 1. FL spectra of the NTTA FONs (NTTA 10^{-5} M) in different ratios of THF/H$_2$O solution.

prepared in the THF/H$_2$O (v/v = 1:1) solution by adding the THF solution of NTTA at a concentration of 2×10^{-5} M to water, were determined by the field-emission scanning electron microscopy (FE-SEM) as shown in Figure 2. SEM image showed NTTA nanoparticles were monodispersed and uniform. The average size of NTTA nanoparticles measured by photon correlation spectroscopy (PCS) was 100 nm. The relative standard deviation (R.S.D) established at five replicate measurements was 4.3%.

The colloidal stability of the NTTA nanoparticles was estimated at room temperature (Fig. S1). It was found that the FL intensity of NTTA nanoparticles was increased slightly in the first four days,

and then FL intensity stayed basically the same, which showed that the FONs were quite stable. In order to study the molecular recognition ability of the NTTA FONs, the FL titration of NTTA monomer in THF and NTTA FONs in water with various cations was conducted to examine the selectivity. Figure 3 shows the effect of 10^{-4} M relevant cations on the FL intensity of NTTA FONs, including Na$^+$, Ca^{2+}, Co^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ag$^+$, Pb^{2+}, and Hg^{2+}. Only Ag$^+$ and Hg^{2+} have quenched the luminescence of NTTA FONs over other cations, selectively. However, Ag$^+$ has a stronger effect on the luminescence of NTTA FONs compared with that of Hg^{2+}.
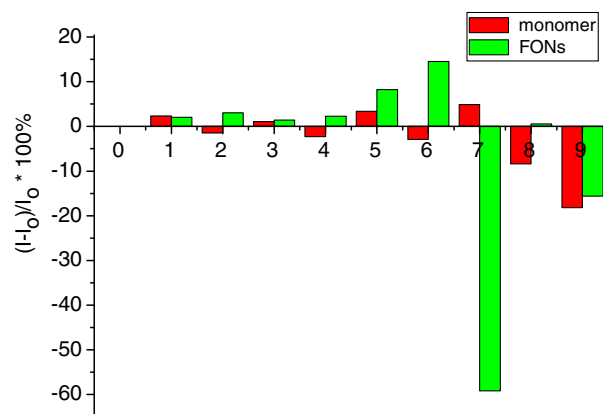

Figure 3. Effects of 10^{-4} M relevant cations on the FL intensity of the NTTA monomer and the FONs (from 0 to 9:0, Na$^+$, Ca^{2+}, Co^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ag$^+$, Pb^{2+}, and Hg^{2+}).
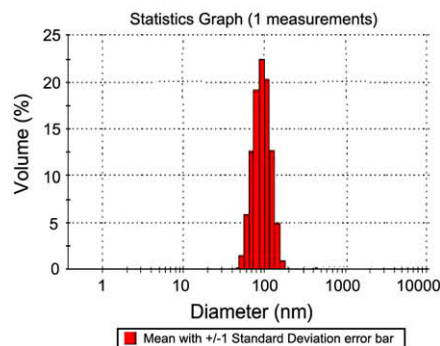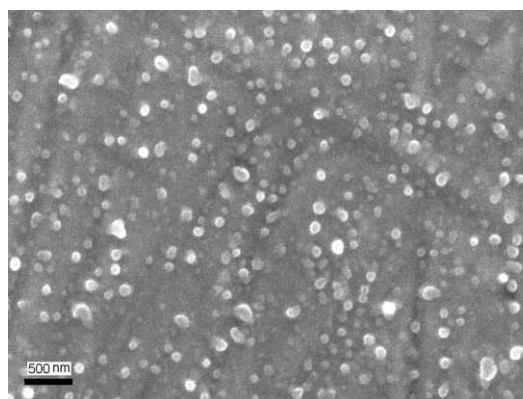

Figure 2. Typical SEM images (left) and size distrubution (right) of NTTA FONs prepared in 2×10^{-5} M THF/H$_2$O solution with v/v of 1:1 (scale bars is 500 nm).
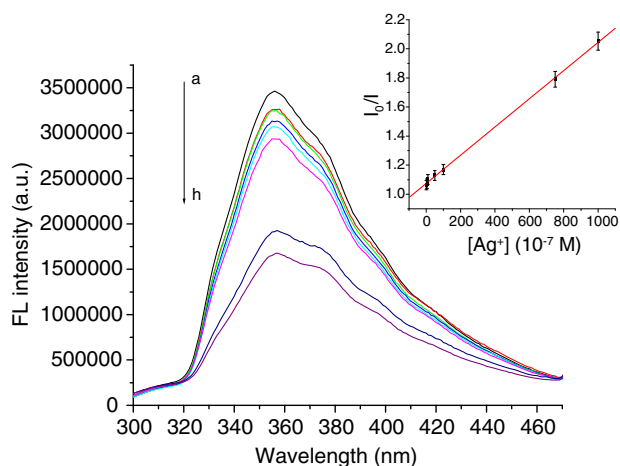
Figure 4. Effect of Ag⁺ ion concentration on FL intensity of NTTA FONs (from a to h: 0, 10^{-7}, 5×10^{-7}, 10^{-6}, 5×10^{-6}, 10^{-5}, 7.5×10^{-5}, 10^{-4} M). Inset: Stern–Volmer-type description of the data showing a linear fit throughout the Ag⁺ concentration range.

To further explore the selectivity of NTTA FONs for Ag⁺, competition control experiments were performed for NTTA FONs with only Ag⁺ and with other background metal ions such as Na⁺, Ca²⁺, Co²⁺, Mn²⁺, Cd²⁺, Cu²⁺, Pb²⁺, and Hg²⁺. As shown in Figure S2, other metal ions resulted in nearly no disturbance to the selective sensing of NTTA FONs toward Ag⁺. This can be attributed to the former containing thiourea NHC=S and thiadiazole groups, which are preferable to complex the more polarizable heavy metal ions especially Ag⁺ due to cation–p interactions. The phenomenon may also reflect the 'principle of hard and soft acids and bases' introduced by Ho.[24] But for NTTA monomer, all cations have little effect on the FL of NTTA. It is rationalized that the NTTA FONs play an important role in selective luminescence response to Ag⁺. Comparing with the NTTA monomer, the FONs make functional group of the binding sites congregate, which provides an appropriate condition for the enrichment of Ag⁺ on the surface of the FONs.

As shown in Figure 4, the FL emission is progressively quenched at a concentration of 0–100 μM by the addition of Ag⁺. Furthermore, it is found that the silver ions quenched the FL intensity of the FONs in a concentration-dependent manner that is best described by a Stern–Volmer-type equation,[25] which could be used to develop a method to determine the concentration of Ag⁺.

$$I_{max}/I = 1 + K_{SV}[Q],$$

where I and I_{max} are the FL intensities of the FONs at a given Ag⁺ concentration and in Ag⁺ free solution, [Q] is the given Ag⁺ concen-

tration. Figure 4 shows the Stern–Volmer quenching curve describing the I_{max}/I as a function of Ag⁺ concentration, the detection limit of 4.7×10^{-8} M (5 ppb) is calculated following the 3σ IUPAC criteria.

The observed luminescence emission quenching at the concentration 0–100 μM of Ag⁺ may be attributed to Ag⁺ intercalation that induces the FONs aggregation, which caused the fluorescence intensity quenching, which is supported by a SEM image (Fig. 5A). The average size of FONs aggregation measured by PCS was 1680 nm (Fig. 5B).

Interestingly, adding 5×10^{-4} M of Ag⁺ after 5h, the color of the FONs solution changed from colorless to pink, red-brown, brown along with the time (Fig. S3) as shown in Figure 6; after 24 h, the color of the solution changed to dark brown. Finally, appreciable precipitation was formed and visualized by the naked eye in the system. However, the addition of other metal ions had no effect on the color of NTTA FONs, which also indicated that NTTA FONs responded selectively to Ag⁺. And also, all metal ions had no effect on the color of NTTA monomer solution (Fig. S3).

The possible colorimetric mechanism is discussed, as shown in Scheme 2. The aggregation of organic nanoparticles was induced by Ag ions in a short time. Then, Ag ions adsorbed on the surface of NTTA FONs formed Ag ions-capped FONs. Under irradiation of

Figure 6. Photographic image of FONs solutions adding 5×10^{-4} M relevant metal ions after 24 h (from 0 to 9: 0, Na⁺, Ca²⁺, Co²⁺, Mn²⁺, Cd²⁺, Cu²⁺, Ag⁺, Pb²⁺, and Hg²⁺).
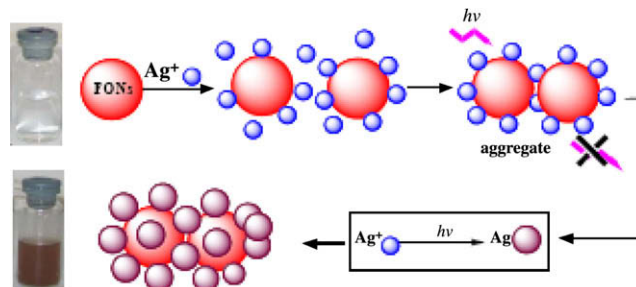
Scheme 2. Schematic illustration of a possible structure of Ag nanoparticles coated NTTA FONs aggregates.
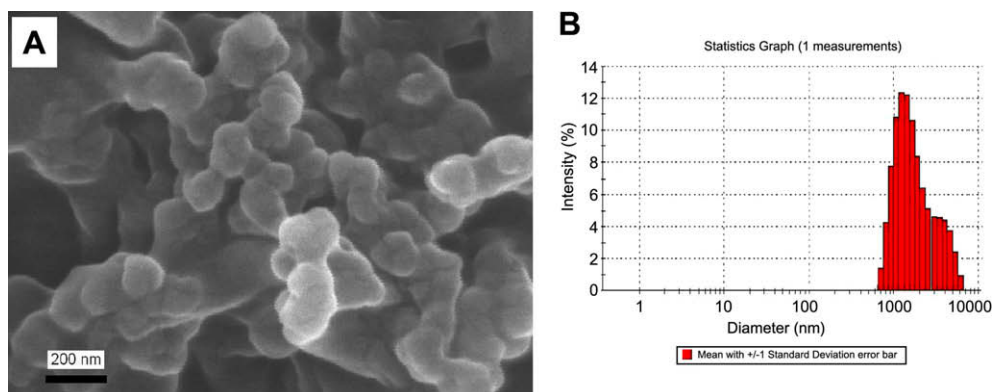

Figure 5. SEM images (A) and size distribution (B) of NTTA FONs after adding 5×10^{-4} M Ag⁺ (scale bars is 200 nm).

light, the Ag ions were slowly reduced to form very small silver nanoparticle, which was proved by TEM, XPS, and time-dependent UV experiments (Figs. S4–S6). Thus, Ag nanoparticles coated on the surface of FONs aggregate, which resulted in the color change of FONs solution to dark brown, gradually.

In summary, we have synthesized the NTTA FONs by reprecip-itation method. The FONs can potentially be employed as a highly sensitive and selective fluorescent and colorimetric probes for Ag⁺. Quenching of the luminescence emitted by the synthesized nano-particles allows the determination of Ag⁺concentration as low as 4.7×10^{-8} M (5 ppb). Furthermore, molecular recognition of other organic nanoparticles is in progress in our laboratory, which should spark a broad spectrum of interest due to its great versatil-ity and flexibility for future applications.

Acknowledgments

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.10.077.

References and notes

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22. *Synthesis of NTTA*: To a solution of 5-amino-1,3,4-thiadiazole-2-carboxylic acid **1** (9 mmol) in dry DMF (10 mL) was added 2-(naphthalen-2-yloxy)ethanoyl isothiocyanatearoyl isocyanates **2** (9.9 mmol) at room temperature. After the reaction mixture was stirred and heated at 60 °C for 3 h under argon atmosphere, the mixture was concentrated and purified by column chromatography on silica gel to give the NTTA as a pale yellow powder in 70% yield. ^{1}H NMR(CDCl$_3$, 400 MHz) δ 4.92 (s, 2H, OCH$_2$), 7.28–7.89 (m, 7H, naphthyl H), 7.81 (s, 1H, NH), 8.90 (s,1H, NH), ^{13}C NMR (150 MHz, DMSO-d_6) δ: 66.3, 107.2, 118.6, 124.1, 126.6, 126.9, 127.6, 128.9, 129.5, 134.1, 148.7, 149.1, 149.5, 155.7, 158.4, 167.3. ESI-MS: $m/z = 388$ (M$^+$). Anal. calcd for C$_{16}$H$_{12}$N$_4$O$_4$S$_2$: C, 49.47; H, 3.11; N, 14.42. Found: C, 49.44; H, 3.15; N, 14.39.
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