Microwave-assisted synthesis of highly fluorescent nanoparticles of a melamine-based porous covalent organic framework for trace-level detection of nitroaromatic explosives

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ABSTRACT

Covalent organic frameworks (COFs) are a new generation of porous materials constructed from light elements linked by strong covalent bonds. Herein we present rapid preparation of highly fluorescent nanoparticles of a new type of COF, i.e. melamine-based porous polymeric network SNW-1, by a microwave-assisted synthesis route. Although the synthesis of SNW-1 has to be carried out at 180 °C for 3 d under conventional reflux conditions, SNW-1 nanoparticles could be obtained in 6 h by using such a microwave-assisted method. The results obtained have clearly demonstrated that microwave-assisted synthesis is a simple yet highly efficient approach to nanoscale COFs or other porous polymeric materials. Remarkably, the as-synthesized SNW-1 nanoparticles exhibit extremely high sensitivity and selectivity, as well as fast response to nitroaromatic explosives such as 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenylmethylnitramine (Tetryl) and picric acid (PA) without interference by common organic solvents, which is due to the nanoscaled size and unique hierarchical porosity of such fluorescence-based sensing material.

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1. Introduction

Rapid detection of high explosives with sensitivity and selectivity is of great significance in public security, military applications and environmental monitoring [1,2]. Many chemical explosives like 2,4,6-trinitrotoluene (TNT) and picric acid (PA) usually contain nitroaromatic groups, which have electron accepting capability. Therefore, the electron-rich chemosensor based on fluorescence quenching has been regarded as one of the most promising approaches for detection of the electron-withdrawing nitroaromatic explosives [3–9]. Thus far, a wide variety of fluorescent conjugated polymers [10–16], small molecule fluorophores [17–23] and metal-organic frameworks [24–30] have been reported. Among these competing devices, the polymer-based fluorescent sensors has been demonstrated to be highly sensitive and selective [31]. However, many bulky conjugated polymers or dense polymer layers exhibit slow fluorescent quenching responses [32,33], which is due to diffusion of explosive molecules was restricted into the materials.

Covalent organic frameworks (COFs) are a new generation of porous materials constructed from light elements, such as H, B, C, N and O, which are linked by strong covalent bonds [34–36]. A significant amount of previous researches have focused on the construction of functional COFs for gas storage [37–39]. Another potential application for COFs might be its use as fluorescent materials for sensing, which is due to their strong fluorescence [40]. Very recently, Schwab and Thomas et al. [41] developed a novel series of porous COFs, i.e. Schiff base network (SNW) series, constructed from melamine and di- or trialdehydes. For example, a melamine-based polymeric network SNW-1 with microporosity could be synthesized by a polycondensation reaction of melamine and terephthalaldehyde in dimethylsulphoxide. Although it has clearly been demonstrated that formation of the highly cross-linked polymeric network can be achieved from abundant and cheap materials and without the use of any catalyst, the polycondensation reaction of monomers has to be carried out at 180 °C for a long reaction time (3 d) using a traditional heating method.

Herein, we present a facile yet highly efficient synthesis of highly fluorescent nanoparticles of hierarchically micro- and mesoporous SNW-1 by a microwave (MW)-assisted method. MW-assisted approach has become a widely employed approach in organic synthesis and materials preparation [42,43]. More recently, the use of microwave synthesis strategy has also been demonstrated to display significant advantage over traditional heating methods in the preparation of COF [44] and covalent triazine-based framework (CTF) [45]. In the present work, we describe rapid synthesis

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of highly fluorescent nanoparticles of melamine-based polymeric network SNW-1 and their application for highly sensitive and selective detection of nitroaromatic explosives. The results reveal that MW-assisted synthesis is an energy- and time-efficient approach to porous polymeric network. Moreover, SNW-1 nanoparticles exhibit high sensitivity and selectivity, as well as fast fluorescence response to nitroaromatic explosives, reaching a very low detection limit, which is due to nanoscaled size and unique hierarchical porosity, as well as significant fluorescence quenching effects of this kind of novel fluorescence sensing material.

2. Experimental

2.1. Materials

Terephthalaldehyde, melamine, nitrobenzene (NB), 4-nitrotoluene (4-NT), 4-nitrophenol (NP), 2,4-dinitrotoluene (DNT), picric acid (PA) were purchased from Sinopharm (Shanghai) Chemical Reagent Co. Ltd., China. 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenylmethylnitramine (Tetryl) standard solutions were purchased from aladdin and J&K Scientific Ltd., China, respectively. All other chemicals were of reagent grade quality, and were obtained from commercial sources and used without further purification. All water used in the experiments was deionized.

2.2. Preparation

Nanoparticles of porous polymeric network SNW-1 were synthesized by a polycondensation reaction of melamine and terephthalaldehyde in dimethylsulphoxide. In a typical synthesis, terephthalaldehyde (1.00 g, 7.5 mmol) and melamine (0.63 g, 5.0 mmol) were dissolved in 50 ml of dimethylsulfoxide (DMSO), and transferred into a 100 ml round flask. Then, the round flask was put in a microwave oven (Glanz P70D20TJ-D3, Shenzhen, China). After being refluxed 6 h under nitrogen atmosphere at 280 W microwave power output, the reaction product was allowed to cool to room temperature. The off-white powder was filtered by filtration over a Büchner funnel and washed with acetone, dichloromethane, tetrahydrofuran (THF), respectively. Finally, the sample was dried 5 h at 120 °C in vacuum (0.01 MPa). The sample shows remarkable thermal stability with its thermal gravimetric analysis (TGA) up to 400 °C. Furthermore, SNW-1 sample is stable and insoluble in water and in common organic solvents such as THF, DMSO, N,N-dimethylformamide (DMF), ethanol, acetone, acetonitrile and benzene.

2.3. Characterization

Infrared spectra (KBr pellets) were obtained in the 400–4000 cm^{-1} rang using a Nocolet Nexus 870 FTIR spectrometer. Transmission electron microscopy images were carried out on a JEOL JSM-2100 electron microscope operating at 200 KV. Nitrogen sorption-desorption isotherms were measured at 77 K using a Micromeritics 2020M+C system after the sample was first degassed at 120 °C overnight. Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was determined by both the Barrett–Joyner–Halenda (BJH) and the Horvath–Kawazoe (HK) methods. TGA measurement was carried out using a Pyrisl TGA-1 in a nitrogen atmosphere at a heating rate of 20 °C min^{-1} in the temperature range of 50–800 °C. The elemental analysis of C, N and H was carried out on a Perkin-Elmer 2400 elemental analyzer. Fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Solid-state ^{13}C NMR spectrum was obtained on a Bruker AVANCE III 400 spectrometer.

2.4. Sensing of nitroaromatic explosives

For fluorescence sensing of nitroaromatics, corresponding fluorescence spectra of the sample were recorded after injecting various amounts of concentrations of nitroaromatics into a 1-cm cuvette containing 2.00 ml of 10% THF aqueous suspension of SNW-1 nanoparticles. Variation of emission intensity with concentration of every kind of nitroaromatic compound was recorded, respectively. For the time-dependent fluorescence quenching experiment of DNT in vapor phase, a slice of quartz glass coated with SNW-1 nanoparticles was placed in a sealed quartz cuvette containing small amounts of analyte deposited onto cotton to ensure constant vapor pressure, and then the corresponding fluorescence spectra of the sample were recorded at an interval of 10 s upon excitation at 370 nm.

Caution: TNT, Tetryl and PA should be used with extreme caution owing to their high explosion.

3. Results and discussion

3.1. Preparation of SNW-1 nanoparticles

The reaction of melamine and terephthalaldehyde in dimethylsulfoxide under inert atmosphere at 280 W MW power output for 6 h (Fig. 1) resulted in SNW-1 nanoparticles in a yield of more than 60%. The chemical structure of sample was confirmed by solid-state ^{13}C NMR spectroscopy, Fourier transform infrared (FT-IR) spectroscopy and elemental microanalysis. The solid-state ^{13}C NMR spectrum of SNW-1 shows three resonances at 48, 127 and 167 ppm, as shown in Fig. S2. The resonance at 48 ppm reveals the tertiary carbon atoms, indicating that the polycondensation reaction is completed. The signal at 127 and 167 ppm can be attributed to the CH aromatic carbons of the benzene and the carbon atoms present in the triazine ring, respectively, which is consistent with ^{13}C NMR previously reported results for SNW-1 [41]. The FT-IR spectrum of the sample reveals the existence of triazine rings and benzene rings, which is confirmed by the appearance of several strong bands in the 1466–1582 cm^{-1} region, as shown in Fig. S3, clearly indicating the complete polycondensation of melamine and terephthalaldehyde. Additionally, the disappearance of band at 1700 cm^{-1} corresponding to carbonyl group is also indicative of a complete polycondensation reaction [41]. Chemical composition of SNW-1 by the MW-assisted method was also confirmed by elemental microanalysis. The C, N and H contents were determined to be 36.32, 46.58, and 4.97, respectively, which is consistent with elemental analysis result for SNW-1 as reported previously [41]. Remarkably, the reaction time of the synthesis of SNW-1 nanoparticles could substantially be reduced to 6 h using MW-assisted method, while all melamine-based polymeric network SNWs were obtained under reflux conditions for 3 d in dimethylsulfoxide as reported previously [41].

Fig. 2 shows the representative TEM image of SNW-1 nanoparticles prepared at a power output of 280 W MW for 6 h. The result suggests that the size of the as-prepared SNW-1 particles is about 20–50 nm. The nitrogen sorption–desorption measurement clearly reveals porosity of the sample obtained, as shown in Fig. 3. Unlike the microporous SNW-1 prepared for 3 d under traditional condition, the SNW-1 nanoparticles obtained by microwave method exhibit a type IV isotherm. A pronounced hysteresis loop was observed upon desorption, revealing the microporous framework with mesopores formed by close-packed nanoparticles. Its Brunauer–Emmett–Teller (BET) surface area was determined to be
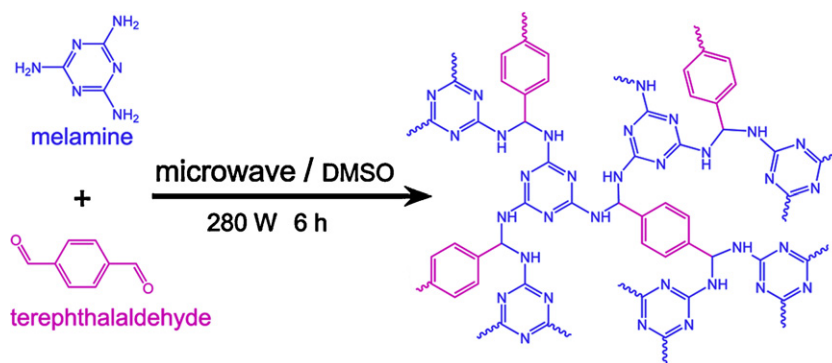
Fig. 1. A schematic illustration of the polycondensation of terephthalaldehyde and melamine to form polymeric network SNW-1 by using a MW-assisted method.
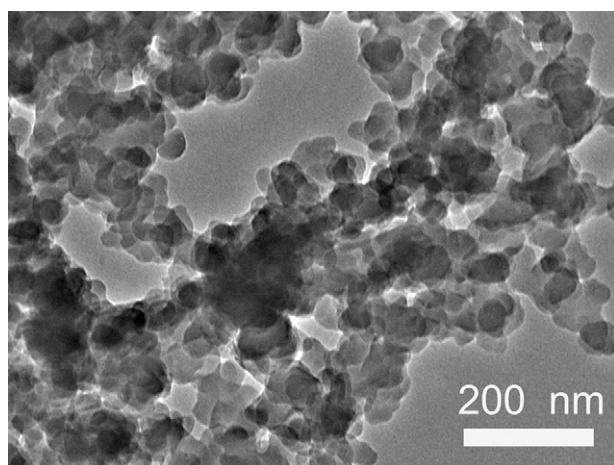

Fig. 2. Representative TEM image of SNW-1 nanoparticles.

476 m^2 g^{-1}, which is smaller than that of SNW-1 prepared by a conventional polycondensation for 3 d. This may be attributed to rapid polycondensation of the monomers under such a microwave irradiation condition. Furthermore, a total pore volume of 1.26 cm^3 g^{-1} was found for SNW-1 nanoparticles, which is comparable with that of sample prepared by conventional method. Pores size distributions were further estimated by Horvath–Kawazoe (HK) and Barrett–Joyner–Halenda (BJH) methods, respectively (Fig. 3b). Remarkably, SNW-1 nanoparticles obtained by microwave method

show a hierarchical pore system from micro- to macropores. A macropore system was also found around 40 nm, besides a micropore system with a size of 1 nm (Fig. 3b). It is well known that hierarchically porous materials allow for improved accessibility and molecular transport for adsorption, sensing, and catalysis, which is due to their unique hierarchically porous structures [46]. As a result, fluorescent porous SNW-1 nanoparticles would benefit, as an excellent candidate for sensing of organic molecules, from having a nanoscale particle size, as well as a hierarchically micro- and macroporous structure, to improve diffusion of analyte molecules in pores of the solid, which is due to both widening the pores and shortening the diffusion path length.

3.2. Fluorescence spectrometric titration experiments

SNW-1 nanoparticles exhibits a remarkable fluorescent emission feature in both suspension and solid-state. Fluorescence quenching experiments reveal that fluorescent emission of SNW-1 nanoparticles could be significantly quenched by nitroaromatic compounds such as NB and DNT in THF or acetonitrile solutions, indicating high sensitivity of SNW-1 nanoparticles for sensing of nitroaromatics in organic solvents. However, most pollutants are usually present in aqueous solution, and quickly and quantitatively detecting them in situ is more necessary and highly desirable from the viewpoint of practical use. To make the sensing material more practical for their applications, fluorescence sensing of nitroaromatic explosives, such as NB, NT, DNT, TNT, Tetryl and PA, in aqueous solutions was further investigated.
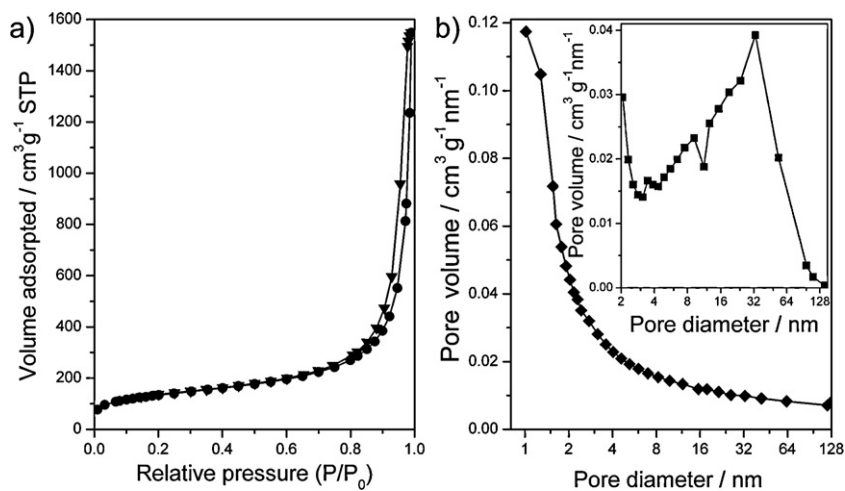

Fig. 3. (a) N$_2$ adsorption–desorption isotherms of SNW-1 nanoparticles and (b) pore size distribution by HK model. Inset: mesoporous size distribution of SNW-1 by BJH model.
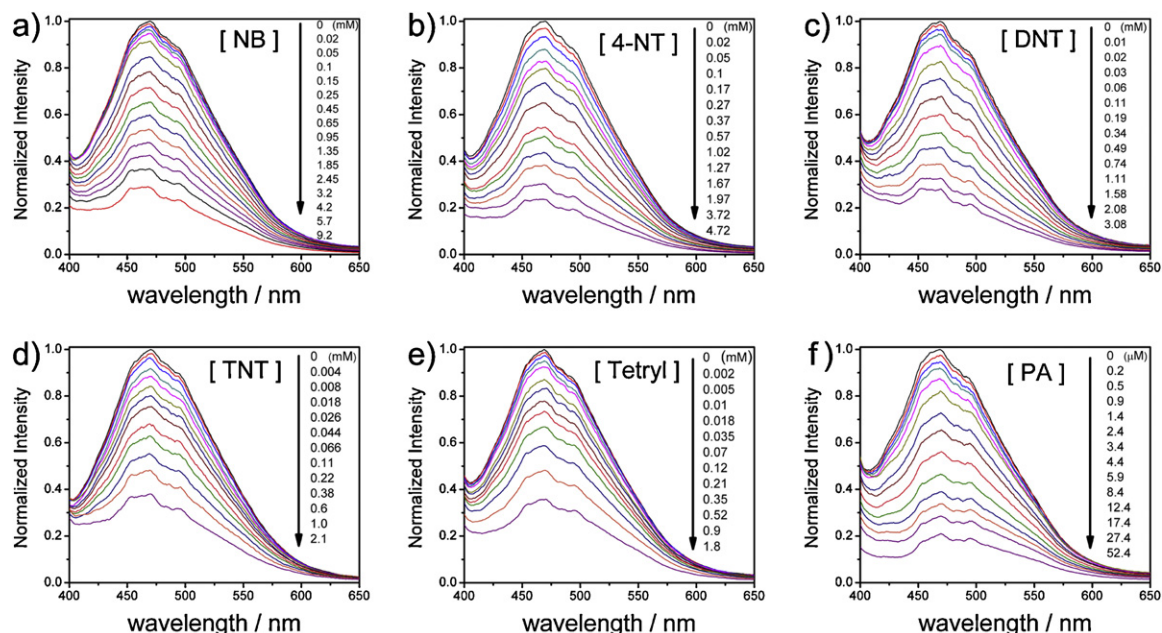
Fig. 4. Fluorescence quenching of SNW-1 nanoparticles (2 mg) with nitroaromatics (NB, 4-NT, DNT, TNT, Tetryl and PA) in a 10% THF aqueous solution (2 ml).

It is well known that solvent polarity and the local environmental have profound effects on the emission spectral properties of fluorophores [47]. The aggregation state of nanoparticles of the sensing materials has also been found to show significant effects on their fluorescence emission properties due to "aggregation-caused quenching" (ACQ) or "aggregation-induced emission enhancement" (AIE), and aggregation state of the nanoparticles can be tuned by adding organic solvents or water into nanoparticles suspension [48]. Although emission intensity of SNW-1 nanoparticles in aqueous solution is strong enough for sensing of nitroaromatic explosives, fluorescence emission spectra of the sample in aqueous solutions containing various THF contents were still measured with the hope of observing solvent-induced fluorescence emission enhancement as reported previously [19] and thus improving sensitivity of the SNW-1 nanoparticles for nitroaromatic explosive determination. Fig. S4 shows variation of emission intensity at 467 nm with volume-fraction of THF solution. The suspensions of SNW-1 nanoparticles (1 mg ml^{-1}) in aqueous solutions containing various THF concentrations display a strong fluorescent emission at room temperature with an emission peak at 467 nm upon excitation at 370 nm, which accords with its solid state fluorescence spectra. Remarkably, SNW-1 nanoparticle suspensions exhibit significantly enhanced fluorescence emission with an increase in THF concentration, which may be due to the solvent-caused changes in aggregation state of SNW-1 nanoparticles in aqueous solution after the addition of THF to the SNW-1 suspensions.

The sensing of nitroaromatic explosives using SNW-1 nanoparticles in THF–water (1:9, v/v) mixture was first quantitatively analyzed by a fluorescence spectrometric titration experiment as described previously [49]. The detection approach requires measurement of fluorescence quenching of SNW-1 nanoparticles suspensions after the addition of different concentrations of nitroaromatic compounds. As shown in Fig. 4, strong fluorescence quenching effects were observed for all nitroaromatics, and fluorescence quenching efficiencies of the SNW-1 nanoparticles in THF–water mixture are in the order of PA ≫ Tetryl ≈ TNT > DNT > 4-NT > NB. Upon increasing the concentrations of NB, 4-NT, DNT, TNT, Tetryl, PA to 9.2, 4.7, 3.1, 2.1, 1.8 mM, and 52 μM, respectively, fluorescence quenching efficiencies exceeded 80% for all analytes. The result suggests that the fluorescence property of SNW-1

nanoparticles is highly sensitive to nitroaromatics, which is mainly due to transfer of photoexcited electrons from the excited luminescence network donor to the electron-deficient nitroaromatic acceptors and strong intermolecular interactions such as π–π stacking effects between triazine rings in the polymer network and aromatic rings of nitroaromatic compounds.

As one of the common measures, the Stern–Volmer constant (K_{sv}) is usually used to allow a comparison of quenching efficiency for various analytes. As a result, the fluorescence quenching effect was also investigated by the Stern–Volmer model:

$$\frac{I_0}{I} = 1 + K_{sv}\,[M] \tag{1}$$

where I is the fluorescence intensity at analyte concentration [M], I_0 the intensity at [M] = 0, and the K_{sv} the quenching effect coefficient of the sensing material.

As can be seen in Fig. 5, all of the linear correlation coefficients R approach to 1, indicating that fluorescence quenching effects of NB,
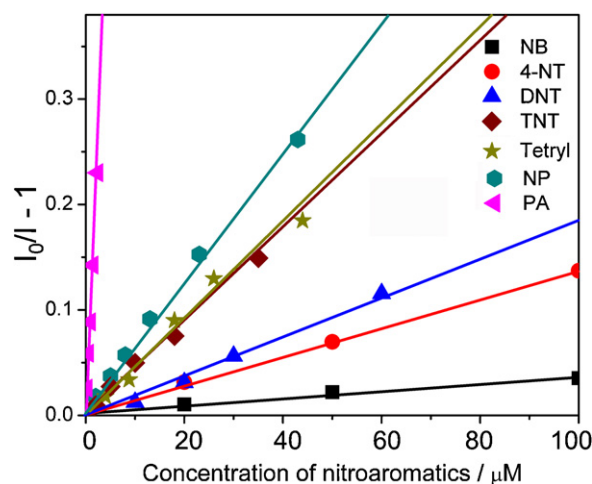

Fig. 5. Stern–Volmer plots of fluorescence quenching of SNW-1 nanoparticles (2 mg) with NB, 4-NT, DNT, TNT, Tetryl, NP and PA in 2 ml 10% THF aqueous solution, respectively.

Table 1
Summary of linear correlation coefficients (R), quenching effect coefficients (K_{sv}) and detection limit in the presence of nitroaromatics for SNW-1 at room temperature.

Analyte	R	K_{sv} (M^{-1})	Detection limit (μM)	Standard error (±)
NB	0.9962	392	7.7	2.5%
4-NT	0.9986	1357	4.2	2.1%
DNT	0.9961	1804	2.8	2.5%
NP	0.9984	5961	0.79	1.4%
TNT	0.9916	3800	1.51	2.3%
Tetryl	0.9952	4180	1.47	2.1%
PA	0.9965	94,630	0.05	2.7%

4-NT, DNT, TNT, Tetryl and PA on fluorescence emission intensity of SNW-1 nanoparticles well fit the Stern–Vlomer model. As shown in Table 1, the quenching constants for NB, 4-NT, DNT, TNT and Tetryl are comparable with many representative sensing materials, such as phosphole oxide [19], as well as polymetalloles and metallole copolymers reported very recently [13]. Significantly, a much larger K_{sv} value (94,630 M^{-1}) was observed for SNW-1 nanoparticles for fluorescence sensing of PA, revealing extremely high sensitivity of SNW-1 nanoparticles for PA detection, which made nanoscale SNW-1 one of the best sensitive fluorescence-based sensing materials [13,19,50–58] (see Fig. 6 and Table S2). This may be attributed to hydrogen-bond formation between the secondary amine of SNW-1 nanoparticles and the hydroxyl of PA molecule or the formation of a Meisenheimer complex [2]. The UV spectra of the mixtures of PA with suspension of SNW-1 nanoparticles in THF/H$_2$O (1:9, v/v) mixture were also measured to clarify intermolecular interactions between SNW-1 framework and PA. As can be seen from Fig. S5, the addition of PA to the suspension of SNW-1 nanoparticles led to an obvious blue shift of the absorption band peak from 261 to 244 nm, which can be ascribed to strong molecular interactions between the network and PA molecules. Such strong interactions between SNW-1 nanoparticles and PA may facilitate the charge transfer between them, as demonstrated in the fluorescence spectrometric titration experiments mentioned above.

To have a better understanding of fluorescence quenching mechanism, a control experiment was also carried out by choosing p-nitrophenol (NP) as a model analyte (see Fig. S6). K_{sv} for NP was estimated to be 5961 M^{-1}, which is much higher than those of NB, 4-NT, DNT, TNT and Tetryl, also indicating phenolic hydroxyl in nitroaromatic compounds plays an important role during the fluorescence quenching of indicator. In addition to sensitivity of a kind of sensing material, high performance of solvent-independent
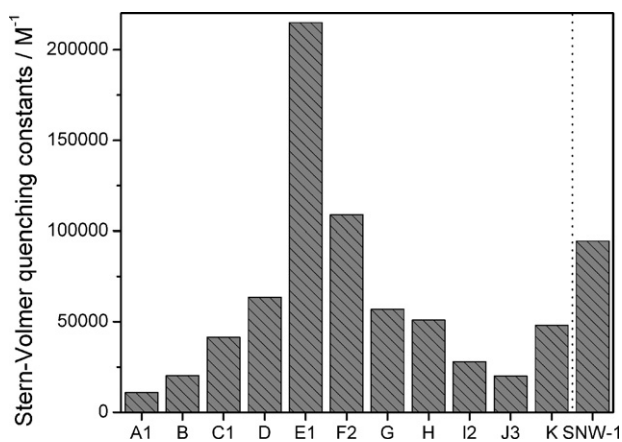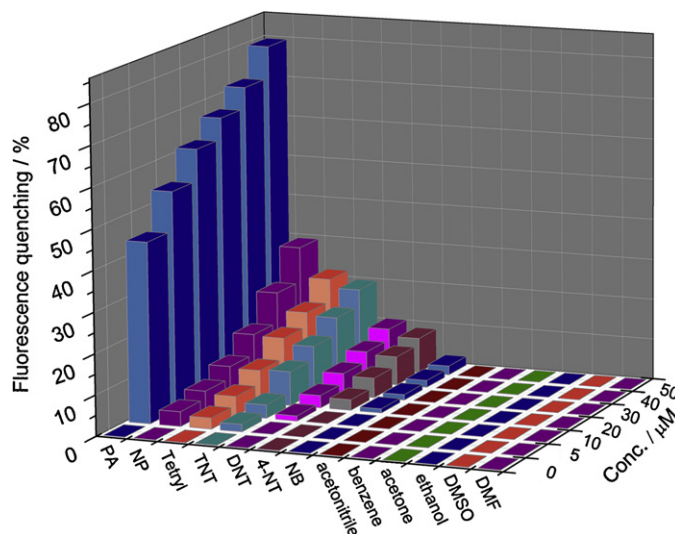
Fig. 7. Fluorescence quenching results of nitroaromatic explosives and commonly found interferents, including N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol, acetone, acetonitrile, benzene, to the emission of the SNW-1 nanoparticles at various concentrations in THF/H$_2$O (1:9, v/v) mixture.

fluorescence properties are of crucial for selective sensing of nitroaromatic explosives. Fig. 7 shows the results of the fluorescence quenching efficiencies of SNW-1 nanoparticles (2 mg) with various interferents and nitroaromatics at different concentrations in 2 ml 10% THF aqueous solution when excited at 370 nm. Significantly, common organic chemicals such as DMF, DMSO, ethanol, acetone, acetonitrile, benzene have almost no effect on the emission intensity of the suspensions of SNW-1 nanoparticles, clearly reveals high selectivity of SNW-1 nanoparticles for the sensing of nitroaromatic compounds especially picric acid.

The detection limit of SNW-1 nanoparticles for sensing of nitroaromatic compounds were also investigated based on fluorescence titration experiments by using a reported method [59]. As expected, calculation of the detection limits (see Table 1) once again proved that the response of the SNW-1 nanoparticles to nitroaromatic explosives is highly sensitive. The detection limits for NP, Tetryl, TNT, DNT, 4-NT, and NB are approximately 7.9×10^{-7}, 1.47×10^{-6}, 1.51×10^{-6}, 2.8×10^{-6}, 4.2×10^{-6}, and 7.7×10^{-6} mol L^{-1}, respectively. Remarkably, the detection limit of SNW-1 nanoparticles for sensing of PA was determined to be 5.0×10^{-8} mol L^{-1}, corresponding to 11.5 ppb. This value is quite lower than that of silicon-containing hyperbranched polymer (1 ppm) [51], functionalized siloles (0.1 ppm) [53], monolayer-chemistry-based fluorescent sensing films (3.2×10^{-7} mol L^{-1}) [54], anthracene/porphyrin dimer (1.5×10^{-7} mol L^{-1}) [60], and close to that of pyrene-functionalized fluorescent film (1.0×10^{-8} mol L^{-1}) [55] and hexaphenylsilole/chitosan composite film (2.1×10^{-8} mol L^{-1}) [59] reported very recently by Fang et al., and thin films of polysilole (6 ppb) reported by Sailor and Trogler [61]. These results demonstrated once again high sensitivity of SNW-1 nanoparticles for nitroaromatic explosive detection in aqueous solution.

3.3. Detection of DNT vapor

Another challenge for designing novel vapor sensors is to improve sensors with fast response, which is very important for their practical application. 2,4,6-trinitrotoluene (TNT) is one of the most widely used explosives in military application and terrorist activities [62,63]. However, direct sensing of DNT is often used as a substitute for monitoring of TNT [16,18,28,31,32,64], because

Fig. 6. Comparison of the Stern–Volmer quenching constants of representative sensing materials in different sensor systems with PA in solutions (detail K_{sv} constants and chemical structures in different sensor systems with picric acid reported previously and investigated in the present work in Table S2).

Table 2
The limit of detection of different sensor systems with DNT reported previously and investigated in the present work.

Sensors	Detection limit	Reference
Molecularly imprinted short-alkyl-chain self-assembled monolayers	7.6 ppm in solution	[64]
Porous silicon films	2 ppb in vapor	[66]
Phenothiazine-based oligomers	40 ppb in vapor	[67]
Fluorescent-labeled imprinted polymer	5.48 ppm in solution	[68]
Nanoscale melamine-based porous polymeric network	0.51 ppm in solution 9.8 ppb in vapor	This work
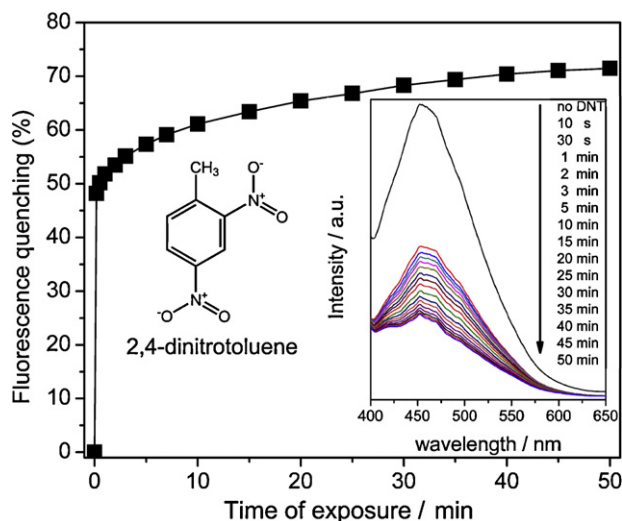
Fig. 8. Time-dependent fluorescence quenching by DNT vapor. Inset: the corresponding fluorescence spectra before and after exposure to the saturated DNT vapor.

DNT is an inevitable by-product present in TNT samples resulting from the manufacturing process and the saturated vapor pressure of DNT (ca. 100 ppb) is much higher than that of TNT (ca. 5 ppb) at room temperature [65]. Consequently, additional experiments were carried out to investigate the time-dependent fluorescence quenching by DNT vapor. Fig. 8 illustrates the time-dependent fluorescence quenching of the as-synthesized sample before and after exposure to the saturated DNT vapor. As expected, fluorescence quenching efficiency increased sharply in 10 s, suggesting ultrafast fluorescence response rate of SNW-1 nanoparticles to nitroaromatics in comparison with most fluorescence-based chemical sensitive materials reported previously (see Table S1). The detection limit of SNW-1 nanoparticles for DNT vapor was calculated to be 9.8 ppb, which is comparable with porous silicon films [66], but much lower than that of molecularly imprinted short-alkyl-chain self-assembled monolayers [64], phenothiazine-based oligomers [67], and fluorescent-labeled imprinted polymer [68] (see Table 2). Such high performance of SNW-1 nanoparticles may result from nanosized dimensionalities of SNW-1 particles (40 nm) and hierarchically micro- and mesoporous structure as mentioned above. Such a hierarchically porous structure and nanoscaled dimensionalities of the sensing material obviously improve accessibility of the guest molecules to the sensing sites and shorter diffusion path lengths, thus promoting response rate of SNW-1 nanoparticles for sensing of nitroaromatic explosives.

4. Conclusion

In conclusion, we present here rapid synthesis of nanoparticles of a highly fluorescent melamine-based polymeric network SNW-1 by a MW-assisted method, and their application in detection of nitroaromatic explosives. The results suggest that microwave synthesis is a simple yet highly efficient method for preparing nanoscales porous polymeric materials. Significantly, fluorescence property of the nanoparticles was found to be highly sensitive and selective, as well as rapidly responsive to nitro explosives including PA, DNT, TNT and Tetryl. Interferents such as common organic solvents show little effect upon the fluorescence emission of the SNW-1 nanoparticles in aqueous solution. This makes nanoscale porous conjugated polymers or nanoscale COFs as promising fluorescence sensory materials for nitroaromatic explosives with a detection limit down to ppb level as judged with DTN and picric acid.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2012.04.025.

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