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ARTICLE

Highly Selective and Sensitive Fluorescent Zeolitic Imidazole Frameworks Sensor for Nitroaromatic Explosive Detection

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Nitroaromatic explosives, such as 2-4-6 trinitrotoluene (TNT) are dangerous materials that pose safety and environmental risks. Even though many sensors have been reported for the detection of nitroaromatic explosives, a facile, rapid, cost-effective sensor is still sought-after in the field. Here we demonstrate a facile and rapid method to synthesize a fluorescent metal-organic framework for the highly selective and sensitive detection of nitroaromatic explosives. Zeolitic imidazole framework-8 (ZIF-8) is synthesized and enhanced with fluorescent 8-hydroxyquinoline zinc (ZnQ). The synthesized material shows visible colour changes upon exposure to TNT from ivory to light red. In addition, fluorescence quenching is noted under UV illumination when the ZnQ@ZIF-8 is exposed to TNT. The ZnQ@ZIF-8-coated paper sensors show the highest fluorescence quenching at an emission wavelength of 455 nm with TNT concentration as low as 1 ppm. Therefore, the proposed strategy not only offers a fast and convenient protocol for selective detection of TNT but also offers great potential in practical applications, especially for airport/railway security inspection and prevention of terrorist attacks.

1. Introduction

The detection of explosives is very important for maintaining public safety and minimizing environmental pollution. Nitroaromatic explosives, such as 2-4-6 trinitrotoluene (TNT), are dangerous contaminants in military bases and munitions facilities [1]. They also pose public safety risks. Canines are one of the primary detection methods used at airports, ports and borders [2]. However, their performance degrades over time when they get tired. Ionization mass spectroscopy is another common detection method, but the bulky instruments required for this technique poses limited portability. Generally, colorimetric chemical sensors are more compact and cost-effective than desk-top mass spectrometers. The nitro groups within nitroaromatic explosives have strong electron accepting capabilities that cause a photoinduced electron transfer [3-6]. This results in fluorescence quenching or visible colour changes that can be detected through different assays typically using conjugated polymers [7]. Alternatively, metal-organic frameworks (MOFs) are another branch of materials that have shown promise for molecular storage, sensing [8], catalysis, and separation [9]. Recently, luminescent microporous MOFs have emerged as promising materials for explosives sensing [10]. They are also appealing because the surface area, functionality, pore size and topology can be controlled during synthesis [11].

Zeolitic imidazole frameworks (ZIFs) are one type of MOFs that offer chemical and thermal stability, good dispersibility in nanocomposites, anti-interference properties and size-selectivity [12]. ZIF-8 is the most commercially available form of ZIFs. However, it requires complicated synthesis procedures and produces a large amount of by-products [13, 14]. Recently, we demonstrated a sonochemical method to fabricate ZIF-8 in approximately 5 minutes [15]. However, this method still requires intensive energy and sonication equipment. ZIF-8 has been extensively studied in literature and showed viability for explosive detection [13]. In this paper, a rapid and facile synthesis of a fluorescent MOF has been demonstrated. Fluorescent 8-hydroxyquinoline zinc material is encapsulated within ZIF-8 in-situ to enhance fluorescent properties of ZIF-8. We identified the highly fluorescent inorganic metal complex: Zn-(bis-8-hydroxyquinoline), termed as ZnQ, for encapsulation within the internal pores of ZIF-8. It worth to mention that, ZnQ is one of the relatively smaller and yet highly luminescent quantum yield metal complexes amongst the other metal quinolate series (e.g. Alq3, Gaq3, Inq3) [16]. Here ZnQ is selected owing to the shared Zn ions for ZIF-8 synthesis. The reaction time is varied to control the crystal morphology, but changes in turbidity of the solution suggest that crystals are formed after less than 30 sec. of reaction time. This synthesis strategy overcomes the drawback noted in literature for ZnQ encapsulation within ZIF-8 [16]. The synthesized ZnQ@ZIF-8 are coated on a filter paper or suspended in ethanolic solution for TNT sensing experiments. ZnQ@ZIF-8 exhibits high sensitivity and selectivity towards TNT. Visible colour changes and fluorescent quenching are noted immediately after exposure to TNT.

2. Materials and methods

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2.1. Materials

All chemicals are of analytical grade and used without further purification. 2-methylimidazole (2-MIM, 99%, Sigma-Aldrich), N, N-dimethylformamide (DMF, 99.8%, VWR), triethylamine (TEA, 99%, Alfa Aesar), Zinc acetate dihydrate (98%, VWR), 8-Hydroxyquinoline (8-Q, 99%, VWR), 2,4,6-trinitrotoluene (TNT, 1000 ppm, VWR), 3-nitrotoluene (3NT, 1000 ppm, VWR), 2,4-dinitrotoluene (2,4-DNT, 99%, Sigma Aldrich), 2,6-dinitrotoluene (2,6-DNT, 99%, Sigma Aldrich), acetonitrile (ACN, 99%, VWR), ethanol (98%, VWR), methanol (98%, VWR), acetone (98%, VWR), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX, 1000 ppm, VWR) and distilled deionized water (DDW) are used.

2.2. Preparation of Precursor Solutions and Synthesis of ZIF-8 and ZnQ@ZIF-8

For the preparation of ZIF-8, 0.8 g of 2-MIM is dissolved in 5 mL of DMF and 0.5 mL of TEA as a deprotonating agent. This is termed as solution A. Solution B is formed by dissolving 0.9 g of zinc acetate dihydrate in 5 mL of DMF. The two solutions A and B are then mixed in one vial. The white crystals of ZIF-8 are immediately formed and noticed. Visible turbidity changes are noticed and crystal formation is verified by scanning electron microscopy. The final product is separated by centrifugation at 8000 rpm and then dried at 80 °C under vacuum overnight. For the synthesis of functionalized MOF, ZnQ@ZIF-8, simple mixing of a solution containing Zn ions and 8-Q (0.8 g zinc acetate and 0.05 g 8-Q in 5 mL DMF) with solution A is performed. To avoid the formation of ZnQ only, we have maintained a constant ratio of Zn^{2+} : 2-MIM (i.e. ZIF-8 formation) and adjusted the quantity 8-Q to coordinate with free Zn^{2+} [16]. After mixing both together, the ivory crystals of ZnQ@ZIF-8 are noticed immediately. The final product of ZnQ@ZIF-8 is separated by centrifugation at 8000 rpm then dried at 80 °C under vacuum overnight. To ensure that the guest species (ZnQ) are not left adhered to the MOF surface, the product is washed thoroughly twice using solvents that solubilize the guest species (first using DMF, followed by methanol, ethanol, and acetone). The washing step is carried out with simultaneous sonication (10 minutes per solvent, then centrifugation) to further expedite the removal of external guest species.

2.3 Materials characterization techniques

A field emission scanning electron microscope (FE-SEM, Quanta™ 250) is used to determine and analyze the morphologies of the ZIF-8 and ZnQ@ZIF-8. An X-ray diffractometer (XRD, Rigaku Multiflex) is used to characterize the crystalline structure of the ZIF-8 and ZnQ@ZIF-8. Fourier Transform Infrared (FTIR) Spectroscopy instrument (Nicolet Nexus 470, USA) is used measure the transmittance spectra in the range of 4000–500 cm^{-1} with a spectral resolution of 4 cm^{-1} . Raman spectroscopy instrument (Bruker Raman II, Laser (1064 nm) Power 300 mW, USA) is used to measure the Raman spectra of both ZIF-8 and ZnQ@ZIF-8. The Brunauer-Emmett-Teller (BET) measurements are performed using a surface area analyzer (NOVA 3000e, USA) to determine the surface area of ZIF-8 and ZnQ@ZIF-8. Gas chromatography-mass spectroscopy

(GC-MS) instrument (Agilent, USA) is used to determine the ratio of 8-Q to 2-MIM in ZnQ@ZIF-8. ZnQ@ZIF-8 is dissolved using diluted sulphuric acid then the linkers (2-MIM and 8-Q) are solvent extracted with hexane. The solution is then injected to GC-MS to see the composition ratio.

2.4 Nitroaromatic explosive sensing experiments

For the detection of TNT, a piece of filter paper (36 mm in diameter) is immersed in the fluorescent ZnQ@ZIF-8 colloidal solution for 10 min. The filter paper then is removed from the solution and dried at 80 °C under vacuum for 1 hr. The gravimetric calculation shows that approximately 0.05 g of ZnQ@ZIF-8 is loaded on the filter paper. To demonstrate its application as a paper-based sensor for TNT detection, 1 μL drops of TNT solution diluted to different concentrations are applied at room temperature. In addition, standard solutions of 3NT, RDX, 2,4-DNT, 2,6-DNT and ACN are applied to test chemical selectivity. Thereafter, the paper-based sensor is imaged with an optical camera. In addition, the fluorescent optical images under the irradiation of a UV lamp (λ_{ex} = 365 nm) are taken and the fluorescence intensities at different emission wavelengths are captured by a fluorescence microscope (Olympus IX71, USA) using Volocity™ software. UV-visible spectrophotometer (Ocean Optics, Flame-S, USA) is used to measure the UV-vis reflectance spectra of the ZnQ@ZIF-8 coated paper sensor before and after applying various standard solutions.

To carry out the fluorescence titration for TNT, 10 mg of the finely ground ZnQ@ZIF-8 is added to 120 mL of ethanol. After the sonication of this mixture at room temperature for 30 min, a suspension of ZnQ@ZIF-8 in ethanolic media is obtained. Then 4.5 mL of the suspension is pipetted to a 5 mL volumetric flask; after that a different amount of TNT dilutes solution is added. The volume of the suspension containing TNT is adjusted to 5 mL by ethanol, giving a different concentration of TNT in the ZnQ@ZIF-8 fluorescent crystal probe. Finally, this suspension is transferred to a quartz cuvette followed by monitoring emission intensity upon excitation at 365 nm using the UV-visible spectrophotometer with fluorescence measurement setup. It is worth to note that we take the reading three time and then collect the average data.

3. Results & Discussion

In this study, the ZIF-8 material was selected as a nanoporous host structure, within which we in-situ encapsulate a fluorescent guest material ZnQ. ZIF-8 has a large void size of 13.32 Å × 11.18 Å [16] which enables the luminescent materials to settle inside, as illustrated in Figure 1. ZIF-8 has naturally smaller window apertures which may obstruct the true advantage of having a larger internal void space. Indeed, recent studies showed that only small gas molecules could penetrate the internal void space of ZIF-8 upon application of a threshold pressure [17]. ZIF-8 nanocrystals could be formed in less than one minute (via simple mixing of solution A and B) as shown in Figure 1 A reaction. The strategy of in situ synthesis and guest

encapsulation to construct a host-guest MOF hybrid composite with tunable guest-induced electronic and optical emission properties is illustrated in Figure 1 B reaction. The key point is to choose suitable guest materials that can be easily encapsulated in ZIF-8 voids. ZnQ is one of the relatively smaller and yet highly fluorescent metal complexes [18]. The molecular dimensions of the ZnQ metal complex is approximately $11.74 \text{ \AA} \times 6.49 \text{ \AA}$ (with van der Waals radii), which is geometrically favourable for encapsulation within the void space of ZIF-8 [16].

Figure 1. Schematic diagram illustrating the strategy of the in-situ encapsulation of ZnQ guest in the ZIF-8 voids.

3.1 Morphological and structural characterization of ZIF-8 and ZnQ@ZIF-8

Visual inspections indicate that the pure white crystalline dried product (ZIF-8) is obtained from the reaction of zinc acetate dihydrate with 2-MIM in DMF. However, the reaction of zinc acetate dihydrate and 8-Q with 2-MIM in DMF yields ivory colour crystals of ZnQ@ZIF-8. Scanning electron microscopy confirms a rhombic dodecahedral morphology of ZIF-8 (twelve facets) [15] and its crystal size in the range of 100 nm to 300 nm as shown in Figure 2(a). In contrast, we recognize from Figure 2(b) that the encapsulation process of the ZnQ guest within ZIF-8 has resulted in a relatively larger crystal size distribution between 300 nm and 900 nm. We attribute that the supportive self-assembly for ZnQ within ZIF-8 could influence the growth of ZIF-8 nanocrystals.

Figure 2. SEM images of (a) ZIF-8 and (b) ZnQ@ZIF-8.

Figure 3 presents the structural data of the pure ZIF-8 material compared with its ZnQ guest-encapsulated. Powder X-ray diffraction (PXRD) patterns and simulated pattern in Figure 3(a)

show the structural crystallographic planes of ZIF-8 (black) match well with those of simulated ZIF-8 (blue) and literature [14, 19]. We find that the ZIF-8 has retained its pristine structural form, upon encapsulation with ZnQ guest, for which no major structural changes have been observed between two PXRD patterns. However, we noticed a slight intensity enhancement in case of ZnQ@ZIF-8 (red) which may be attributed to a relatively larger crystal size distribution. Vibrational spectroscopy data measured by Raman spectroscopy have been used in order to confirm the ZIF-8 structure. Figure 3(b) shows the Raman spectra of ZIF-8 (black) and ZnQ@ZIF-8 (red), respectively. The major Raman peaks of ZIF-8 are observed at 168 cm^{-1} ($\nu \text{ Zn-N}$), 273 cm^{-1} ($\nu \text{ Zn-N}$), 687 cm^{-1} (Imdz ring), 1146 cm^{-1} ($\nu \text{ C-N}$), 1180 cm^{-1} ($\nu \text{ C-N} + \text{N-H}$), 1187 cm^{-1} ($\nu \text{ C-N}$), 1462 cm^{-1} (C-H bending of methyl group), 1509 cm^{-1} ($\nu \text{ C-C}$), 2931 cm^{-1} (methyl $\nu \text{ C-H}$), 3114 cm^{-1} , and 3138 cm^{-1} (Imdz $\nu \text{ C-H}$) [20-23]. FTIR spectra in Figure 3(c) further demonstrate matching signatures in agreement with the pristine ZIF-8 compound. At higher frequencies ZIF-8 showed three contributions. First one is a broad peak between 3500 and 3200 cm^{-1} that corresponds to the stretching of the N-H bond due to protonated imidazole [13, 24], and the other two are the small peaks present at 3135 cm^{-1} and 2926 cm^{-1} , which can be attributed to C-H stretching vibrational modes of the imidazole ring and of the methyl group present in the organic linker [25]. The peak at 1590 cm^{-1} could be due to the C=N stretch modes whereas the peak at 1457 cm^{-1} corresponds to the entire ring stretching [24]. Several spectral bands seen in the range 1350 to 900 cm^{-1} that could be attributed to the in-plane bending of the ring and the peaks at 760 and 690 cm^{-1} are associated with aromatic sp^2 C-H bending [26]. Together we conclude that ZIF-8 has retained its pure structural form, even upon encapsulation with ZnQ guests, for which no major structural changes have been observed. This behaviour is similar to examples shown in the literature which reported no change in the structural X-ray diffraction pattern upon guest molecule encapsulation in the ZIF-8 host compounds [16, 24, 27, 28].

The BET measurements show a loss in the surface area of the pristine ZIF-8 upon the encapsulation of ZnQ. The pristine ZIF-8 has a surface area of $846 \text{ m}^2/\text{g}$. After encapsulating ZnQ to ZIF-8 pores (ZnQ@ZIF-8), the surface area is decreased to $705 \text{ m}^2/\text{g}$ which is 16.5 % reduction in surface area which suggest the loading ratio of ZnQ to ZIF-8. The adsorption-desorption isotherms of N_2 on ZIF-8 and ZnQ@ZIF-8 at 77 K are presented in supplementary material section S1. In addition, the peak area calculations with GC-MS data (see supplementary information section S2) result in composition ratio of 18.52% of 8-Q, 80.5% of 2-MIM, and 0.98% of impurities.

Fluorescence emission spectra in Figure 3(d) provide evidence of host-guest intermolecular interactions responsible for the red-shifted emission spectrum in ZnQ@ZIF-8. It can be seen that the maximum emission peak of ZnQ at $\sim 420 \text{ nm}$ has redshifted by $\sim 100 \text{ nm}$ to a higher wavelength of $\sim 520 \text{ nm}$, which occurred upon encapsulation of ZnQ guests inside ZIF-8.

Figure 3. Structural characterization of ZIF-8 (black) and ZnQ@ZIF-8 (red): (a) Powder X-ray diffraction patterns with comparison to that of simulated ZIF-8 (blue), (b) Raman vibrational spectra (ν : stretching, δ : bending), (c) FTIR spectra in transmission mode and (d) Fluorescence emission spectra of ZnQ (purple) and ZnQ@ZIF-8 (red) excited at $\lambda_{\text{ex}} = 365$ nm.

3.2 Visible colorimetric and fluorescent nitroaromatic explosive sensing

Interestingly, we observe a visible colour change upon the application of different concentrations of TNT to the ZnQ@ZIF-8 coated paper sensor as shown in Figure 4(a). The colour has been changed from ivory to light red in approximately one minute which indicates an interaction between the analyte (TNT) and the sensing materials (ZnQ@ZIF-8). Nitroaromatics are good examples of electron-deficient molecule, making them ideal targets for nucleophilic aromatic substitutions [7]. TNT is an electron-deficient molecule because of three-electron withdrawing nitro group. Thus, the interaction between the electron-deficient aromatic core of TNT and the electron-rich ZnQ@ZIF-8 favours the formation of donor-acceptor electron-transfer mechanism which consequently causes a colour change in visible range. It is worth to mention that there are no colour changes upon addition of TNT to either ZIF-8 or ZnQ coated paper. It should be noted that lowest TNT concentration that causes visible colour change which we can observe with our bare eyes is 3 ppm. However, the colour is very faint so the optical image is not included in Figure 4(a). As shown in Figure 4(b), with increasing TNT concentration, absorption of light around 500 nm wavelength increases which results in colour change in visible region. UV-vis reflectance spectra measurements also show no interaction after the addition of 3NT, RDX and ACN as shown in Figure 4(c). However, there are some changes in reflectance spectra with the addition of 1000 ppm of 2,4-DNT or 2,6-DNT which implies that TNT by-products in high concentrations are also detectable with this paper sensor.

Figure 4. (a) Optical images of the ZnQ@ZIF-8 coated paper sensor as a function of TNT concentrations. The colour changes from ivory to light red with increasing concentrations of TNT. All scale bars are 1 cm. (b) UV-vis reflectance spectra as a function of TNT concentrations, (c) UV-vis reflectance spectra with different nitroaromatic compounds (1000 ppm 3NT, 1000 ppm RDX, 1000 ppm 2,4-DNT, 1000 ppm 2,6-DNT, ACN and 1000 ppm TNT).

Upon exposure of TNT to the ZnQ@ZIF-8 coated paper sensor, fluorescence quenching is also noted under a portable UV light irradiation ($\lambda_{\text{ex}} = 365$ nm). Figure 5(a) shows optical images of the ZnQ@ZIF-8 coated paper sensor as a function of TNT concentrations under the UV light. Bluish-green fluorescence colour becomes darker as TNT concentration increases. The fluorescence intensities at different emission wavelengths ($\lambda_{\text{em}} = 455$ nm, 525 nm and 605 nm) captured by a fluorescence microscope are plotted in Figure 5(b). It is noted that the highest fluorescence quenching always occurs in the blue emission regime at 455 nm (see supplementary material section S3). Similar performance has been noted in literature because 455 nm matches the absorption spectrum of TNT-amine complexes [29]. The fluorescence quenching is defined as in the equation (1) where I is the maximum fluorescence intensity after exposure to TNT and I_0 is the maximum fluorescence intensity of the ZnQ@ZIF-8 before exposure.

$$\text{Fluorescence Quenching} = 1 - \frac{I}{I_0} \quad (1)$$

The standard TNT solution comes in ACN and diluted with ACN. Therefore, it is important to test the response to ACN, as well as other nitroaromatic compounds to show that TNT is the real cause of the fluorescence quenching. The intensity of the bluish-green fluorescence is not much influenced by the addition of other nitroaromatics including 3NT, RDX and ACN as shown in Figure 5(c) (see supplementary material section S4). However, some changes in fluorescence quenching upon addition of 2,4-DNT and 2,6-DNT are observed which implies that TNT by-products in high concentration are also detectable with this paper sensor (see supplementary material section S4). This lower interaction with DNTs compared to TNT further confirms the primary interaction happens between the sensing material (ZnQ@ZIF-8) and the toluene ring. However, the numbers and positions of the nitro group have an effect on the interaction extent.

Figure 5. (a) Optical images of the ZnQ@ZIF-8 coated paper sensor as a function of TNT concentrations under UV irradiation ($\lambda_{\text{ex}} = 365 \text{ nm}$). The bluish-green fluorescence color becomes darker with increasing concentrations of TNT. All scale bars are 1 cm. (b) Fluorescence quenching at different emission wavelengths ($\lambda_{\text{em}} = 455 \text{ nm}$, 525 nm and 605 nm) for the ZnQ@ZIF-8 coated paper sensor as a function of TNT concentrations from 1 to 100 ppm. (c) Fluorescence quenching at different emission wavelengths ($\lambda_{\text{em}} = 455 \text{ nm}$, 525 nm and 605 nm) for the ZnQ@ZIF-8 coated paper sensor with different nitroaromatic compounds (ACN, 1000 ppm 3NT, 1000 ppm RDX, 1000 ppm 2,4-DNT, 1000 ppm 2,6-DNT, and 1000 ppm TNT).

3.3 Fluorescent TNT sensing in liquid phase

Upon excitation at 365 nm, the ZnQ@ZIF-8 in ethanolic solution has shown an emission maximum at 510 nm which is attributed to a π^* to n or a π^* to π transition [30]. ZnQ encapsulation process greatly enhances the fluorescence emission spectrum of ZIF-8. Moreover, the electron rich properties of ZnQ materials influence the electronic interaction between the analyte material (TNT) and the sensing material (ZnQ@ZIF-8). Upon addition of TNT to solutions of ZnQ@ZIF-8, fluorescence is rapidly quenched. Measurements are conducted one minute after the addition of TNT. As shown in Figure 6, a titration curve

Sensing Material	Colorimetric LOD	Fluorescent LOD	Selectivity	Ref
Polyethylene imine capped copper nanoclusters	0.05 nM	14 pM	TNT only	[31]
Dicyclohexylamine entrapped polyvinylchloride with diethylphthalate	0.013 M	N/A	Tetryl(2,4,6-trinitrophenyl-N-methylnitramine) and TNT	[32]
Polyethylenimine with pyrene moieties	N/A	145 pM	Not selective to DNT versus TNT	[33]
Fluorescein 5(6)-isothiocyanate functionalized-per-6-NH ₂ - β -CD	N/A	20 nM	TNT only	[34]
Molecularly imprinted polymers capped carbon dots	N/A	17 nM	TNT in water only	[35]
Bovine serum albumin functionalized fluorescent gold nanoclusters	N/A	10 nM	TNT and 4-nitrophenol	[36]
PCN-224	N/A	460 nM	TNT	[37]
Fe ₃ O ₄ @Tb-BTC	N/A	50 μ M	TNT, 2,4DNT and 2,6DNT	[38]
ZnQ@ZIF-8	1.2 μ M	212 nM	TNT only	This work

of the fluorescence peak intensity of ethanolic solutions containing 1 mg/mL of ZnQ@ZIF-8 is generated as a function of TNT concentrations ranging from 100 ppb to 1 ppm. The quenching efficiency increased with increasing the TNT concentrations. The fluorescence turn-off signal is also easily distinguished by the naked eye under a UV lamp using UV goggle (Figure 6(a)), demonstrating the applicability of ZnQ@ZIF-8 for real-time sensing of TNT. Figure 6(b) shows the linearity range of this sensor. After curve fitting, the best linear fitting ($R^2 = 0.9949$) is at a lower TNT concentration range that is attributed to either static or dynamic quenching. The fluorescence quenching also follows the Stern-Volmer equation shown in equation (2), where $[Q]$ is the concentration of analyte. K_{sv} values are calculated to be 1349 M^{-1} for paper sensors and 820.9 M^{-1} for liquid sensors. The limit of detection (LOD) can be calculated using a signal-to-noise ratio of 3 ($3\sigma/K_{sv}$, where σ is the standard deviation of 5 blanks). This corresponds to a LOD of 398 nM and 212 nM, respectively. The LOD for colorimetric sensors is calculated from the standard deviation in the blank (s_b), intercept error (s_i) and the slope of the responses (m) for 4 separate sensors. A confidence factor (k) of 3 is chosen to yield a confidence level of 99.87%. The intercept error is determined from plotting the responses from 1-20 ppm. As a result, the LOD could be calculated with equation (3) to be 1.2 μ M with colorimetric sensors. A comparison table is shown in Table 1. The LOD is slightly higher than that of others.

However, other works use long and complex synthesis techniques, and some may also use buffer solutions during sensing [31]. The advantages of this work include the rapid and facile synthesis technique, and an ability to perform colorimetric sensing and fluorescent sensing in the solid or liquid phase without the need for a buffer solution.

A nonlinear behavior was noticed at higher concentrations of TNT (Figure 6(b)), which may be attributed to a self-absorption or an occurrence of an energy transfer process between TNT and ZnQ@ZIF-8.

$$\frac{I_0}{I} = 1 + K_{sv}[Q] \quad (2)$$

$$LOD = \frac{k[s_B^2 + s_L^2]^{\frac{1}{2}}}{m} \quad (3)$$

Figure 6. (a) Fluorescence emission intensity upon incremental addition of TNT ($\lambda_{ex} = 365$ nm). The inset shows the visual color change under UV light. (b) Fluorescence quenching with ethanolic solution of ZnQ@ZIF-8 at different TNT concentrations from 100 ppb to 1 ppm. The inset shows a linear fitting curve at lower concentration ranges.

Table 1. Comparison table of various TNT colorimetric and fluorescent sensors.

3.4 Sensing Mechanism

It has been reported that a single dried TNT particle has an aerodynamic diameter of approximately $1.08 \mu\text{m}$ [39] which is larger than the pore size of ZIF-8. Therefore, adsorption of dried TNT particles is an unlikely mechanism. The TNT sensing mechanism for ZIF-8 has been commonly reported as a donor-acceptor electron transfer [40, 41]. Moreover, ZnQ was also reported as electron rich molecule [42] which greatly support the proposed mechanism of interaction between TNT and ZnQ@ZIF-8. At photoexcitation of molecule-sensors, the electron makes a transition to the molecular orbital of higher energy. In the absence of quencher, the reverse transition is accompanied by fluorescence as shown in the Figure 7. The photo excited molecule, called the donor (ZnQ@ZIF-8), has a larger band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (4.4 eV) [16] than the acceptor (TNT) which has lower band gap (0.4131 eV) [43]. Both static and dynamic quenching are frequently a matter of photoinduced electron transfer between the excited-state of the sensor, and the ground state of the explosives [7]. Upon contact with the nitro compound the excited electron of molecule-sensor returns to the ground state not participating in the radiative transition, which is observed experimentally as fluorescence quenching. The energy

difference between HOMO and LUMO is a driving force (DF) of fluorescence quenching process. In most cases, the static fluorescence quenching is prevalent and therefore it is often used in nitroaromatic compounds luminescent detection. The additional -NO₂ group on TNT versus DNT explains the higher magnitude of changes. This phenomenon is attributed to both fluorescence quenching and visible color change.

Figure 7. The mechanism of fluorescence quenching by contact of chemical sensor (ZnQ@ZIF-8) and nitro compounds (TNT). LUMO - the lowest unoccupied molecular orbital, HOMO - the highest occupied molecular orbital, DF - driving force. The blue and red arrows indicate the electron spin directions and red dotted arrows represent the radiative and non-radiative transitions of electron, respectively.

Conclusions

In conclusion, ZIF-8 is successfully synthesized in situ without the need of excessive energy. ZnQ is encapsulated into the pores of ZIF-8 in-situ to form a strong fluorescent MOF. The ZnQ@ZIF-8 solution is coated on a filter paper and dried in a vacuum oven to make cost-effective and disposable nitroaromatic explosives sensors. The paper-based sensors showed the most visible colour change upon application of TNT, but not other nitroaromatics such as 3NT and RDX. In addition, the most fluorescence quenching under UV irradiation ($\lambda_{ex} = 365$ nm) occurs upon application of TNT at an emission wavelength of 455 nm. Visible colorimetric changes and fluorescence quenching are noted down to TNT concentrations of 1 ppm. In liquid phase, the fluorescence quenching is observed down to TNT concentration of 100 ppb. It is envisioned that this strategy can be extended to nano-caging and nano-manipulation of a wide variety of light-sensitive fluorophores combined with the diverse family of MOFs for different chemical sensing applications.

Conflicts of interest

There are no conflicts to declare.

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