Rapid and Specific Aqueous-Phase Detection of Nitroaromatic Explosives with Inherent Porphyrin Recognition Sites in Metal–Organic Frameworks

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Ⓢ *Supporting Information*

ABSTRACT: Development of a rapid and effective method for the detection of 2,4,6-trinitrotoluene (TNT) in aqueous phase has attracted great attention. In this work, the fluorescent porphyrin-based metal−organic frameworks (MOFs) of PCN-224 were successfully exploited as a fluorescent probe for the rapid and selective TNT detection in water media. This strategy combined the advantages of fluorescent porphyrin molecules and porous MOFs, which not only overcame the aggregation of hydrophobic tetrakis(4-carboxyphenyl)porphyrin (TCPP) recognition sites but also promoted TNT to interact with recognition sites in virtue of the high surface and intrinsic open structure of MOFs. As a result, a rapid response time of as short as 30 s was obtained for the elaborated fluorescent probe. Meanwhile, the bright red emission of porphyrin units in PCN-224 could be proportionally quenched in correlation with the applied TNT level through the formation of TNT-TCPP complex in the ground state. The specificity of the employed sensory platform for TNT recognition was scarcely affected by other possible coexistent interfering species. Furthermore, this fluorescent PCN-224 probe presented a much higher quenching efficiency for TNT than other structurally similar nitroaromatic compounds and was successfully applied for the quantitative detection of TNT in the mixed nitroaromatic explosive samples. This prefigured their great potentials of practical TNT detection in water media for public safety and security.

KEYWORDS: metal−organic frameworks, TNT detection, fluorescent sensors, aqueous phase, porphyrin
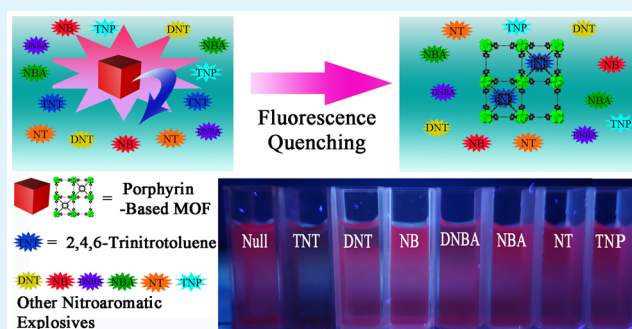
1. INTRODUCTION

The 2,4,6-trinitrotoluene (TNT) is one of the most commonly used explosives for military and industrial purposes.[1] Meanwhile, it is generally a restricted substance in environmental protection and homeland security since residual TNT is highly toxic to biological organisms.[2,3] Therefore, sensitive and reliable TNT detection is of great significance for human health and homeland security.

Although various strategies have been developed for the detection of TNT,[4−6] a simple and rapid technique such as fluorogenic sensing seems more attractive in virtue of its high sensitivity, simple operation, and rapid response time.[7−10] Porphyrins and their derivatives are a group of heterocyclic macrocycle organic compounds, with characteristics of large extinction coefficient in the visible-light region, rigid structure, and excellent chemical stability.[11] These exquisite advantages endow them with a fascinating perspective for the design of long wavelength fluorescent probes to detect nitroaromatic explosives.[12−15] Unfortunately, most porhyrins and their derivatives are hydrophobic. As a result, they are strongly subject to aggregation in aqueous solution due to the strong π−π interaction, greatly influencing their optical properties and inhibiting their fluorescence response to the analytes.[16,17] To address this issue, many types of heterogeneous carriers, such as graphene[18,19] as well as silica nanoparticles,[20−22] have been explored to fabricate stable and reliable sensing systems. However, the fabrication of these sensory platforms often suffers from the low fluorophore loading, nonuniform surface coverage, and fluorophore self-aggregation in the entrapped state. Therefore, it is highly desirable to exploit a facile strategy to fabricate a heterogeneous porphyrin-based fluorogenic sensor for the rapid and selective detection of nitroaromatic compounds in aqueous solution.

Metal−organic frameworks (MOFs) are permanent porous crystals composed of metal clusters and organic ligands structured by coordination bonds.[23−25] They have been

Scheme 1. Schematic Illustration for the Construction of PCN-224 LMOFs and Their Sensing Mechanism for the Rapid and Specific TNT Detection with Porphyrin Units in TCPP as the Inherent Bridging Struts, Recognition Sites, and Fluorescent Reporter
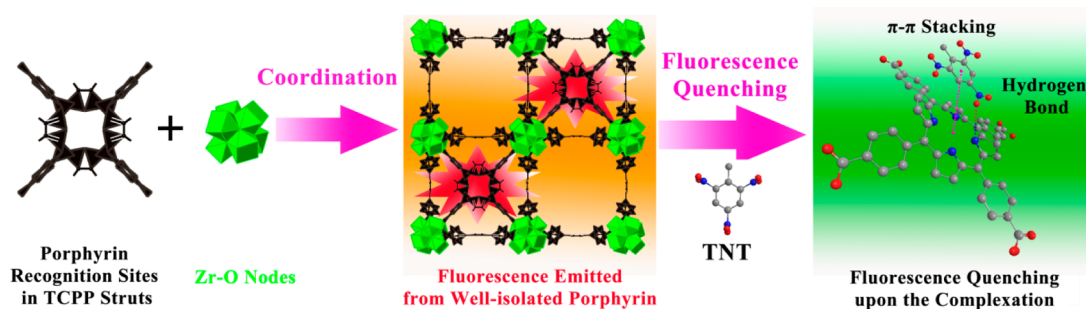
regarded as one of the leading candidates for sensing materials thanks to their outstanding merits such as high surface areas, versatile framework compositions, and exposed active sites.[26−28] Especially, luminescent MOFs (LMOFs) have been successfully exploited as a unique class of sensing platform in the analytical science community.[29−33] Up to now, many efforts have been devoted to applying LMOFs for the detection of nitroaromatic explosives.[34−46] However, most of the reported LMOFs are used in organic or gas phase because the employed MOFs are generally characteristic of poor hydrolytic stability. It seems that aqueous-phase detection is more preferred for the in-field selective probing of nitro explosives in soil or groundwater,[47] in which field quantum dots sensors have been successfully applied.[9,10] Therefore, an urgent need exists to exploit the water-resistant LMOFs for practical explosives detection, although a few recent encouraging works came to touch on this vital topic.[48−50]

It has been verified that porphyrin-based MOFs of PCN-224 possess exceptional chemical and thermal stability due to the strong interaction between Zr−O clusters and carboxylate in tetrakis(4-carboxyphenyl)porphyrin (TCPP) molecules (Scheme 1).[51,52] Additionally, porphyrin is an inherent component as the organic struts for the construction of the open framework of PCN-224, so that the multistep procedures for the introduction of porphyrinic groups could be effectively avoided. This strongly prompts us to propose that PCN-224 could hopefully offer a new platform to fabricate a long wavelength emission sensor for the detection of TNT. We conceive that porphyrin units could serve as bridging struts, recognition sites, and a fluorescent signal reporter for TNT sensing (Scheme 1) upon its integration into the robust and porous PCN-224 network. This sensing system may have several advantages: (1) the aggregation of porphyrin molecules could be effectively avoided since they are well-isolated by the Zr−O nodes in the frameworks of the resultant LMOFs; (2) the open LMOFs structure with high surface area could facilitate TNT diffusion across the frameworks and easily interact with recognition sites; (3) the exceptional chemical stability of PCN-224 favors the aqueous-phase detection of TNT.

As expected, the emission from the elaborated fluorescent probe is similar to that from free TCPP ligands, which should mainly ascribe to the homogeneous distribution of TCPP in the network of the applied LMOFs. On the other hand, TNT explosive forms hydrogen bonds as well as π-stacking with the monomeric TCPP fluorophore in PCN-224 so that it could be specifically recognized in aqueous phase.[12,13] Upon the complexation of TNT with porphyrin units in TCPP linkers,

the fluorescence emission from PCN-224 is progressively quenched correlated with the applied TNT level. In the current work, a rapid response time of as short as 30 s is obtained using this fluorescence quenching sensor for TNT detection. Additionally, the quenching constant (K_{SV}) for TNT is quantified to be 3.5×10^4 M^{-1}, which is approximate five times higher than those of the known porphyrin molecule sensors.[12,13] The specificity of the employed sensory platform for TNT recognition is scarcely affected by other possible interfering species. Furthermore, this fluorescent PCN-224 sensor shows a much higher K_{SV} for TNT than those for other structurally similar nitroaromatic compounds and could be used for the quantitative detection of TNT in mixed nitroaromatic explosive samples.

2. EXPERIMENTAL DETAILS

Chemicals and Materials. TCPP was purchased from J&K Scientific Ltd., Beijing, China. TNT (1.00 mg/mL in methanol), 2,6-dinitrotoluene (DNT), nitrotoluene (NB), 3,5-dinitrobenzoic acid (DNBA), 3-nitrobenzoic acid (NBA), 4-nitrotoluene (NT), benzoic acid (BA), chlorobenzene (CB), and HEPES (4-(2-hydroxyethyl)-piperazine-1-ethanesulfonic acid) were supplied by Sigma-Aldrich. 2,4,6-Trinitrophenol (TNP) was purchased from Xiya Chemical Regent Co., Ltd., Chengdu, China. Other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All reagents were of analytical grade and used as received without additional purification. All of the obtained nitroaromatic compounds were dissolved in ethanol to prepare the stock solution (4.0 mM) before use. The stock solutions of other analytes (4.0 mM) were also prepared by dissolving NaCl, KBr, Na$_2$SO$_4$, NaHCO$_3$, NaNO$_2$, KCl, MgCl$_2$·6H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, CaCl$_2$, Ni(NO$_3$)$_2$·6H$_2$O, and Al-(NO$_3$)$_3$·9H$_2$O in aqueous solutions, respectively.

Synthesis of PCN-224. PCN-224 particles were synthesized in a moderate condition as reported with a slight modification.[52] Briefly, ZrOCl$_2$·8H$_2$O (156.25 mg, 0.485 mmol) was dissolved in 125 mL of dimethylformamide (DMF), and the mixture was sonicated for about 30 min. Then, TCPP (31.25 mg, 0.04 mmol) and acetic acid (31.25 mL, 546 mmol) were added to the solution. After further ultrasonic treatment for 10 min, the solution was placed in a 250 mL vial and heated at 65 °C for 3 days. After cooling to room temperature, the purple solid was collected by centrifugation and washed with DMF (5 × 100 mL). The DMF was then replaced with acetone (5 × 200 mL) at 65 °C over a 5 day period. Finally, the PCN-224 powder was activated at 120 °C *in vacuo* for 24 h.

Fluorescence Detection of TNT and Other Nitroaromatics. The stock solution of PCN-224 with a final concentration of 500 μg/mL was prepared by dispersing PCN-224 in 20 mL of HEPES buffer solution (pH = 7; 20 mM) under ultrasonic condition for 10 min. Then, it was preserved in a refrigerator at 4 °C under dark condition for further use.

For the typical TNT or other explosives detection, 100 μL of PCN-224 stock solution (500 μg/mL) was added into 20 mM HEPES buffer solution (pH = 7.0) and was mixed thoroughly. Then, explosive stock solutions were added to give a series of mixture solutions with different concentrations of analytes. The final volumes of the prepared batches of solutions were kept at 2 mL. The fluorescence spectra were recorded with excitation at 590 nm.

To study the response kinetics, three different samples with TNT concentrations of 0, 20, and 50 μM were prepared by adding TNT to PCN-224 suspension in 20 mM HEPES buffer solution (pH = 7.0). The fluorescence intensities of the resultant mixtures were recorded at different time intervals from 30 to 300 s with excitation at 590 nm.

Selectivity Measurements of TNT. To test the selectivity for TNT detection, different anions, cations, aromatic compounds, and structurally similar nitroaromatic explosives were selected as possible interfering species. The concentrations of various ions and aromatic compounds were set as 50 μM, and the concentrations of the other six nitroaromatic explosives were preset as 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 μM, respectively. The fluorescent measurements were conducted at the same condition as the preceding TNT detection procedures in the presence of various ions and aromatic compounds. Meanwhile, to investigate the interfering effects of the coexistent explosives, each nitroaromatic explosive and TNT were spontaneously added into the PCN-224 suspension for fluorescent measurement. The amounts of the interfering explosives were preset at equivalent moles with TNT in the range of 0−50 μM. The fluorescence spectra were recorded as mentioned previously.

TNT Detection in the Mixed Nitroaromatic Explosive Samples. The fluorescence quantification method was employed to analyze TNT in the mixed nitroaromatic explosive samples. For example, in the TNT/NB mixed sample, 100 uL of PCN-224 stock suspension (500 μg/mL) was injected into 20 mM HEPES buffer solution (pH = 7.0). Then, 10 uL of TNT stock solution (4 mM) and 5 uL of NB stock solution (4 mM) were added into the preceding buffer solution with the final TNT and NB concentrations of 20 and 10 uM, respectively. The final volume of the solution was kept at 2 mL. The fluorescence spectra were recorded with excitation at 590 nm. The measurements were repeated for 4 times to get an average value of the detected TNT concentration. The recovery percentage was calculated to evaluate the deviation degree of the detected value to the real added TNT amount. This fluorescence quantification method was also applied to the other mixed nitroaromatic explosive samples.

Time-Resolved Decay Measurements. To explore the fluorescence quenching mechanism of the current PCN-224 fluorescent probe by TNT, the time-resolved decay measurements of 100 uL of PCN-224 stock solution with different TNT additions (0 and 20 μM) were detected in 20 mM HEPES buffer solution (pH = 7.0). The final volume of the solution was kept at 2 mL. The excitation wavelength was 470 nm, and the emission wavelength was 651 nm.

Instruments and Methods. UV−vis absorption and fluorescence spectra were recorded with a UV-2550 spectrophotometer (Shimadzu, Tokyo, Japan) and a RF-5301PC spectro-fluorophotometer (Shimadzu), respectively. The powder XRD patterns were obtained on a Bruker D8 instrument using Cu Kα radiation (40 kV, 40 mA). N_2 sorption isotherms were recorded with a surface area and pore size analyzer (Micromeritics Tristar 3020). All of the samples were degassed under vacuum for 12 h before measurements. The specific surface area was calculated by the Brunauer−Emmett−Teller (BET) method using adsorption data at a relative pressure lower than 0.15. Field emission scanning electron microscopy (FESEM) was performed on a JEOL JSM6700F electron microscope. Thermogravimetric analysis (TGA) was conducted on a PerkinElmer thermogravimetric analyzer by heating the sample to 600 °C under air atmosphere (50 mL min^{-1}) at a heating rate of 10 °C min^{-1}. Fluorescence lifetime was recorded with a PTI QM/TM/NIR spectrometer (Birmingham, NJ, USA), and the lifetime was calculated using the instrument software (Felix 32).

3. RESULTS AND DISCUSSION

Characterization of PCN-224 Particles. Solvothermal reaction of TCPP with $ZrOCl_2 \cdot 8H_2O$ led to the formation of the purple powder of PCN-224. The powder X-ray diffraction (PXRD) pattern reveals that PCN-224 presents a typical *Im3m* space group consistent with the reported topology (Figure 1),
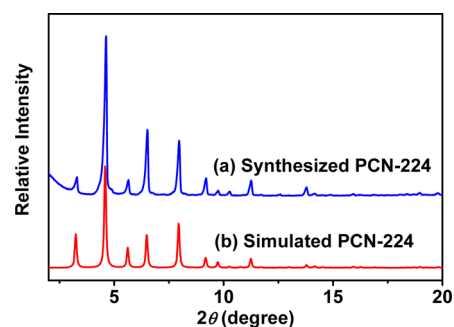
Figure 1. Powder XRD patterns of the (a) as-synthesized and (b) simulated PCN-224 structures.

which has a unit cell parameter of 38.51 Å.[51] Meanwhile, the peak positions match well with the simulated one. The intense diffraction peaks indicate that these particles are highly crystallized. Cubic microcrystals of the obtained PCN-224 exhibit particle sizes of 1−2 μm, as SEM images verified (Figure S1, Supporting Information). The permanent porosity of the activated PCN-224 particles is confirmed by N_2 sorption measurement. As shown in Supporting Information Figure S2, the N_2 sorption curve at 77 K exhibits a type I isotherm with BET and Langmuir surface areas of 1413 and 2111 m^2/g, respectively. Such high surface areas and large pore windows make the recognition sites more accessible for the guest molecules, which might benefit a rapid response of the currently elaborated sensor toward nitroaromatic explosives.

Meanwhile, when PCN-224 particles were soaked in water for several days, the crystalline structure integrity was perfectly preserved (Figure S3, Supporting Information), affirming their excellent chemical stability in a water environment. The TGA profile (Figure 2) reveals that PCN-224 is stable up to around
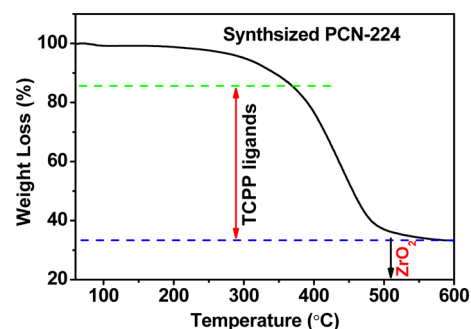
Figure 2. TGA profile for the as-synthesized PCN-224 particles recorded under air flow.

370 °C and shows a 51.3% weight loss (370−550 °C) corresponding to the decomposition of TCPP ligands. The continuous weight loss from 100 to 370 °C is due to the dehydration of the $Zr_6O_4(OH)_4$ nodes to Zr_6O_6.[53] Therefore, PCN-224 exhibits high hydrolytic and thermal stability and meets the critical prerequisites as an ideal platform for
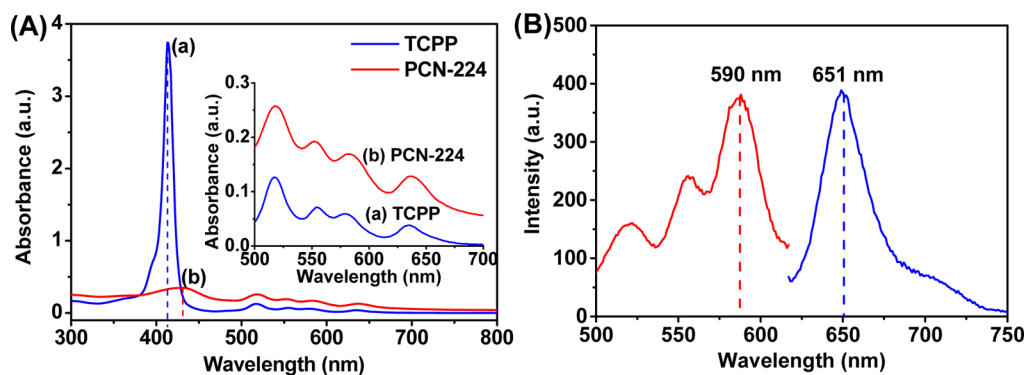
Figure 3. (A) UV−vis absorption spectra of (a) free TCPP ligand (blue) and (b) PCN-224 (red) in HEPES buffer solution (pH = 7; 20 mM) at room temperature. (B) Flucorescence spectra (blue) of PCN-224 (50 mg L^{-1}) in HEPES buffer solution under excitation at 590 nm. The red curve shows the excitation spectrum.

fluorescent sensing in aqueous phase in support of our proposal.

Spectroscopic Properties of PCN-224. Compared with the free TCPP ligands in HEPES buffer solution, the UV−vis absorption spectrum of PCN-224 suspension also presents a Soret band at 430 nm and four Q-bands at 518, 552, 585, and 637 nm (Figure 3A). The peak shapes and positions of the Q-bands of PCN-224 suspension are quite similar to those of the free TCPP ligands. This similarity indicates that TCPP is well-isolated in the particle.[17] The existence of a porous coordination network sterically inhibits the porphyrin fluorophores from approaching each other, which can greatly reduce the aggregation of TCPP recognition sites in good agreement with the spectroscopic observations.[54] Additionally, the Soret band of PCN-224 is significantly broadened and weakened, and demonstrates an obvious red shift from 410 to 430 nm, which is assumedly ascribed to the ligand-to-metal charge transfer (LMCT) upon the strong coordination of TCPP linkers to Zr−O clusters in the framework of PCN-224.[29,55]

In the PL spectra, it is found that the different excitation wavelengths have a negligible impact on the shape and position of the emission peak of PCN-224 (Figure S4, Supporting Information). The PCN-224 suspension in the quartz cuvette emits bright red fluorescence upon illumination even when a UV lamp is used with irradiation wavelength of 365 nm (Figure S5, Supporting Information). By contrast, their fluorescence intensities progressively enhance as excitation wavelengths are increased from 430 to 590 nm. Therefore, an excitation wavelength of 590 nm was chosen in this work. As shown in Figure 3B, the fluorescent spectrum of PCN-224 suspension in aqueous solution exhibits a strong emission peak at 651 nm and a weak emission shoulder at 705 nm, attributed to a typical S$_1$ → S$_0$ state transition of porphyrin.[56] It is also found that the fluorescence emission from PCN-224 MOFs (Figure S6, Supporting Information) is very stable in aqueous solution as verified by a day-to-day fluorescence measurement, benefiting from their high hydrolytic stability. This further endows them with the feasibility as a fluorescent probe in aqueous environment.

Detection of TNT Explosive with PCN-224 Probe. For security-screening and mine-fields analysis, it is very crucial to check out nitroaromatic explosives, especially for TNT, using a simple and rapid method. Therefore, the kinetic characteristic for TNT sensing using the currently developed fluorescent probe was first tested (Figure 4). Upon the addition of TNT
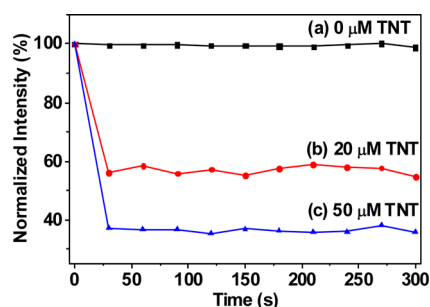

Figure 4. Effect of incubation time on the fluorescent intensities upon the addition of the TNT solutions into the PCN-224 suspension. The TNT concentrations were set as (a) 0, (b) 20, and (c) 50 μM.

(25 and 50 μM) solutions into the PCN-224 suspension, the fluorescence emissions from PCN-224 are instantly decayed within the initial 30 s and maintain an equilibration in the following 5 min. This rapid response probably benefits from the facile diffusion of TNT across the porous PCN-224 framework.[14] Therefore, an incubation time of 30 s was set to ensure reaching the fluorescence equilibrium before measurement for all of the experiments.
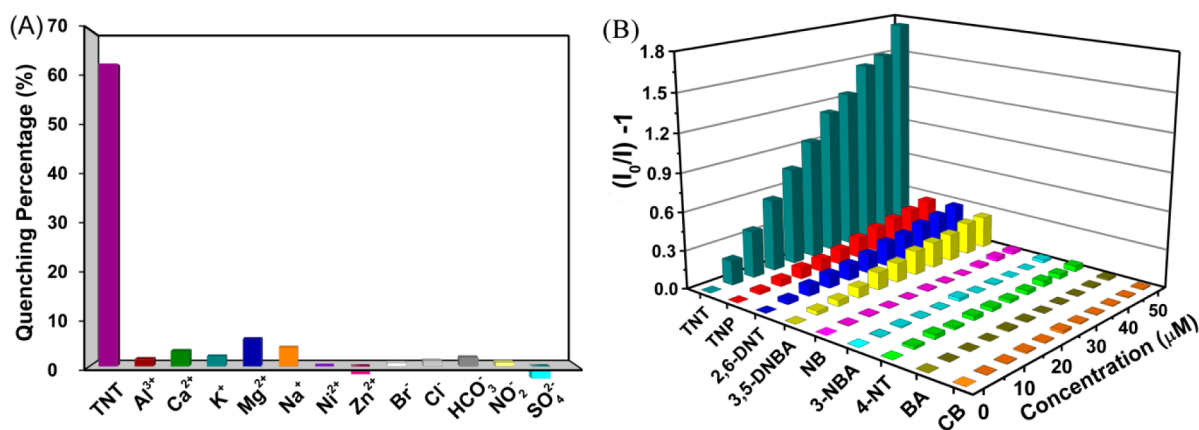
Fluorescence quenching titrations with different TNT addition levels were conducted with an excitation wavelength of 590 nm at room temperature (Figure 5A). It is observed that the fluorescence intensity gradually decreases with the addition of TNT from 0 to 50 μM. The initial fluorescence quenching by TNT could be clearly recognized at low dose concentration (5 μM, red curve in Figure 5A) since the fluorescence reduction is pretty distinct as the titration profile shows. A high florescence quenching percentage is found at 50 μM, which quenches nearly 63% of the initial fluorescence intensity. The naked eye visible red emission of PCN-224 suspension becomes dark upon the addition of 50 μM TNT (Figure S5, Supporting Information), also confirming the capability of TNT for efficient quenching of the fluorescence emission from PCN-224 suspension. Furthermore, the fluorescence quenching efficiency could be analyzed by Stern−Volmer equation as shown in eq 1.

$$\frac{I_0}{I} = K_{SV}[Q] + 1 \tag{1}$$

where I_0 and I represent the fluorescence intensities of PCN-224 suspension before and after the addition of analyte,
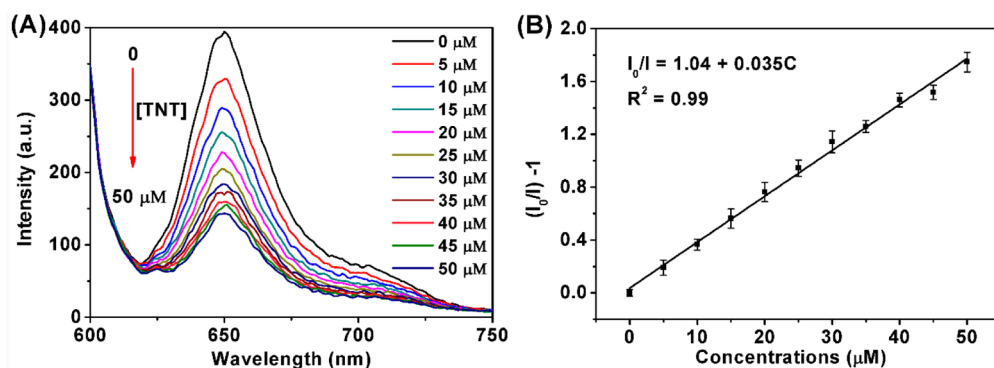
Figure 5. (A) Evolvement of the fluorescence spectra of PCN-224 (50 mg L^{-1}) suspension in HEPES buffer solution (pH = 7; 20 mM) upon the addition of various concentrations of TNT under excitation at 590 nm. (B) Corresponding Stern−Volmer plot of the quenching fluorescence intensity of PCN-224 suspension as a function of TNT concentration.

Figure 6. (A) Percentage of fluorescence quenching of PCN-224 (50 mg L^{-1}) suspension in the presence of different anions and cations (50 μM) at room temperature. (B) Stern−Volmer plots of PCN-224 (50 mg L^{-1}) suspension toward different nitroaromatic explosives (0−50 μM).

respectively; $[Q]$ is the molar concentration of analyte; and K_{SV} is the Stern−Volmer quenching constant.

The Stern−Volmer plot shows a good linear correlation (R^2 = 0.99) in the TNT concentration range of 0−50 μM (Figure 5B). The quenching constant of K_{SV} is an important parameter to describe the fluorescence quenching efficiency, which is quantified to be 3.5×10^4 M^{-1} for TNT. As seen in Supporting Information Table S1, the K_{SV} of PCN-224 is much higher than that of known porphyrin-based molecular sensors for TNT detection in the aqueous solution.[12] Meanwhile, it is comparable to those of reported MOF-based sensors.[48−50] The limit of detection (LOD) is calculated by the fluorescence quenching data using the 3σ IUPAC criteria (3σ/slope).[31] The slope value is taken from a calibration curve for fluorescence intensity against TNT concentration, and the standard deviation σ is calculated by the fluorescence intensity of blank PCN-224 suspension in the absence of TNT (Figure S7, Supporting Information). Then, the LOD is calculated to be 0.46 μM for the current PCN-224 sensor.

Interestingly, although the spectroscopic properties of PCN-224 particles are very similar to that of free TCPP ligands, no such obvious fluorescence quenching effect is found when the PCN-224 particles are replaced with free TCPP ligands (Figure S8, Supporting Information) in the titration experiments. This strongly discloses that the coordination of Zr−O clusters to TCPP ligands in the framework of PCN-224 plays a key role in the detection of TNT. Presumably, TCPP fluorescent molecules used for TNT detection are hydrophobic and tend to aggregate in the water phase. This aggregation significantly deteriorates the accessibility of monomeric porphyrin fluorophore and reduces the fluorescence quenching efficiency by TNT. Compared with free TCPP ligands, the intrinsically open structure of PCN-224 MOFs offers abundant recognition sites, high surfaces, and large pore windows and consequently facilitates TNT recognition and detection. Therefore, this is an effective strategy to prepare a simple and rapid fluorescence sensor for the detection of TNT, which avoids the aggregation of hydrophobic TCPP molecules and enhances fluorescence response efficiency.

Selective TNT Detection. To check the potentials of the PCN-224 fluorescent probe for specific TNT detection, we tested the fluorescence variations of PCN-224 in the presence of various possible coexistent anions (Br$^-$, Cl$^-$, HCO$_3$$^-$, NO$_2$$^-$, and SO$_4$$^{2-}$), cations (Al^{3+}, Ca^{2+}, K$^+$, Mg^{2+}, Na$^+$, Ni^{2+}, and Zn^{2+}), aromatic compounds (BA and CB), and some structurally similar nitroaromatic explosives such as DNT, NB, DNBA, NBA, NT, and TNP.[57] As shown in Figure 6A, the changes of fluorescence intensity toward other ions are almost negligible, clearly evidencing the specificity of the PCN-224 sensor for TNT recognition over other possible interfering ions. Meanwhile, even for some of the nitroaromatic compounds with rather similar chemical structures, their fluorescence quenching efficiencies are much lower than that of TNT (Figure 6B). Furthermore, fluorescent titration measurements of PCN-224 suspension with all of the other nitroaromatic explosives were conducted (Figures S9−S14, Supporting Information), and the

Table 1. Summary of the Stern−Volmer Equations for the Fluorescence Quenching Experiments of PCN-224 Suspension by TNT and Other Structurally Similar Nitroaromatic Explosives

nitroaromatic explosives	K_{SV} ($\times 10^4$ M^{-1})	intercept (μM)	linear range (μM)	correlation (R^2)	SF[a]
TNT	3.5	1.0	0−50	0.99	1
2,6-DNT	0.3	1.1	100−400	0.97	0.09
NB	0.06	1.0	100−400	0.99	0.02
3,5-DNBA	0.5	1.1	50−250	0.97	0.14
3-NBA	0.01	1.0	500−2000	0.95	0.003
4-NT	0.1	1.0	100−400	0.99	0.03
TNP	0.4	1.1	50−200	0.95	0.11

[a]SF represents the ratio between K_{SV} of TNT and that of the other six nitroaromatic compounds.

Stern−Volmer model was also applied to fit the experimental data. It is found that fluorescence quenching could be well-fitted to linear Stern−Volmer plots for all of the other nitroaromatic explosives, and the detailed parameters for each analyte are listed in Table 1. As presented in Table 1, the order of K_{SV} values for the six quenchers is TNT ≫ DNBA > TNP > DNT ≫ NT > NB > NBA. The ratio between K_{SV} of TNT and that of other nitro explosives is defined as the selective factor (SF), which is generally utilized to evaluate the selectivity of PCN-224 toward TNT. The SF values for DNBA, TNP, DNT, NT, NB, and NBA are 0.14, 0.11, 0.09, 0.03, 0.02, and 0.003, respectively, indicating that PCN-224 MOF has a high selectivity toward TNT detection in aqueous solution. In fact, due to the well-known strong tendency to form hydrogen bonding between imino hydrogen of the porphyrin units in TCPP ligands and nitro groups of nitroaromatics as well as π-stacking between porphyrin and nitroaromatics, porphyrin units have relatively large affinity for nitroaromatic molecules.[14] This may provide a strong driving force for fast fluorescent quenching (Scheme 1).[58] The studied nitroaromatic compounds are all of electron-poor analytes. All of them could quench the fluorescence of the porphyrinated PCN-224 due to the electron transfer between electron-rich porphyrin chromophores and these analytes.[59] However, it is different for the fluorescence quenching efficiency. The lack of one (DNT, DNBA) or two (NT, NB, NBA) electron-withdrawing nitro groups might lead to a weaker hydrogen interaction between these nitroaromatic explosives and porphyrin units, rationalizing their relatively weak quenching efficiencies.[60] For TNT and TNP with three nitro groups, the difference of quenching efficiencies should ascribe to the different substituents in their molecules. The presence of a hydrophobic methyl group in TNT could effectively promote the hydrophobic interaction of TNT with hydrophobic porphyrin. By contrast, the electron-rich hydroxyl group in TNP is hydrophilic in nature, which might inhibit the interaction of TNP with hydrophobic TCPP molecules and consequently confine the formation of a TNP-TCPP complex.[13] Therefore, TNT exhibits a stronger quenching efficiency than TNP.

To gain an insight into the proposed quenching mechanism, the fluorescence lifetime was measured by monitoring time-resolved emission decay of PCN-224 suspension at 651 nm. As shown in Figure 7, the fluorescence lifetimes of PCN-224 suspension before and after the addition of TNT are ca. 2.95 and 3.11 ns, which remain essentially unchanged under an excitation wavelength of 450 nm. Generally, a static quenching mechanism should result from a direct binding between the fluorophore and quencher in the ground state while bimolecular collision in the excited state could result in a dynamic quenching.[61] The constant lifetime indicates that a
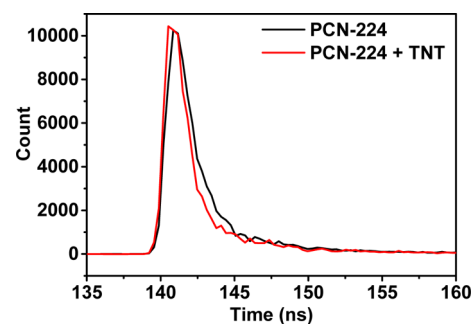

Figure 7. Time-resolved fluorescence decay of the PCN-224 (50 mg L^{-1}) suspension in the absence (black) and presence of TNT (20 μM, red).

static quenching may be the predominant process. The UV−vis spectra of PCN-224 suspension with different TNT were recorded (Figure S15A, Supporting Information) to provide further information about the quenching mechanism. The intensity of the Soret band becomes weakened upon the addition of TNT. Meanwhile, a trough (decrease in absorbance) at 420 nm and a peak (absorbance increase) at 462 nm are clearly observed when we subtract the PCN-224 absorbance spectrum from the PCN-224 + TNT absorbance spectrum (point-to-point subtraction) (Figure S15B, Supporting Information), probably attributing to the formation of a TCPP-TNT complex.[13] This variation trend is similar to the reported free porphyrin molecule sensor through static quenching mechanism for TNT detection.[12,13] Additionally, with the increase of TNT addition, these changes become more visible, indicating that more TNT-porphyrin complex is produced. This confirms the fact that TCPP may form a stable complex with TNT in the ground state via the formation of hydrogen bonding between the hydrogen atoms in pyrrole rings of TCPP and nitro groups in TNT and hydrophobic bonding between the hydrophobic methyl group in TNT and hydrophobic porphyrin rings as well as π-stacking between porphyrin and nitroaromatics.[10,51] As a result, the fluorescent emission of PCN-224 is effectively quenched by the TNT-TCPP complex in the framework of PCN-224 MOFs.

TNT Detection in the Mixed Nitroaromatic Explosive Samples. Since the high specificity is crucial for most probes to be applied in the real sample detection, we further studied the fluorescence quenching of PCN-224 by TNT in the coexistence of other nitroaromatic compounds. As expected, no significant changes of fluorescence intensity are observed in the experiments in which other nitroaromatic compounds are simultaneously added into the TNT-containing detection systems (Figure 8). Meanwhile, almost similar change trends are found for the six selected nitroaromatic compounds,
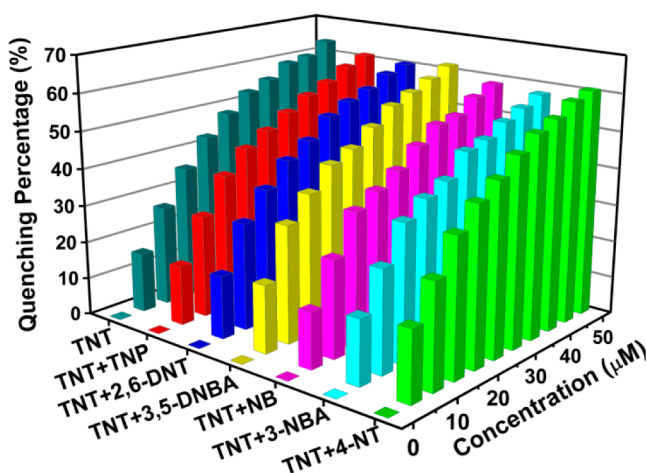
Figure 8. Fluorescence quenching of PCN-224 (50 mg L^{-1}) in HEPES solution (pH = 7; 20 mM) upon the addition of TNT and other nitroaromatic compounds.

explosive. In this elaborated sensory platform, the TCPP ligands are strategically designed as recognition sites and fluorescent signal reporter upon its integration into the robust PCN-224 network. Meanwhile, the specific complexation of porphyrin rings with TNT proportionally quenches the fluorescence emission from TCPP ligands in correlation with the applied TNT level. The exceptional chemical stability of the PCN-224 fluorescent probe rationalizes the detection of TNT in aqueous phase. Additionally, the intrinsic open structure and high surface area facilitate TNT diffusion across the frameworks, benefiting to a short response time and a high quenching constant. The specificity of PCN-224 sensor for TNT recognition is scarcely affected by other possible interfering species so that it could be applied to the quantitative analysis of TNT even in the presence of a large amount of interfering nitroaromatic explosives. Given the ready installation of exposed metal sites in the porphyrin center, this strategy may be a facile and effective method to design rapid and selective porphyrin-based sensors for other analytes with different functionalities of metallic ions in fluorescent porphyrin molecules, which would expand their applications in the fields of chemical and biological sensing.

suggesting that the specificity of PCN-224 for TNT recognition is scarcely affected by other possible coexistent interfering explosives.

To further check the applicability of the elaborated sensory platform, the fluorescence quantification method was employed for the analysis of TNT in the mixed nitroaromatic explosive samples. A recovery study was conducted in the standard TNT solution (20 μM) mixed with various coexistent nitroaromatic explosives, including DNT, NB, DNBA, NBA, NT, and TNP.[62] The concentrations of all of the interfering explosives were set as 10 μM. As shown in Table 2, the mean detected concentration is 20.3 μM for the real concentration of 20 μM TNT in the presence of 10 μM NB. The measurements are repeated for 4 times, and the standard derivation is calculated to be as low as 0.2, indicating that these recovery experiments are reproducible.[63] Other coexistent explosives also have negligible influences on the mean detected concentration (see Table 2). Even in the TNT/DNT/NB/DNBA/NBA/NT/TNP mixture sample in which the total concentration of coexistent explosives reaches 4 times greater than TNT concentration, a good agreement is also observed with the real added and detected TNT concentrations. The resultant recoveries of samples vary from 102% to 107%, suggesting that the newly developed PCN-224 probe is applicable to the quantitative analysis of TNT even in the presence of a large amount interfering nitroaromatic explosives.[62]

4. CONCLUSIONS

In summary, porphyrin-based LMOFs have been successfully developed for the rapid and specific detection of TNT

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures showing SEM images, N$_2$ sorption isotherm, XRD patterns, PL spectra of PCN-224, digital pictures of PCN-224 suspension illuminated with UV lamp in the absence or presence of TNT, PL evolvement of PCN-224 with time, PL evolvement of free TCPP with TNT, fluorescence response curves of PCN-224 to different nitroaromatic compounds, and UV−vis absorption change of PCN-224 with the addition of TNT, text describing the limit of detection for the PCN-224 sensor, and a table comparing sensing features between the current PCN-224 sensor and other reported probes. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01946.

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Notes

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Table 2. Detection of TNT in the Mixed Nitroaromatic Explosive Samples (n = 4^a)

samples	added values (μM)	detected values (μM) $\pm \sigma^b$	recovery (%)^c
TNT/NB	20/10	20.3 ± 0.2	102 ± 1
TNT/DNBA	20/10	21.0 ± 0.4	105 ± 2
TNT/TNP	20/10	20.7 ± 0.6	104 ± 3
TNT/DNT/NB	20/10/10	20.7 ± 0.3	104 ± 2
TNT/NBA/NT	20/10/10	20.5 ± 0.3	103 ± 2
TNT/DNT/NB/DNBA/NBA/NT/TNP	20/10/10/10/10/10/10	21.4 ± 0.7	107 ± 3

^{a}n is the repetitive measurement number. ^{b}Standard derivations are calculated based on 4 times repeated measurements. ^{c}Recovery (%) = 100($C_{mean\ detected}/C_{added\ TNT}$)

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