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Title: Ionic liquids directed syntheses of water-stable Eu- and Tb-organic-frameworks for aqueous-phase detection of nitroaromatic explosives

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Dear Prof. Jin,

Thank you very much for your decision letter on our above-mentioned manuscript. We have carefully revised our manuscript by addressing the concerns expressed the three Reviewers. All changes made in the revised manuscript in response to specific comments of the Reviewers are given in the appended page and are marked in yellow background for your convenience.

Thank you for your courtesy.

Yours Sincerely,

Dr. Shuang-Quan Zang

Responses to Reviewer 1

Comments (1): My comments concern mainly in the aqueous-phase detection of nitroaromatic explosives. Authors presented that the luminescence of MOFs is quenchable by nitroaromatic explosives in aqueous-phase, I saw the intensities of several emitting peaks become weak as the amount of nitroaromatic explosive increases, I want to know how did authors calculate the luminescence intensity, to calculate the peak maximum of one emitting peak or the area of all emitting peak ?

Responses to (1): Thanks for your kind comments. The luminescence intensity refers to the peak maximum of one emitting peak. For **1**, the $^5D_0 \rightarrow ^7F_2$ transition of Eu(III) centered at 610 nm dominates the whole emission spectrum (Fig. 3a), therefore the luminescence intensity was monitored at 610 nm. While for **2**, the dominant band (541 nm) is attributed to the hypersensitive transition $^5D_4 \rightarrow ^7F_5$ of Tb(III) ions (Fig. 3b), therefore the luminescence intensity was monitored at 541 nm.

Comments (2): I also saw that all Stern-Volmer plots in ESI are not linear, however, authors fitted them using linear-fit. Actually, Stern-Volmer luminescence quench mechanism represents the process that the quench rate is proportional to the concentration of quencher. Obviously, the luminescence quench does not obey the Stern-Volmer quench mechanism. Authors should give a reasonable explanation for this situation in the revised version.

Responses to (2): Thanks for your kind comments. The SV plots for NB, TNP, and 2-NT were nearly linear at low concentrations, and subsequently deviated from linearity, bending upwards at higher concentrations (Fig. S9-S11 and S16-S18 in the ESI[†]). The curvature of SV plot may be ascribed to mixed static and dynamics photoinduced electron transfer.

Responses to Reviewer 2

Comments (1): The author might need to give some explanation about stability of the crystal after “fine grinding MOF powder (2 mg)”, e.g., the after sample were evidenced by PXRD and TGA analysis.

Responses to (1): Thanks for your kind comments. First, when the crystals of **1** and **2** were soaked in water for several weeks, retention of crystallinity were observed, as were evidenced by PXRD analysis (Fig. 2), affirming the hydrolytic stabilities. Second, as shown in Fig. S8 and S15 in the ESI†, both of fine grinding powder show the strongest emissions in H₂O and the emission spectra is close to those of solid state sample. Thus the strong emissions and stabilities of fine grinding powder of **1** and **2** in H₂O suspension indicate potentials to be utilized as nitroaromatic explosives sensors in the aqueous phase. Therefore, the fine grinding MOF powder were not further evidenced by PXRD and TGA analysis.

Comments (2): Some missing recent references about detection of nitroaromatic explosives : Inorg. Chem. Front. 2014, 1, 389–392.; Chem. Commun. 2013, 49, 5660–5662.

Responses to (2): Thanks for your kind comments. The two papers are a great helps to us and thus we have cited them.

Comments (3): Another pioneering ionic liquids paper by X. H. Bu (Angew. Chem. Int. Ed.2008, 47, 5434) is highly relevant to this synthesis method.

Responses to (3): Thanks for your kind comments. This paper is a great help to us and thus we have cited it.

Responses to Reviewer 3

Comments (1): I recommend that you use the latest version of ShelXL (currently ShelXL-2014/7) and deposit the resulting full CIF file with the CCDC. This will give us much more information about your structures and enable us to provide more positive feedback than we can do in the absence of the diffraction data.

Responses to (1): Thanks for your kind comments. We have used the latest version of ShelXL (ShelXL-2014/7) and deposited the resulting full CIF file with the CCDC.

Comments (2): Please also make sure that no CheckCif A and B alerts will remain -- and if they do, provide a `_vrf_` entry for each remaining alert.

Responses to (2): Thanks for your kind comments. We have provided a `_vrf_` entry for the one remaining B alert in the cif file.

Comments (3): For future reference: your cif file contains the cif item `'_diffn_reflns_av_sigmaI/netI'`. This item has been superseded and should no longer be used. Please use `'_diffn_reflns_av_unetI/netI'` instead.

Responses to (3): Thanks for your kind comments. We have used `'_diffn_reflns_av_unetI/netI'` instead.

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ARTICLE TYPE

Ionic liquids directed syntheses of water-stable Eu- and Tb-organic-frameworks for aqueous-phase detection of nitroaromatic explosives

Jian-Hua Qin,^{a,b} Bing Ma,^a Xiao-Fei Liu,^a Hong-Lin Lu,^a Xi-Yan Dong,^a Shuang-Quan Zang^{*a} and Hongwei Hou^{*a}⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

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Reactions of lanthanide nitrate, 1,3,5-Benzenetrisbenzoic acid (H₃BTB) and [RMI]Br ionic liquids (RMI = 1-alkyl-3-methylimidazolium; R = ethyl, propyl, butyl, amyl, or hexyl), gave rise to two novel lanthanide metal-organic frameworks (Ln-MOFs) [Ln(BTB)H₂O], where Ln = Eu **1**, Tb **2**. In addition to helping solubilise the starting materials under the reaction conditions there is evidence that [RMI]Br itself can play a structure directing role and is intimately involved in template ordering in [Ln(BTB)H₂O], even though neither [RMI]⁺ cation nor Br[−] anion is occluded into the ultimate structure. **1** and **2** are isostructural and consist of infinite rod-shaped lanthanide-carboxylate building units which are further bridged by trigonal-planar BTB ligands to give a noninterpenetrated open 3D frameworks featuring a (6,6)-connected topology with the point symbol (4⁴·6⁷·8⁴)(4⁸·6⁷). Importantly, the strong emission of **1** and **2** dispersed in water prompted us to explore their application for detection of different nitroaromatics in an aquatic system. **1** and **2** show similar selectivity and sensitivity towards the presence of trace amount of nitroaromatic analytes in aqueous phase, which shows potentials as explosive sensors.

Introduction

Selective and sensitive detection of highly explosive and explosivelike substances has become a serious issue.^{1,2} Nitroaromatic explosives such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrophenol (TNP), and nitrobenzene (NB) are common ingredients of industrial explosives and found in many unexploded land mines worldwide.^{1f} Current high-explosive detection methods rely on the use of canines or sophisticated instruments,^{3-5,1c} which are not very efficient for detection in the field because of limited portability, high cost and great complexity.^{2d,2f} Fluorescence-based detection methods based on the electron transfer and/or energy transfer mechanisms, have attracted increasing attention by virtue of their high sensitivities, portability, short response times, and applicability in both the solid and solution phase.^{1,2} Electron donor conjugated polymers^{1,6} and nanoparticles^{1b-1f,7,8} have been proven to be very effective. As fluorescent sensors metal-organic frameworks (MOFs)^{2,9-11} provide several advantages over conventional fluorophores, owing to their high surface areas, designable architectures and host-guest interactions. The high surface area, which may allow more analyte molecules to come into contact with the MOF surface, imparts them with the capability of transducing the interactions to detectable changes in fluorescence and makes them a potential material for sensing applications. Moreover, for in-field selective detection of nitroaromatic explosives present in soil and ground water, probe working in aqueous media is highly desirable. Up to now, several MOFs have been developed for explosives detection

in liquid phase,^{9,11} however, the precedent of MOFs as explosive sensors in the desired aqueous medium is indeed rare.¹²

Ionic liquids (ILs), a class of salts which are liquid at low temperature and consist of ions only, have received increasing attention as the solvent of choice for the syntheses of crystalline materials such as zeolites and (MOFs).¹³⁻¹⁶ The strong polar of ILs give them a good dissolving capacity to most of inorganic and organic materials, which offers outstanding opportunities for helping solubilise the starting materials and improving the reaction conditions of crystalline materials. Recently, Su group and our group demonstrated the combination of hydro/solvothermal and ionothermal methods.¹⁷ 1,3,5-Benzenetrisbenzoic acid (H₃BTB), as a rigid nonplanar C₃ symmetric organic ligand, has been extensively employed for the constructions of MOFs mainly aimed at gaining porous materials, such as MOF-14, MOF-177, DUT-9, etc.¹⁸⁻²⁰ In fact, the tritopic H₃BTB linker has the potential to provide significantly more topologically different frameworks by changing the reaction condition. Herein we report the fluorescent property and sensing behavior of [Ln(BTB)H₂O] (Ln = Eu **1**, Tb **2**) directed by [RMI]Br ILs (RMI = 1-alkyl-3-methylimidazolium; R = ethyl, propyl, butyl, amyl, or hexyl). In addition to helping solubilise the starting materials under the reaction conditions there is evidence that [RMI]Br itself can play a structure directing role and is intimately involved in template ordering in [Ln(BTB)H₂O], even though neither [RMI]⁺ cation nor Br[−] anion is occluded into the ultimate structure. The excellent hydrolytic stabilities of **1** and **2** allow them to be used in an aquatic system, which is highly desirable for practical applications. As expected,

the two complexes both show high selectivity and sensitivity towards the presence of trace amount of nitroaromatic analytes in aqueous phase, which shows potentials as explosive sensors. It is confirmed that the low porosity and small pore sizes of **1** and **2** exclude the encapsulation of the analytes, which suggests that the fluorescence response mechanism might be attributed to the photoinduced electron transfer from the excited MOF to the electron deficient analytes adsorbed on the particles surface of **1** and **2**.

Experimental section

Materials and physical measurements

All reagents were of analytical grade and obtained from commercial sources without further purification. Elemental analysis for C and H were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range from 4000 to 400 cm^{-1} on a Bruker VECTOR 22 spectrometer. Thermal analyses were performed on a SDT 2960 thermal analyzer from room temperature to 800 $^{\circ}\text{C}$ at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ under nitrogen flow. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/Max-2500PC diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over the 2θ range of 5–50 $^{\circ}$ with a scan speed of 5 $^{\circ}/\text{min}$ at room temperature. Fluorescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer.

Synthesis of [Ln(BTB)H₂O] (Ln = Eu **1**, Tb **2**).

First step: Ln(NO₃)₃·6H₂O (0.20 mmol) and H₃BTB (0.10 mmol) were soaked in 1 mL [RMI]Br solutions in a glass vial (10 mL), which was heated in an isotherm oven more than 100 $^{\circ}\text{C}$ until starting materials dissolved.

Second step: 4 mL mixed solvent of N, N-dimethylformamide (DMF) and H₂O (V/V = 1:1) was added, and then the homogeneous phase was transferred to a 25 mL Teflon-lined stainless steel vessel. The vessel was sealed and heated to 160 $^{\circ}\text{C}$ for 72 h and then cooled to room temperature at a rate of 5 $^{\circ}\text{C}\cdot\text{h}^{-1}$. Yellow prismatic crystals of **1** and **2** were obtained in high yields (85%–94%) especially with [BMI]Br by using the corresponding Ln(NO₃)₃·6H₂O. Elemental analysis calcd (%) for **1** C₂₇H₁₇EuO₇ (605.37): C 53.57, H 2.83, found: C 53.45, H 2.77. IR for **1**: 3393 cm^{-1} (broad), 1583 s, 1407 s, 1246 m, 1012 m, 853 m, 779 s, 659 w, 553 w, 485 m. Elemental analysis calcd (%) for **2** C₂₇H₁₇TbO₇ (612.33): C 52.96, H 2.80, found: C 52.85, H 2.77. IR for **2**: 3426 cm^{-1} (broad), 1608 s, 1535 s, 1403 s, 1187 m, 1013 m, 853 m, 780 s, 553 w, 485 m.

Note that when the cation of the IL altering from [EMI]⁺ to [PMI]⁺, [BMI]⁺, [AMI]⁺ or [HMI]⁺, **1** and **2** could also be successfully obtained, which may attribute to the very similar structure of the ILs' cations. However, when the Br[−] anion of [RMI]Br replaced by Cl[−] or I[−] to study the effects of other halogen anions, only much unspecified impurities rather than any crystals could be found, probably due to the different nucleophilicity and/or the basicity of Cl[−], I[−] and Br[−] anion during the complicated crystallization process. Besides, when the Br[−] anion of [RMI]Br replaced by other anions, such as BF₄[−], ClO₄[−], CF₃SO₃[−], [EMI]PF₆[−], or N(CF₃SO₂)₂[−], the results are the same as Cl[−] or I[−]. Clearly, this change in IL chemistry on alteration of the IL anion has a significant effect on the products of any reaction

carried out in such solvents, due to the fact that the nature of the anion plays an extremely important part in controlling the nature of the IL.

X-ray crystallography

Single crystal X-ray diffraction analyses of **1** and **2** were carried out on a Rigaku Saturn 724 CCD diffractometer (Mo-K α , $\lambda = 0.71073 \text{ \AA}$) at room temperature. The structures were solved by direct methods with SHELXS-97²¹ and refined by the full-matrix least-squares method on F² with anisotropic thermal parameters for all non-H atoms (SHELXL-97)²². The empirical absorption corrections were applied by the SADABS program.²³ The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. The crystallographic data and selected bond lengths and angles for **1** and **2** are listed in Tables S1 and S2 in ESI†. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center. CCDC numbers for **1** and **2** are 1063412 and 1063413, respectively.

Experiments of detecting of nitroaromatic explosives in the aqueous phase

The fluorescence properties of **1** and **2** were investigated in water emulsions at 293 K. The fine grinding MOF powder (2 mg) was dispersed in 1 mM or saturated aqueous solutions (2 mL) of a series of nitroaromatics, treated by ultrasonication for 30 min and then aged for 3 days to form a stable emulsion before the fluorescence studies. The nitroaromatics used in this study were nitrobenzene (NB), 2-nitrotoluene (2-NT), 1,3-dinitrobenzene (1,3-DNB), 1,4-dinitrobenzene (1,4-DNB), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TNP). As a comparison, the emission spectra and fluorescent intensity for **1** (or **2**) dispersed in methyl cyanide (MeCN), and N,N-dimethylformamide (DMF), and even other aromatic compounds, such as benzene (BZ), toluene (TO), bromobenzene (BrBZ), *p*-xylene (PX), were also recorded. In fluorescence titration setup, 2 mg of **1** (or **2**) was dispersed in 2 mL aqueous solution, treated by ultrasonication for 30 min and then aged for 3 days for the next experiment. The fluorescence was measured in-situ after incremental addition of freshly prepared 1 mM or saturated aqueous solutions of each analyte. All the experiments were performed in triplicate and consistent results are reported. The quenching efficiency (%) was estimated using the formula $(F_0 - F)/F_0 \times 100\%$, where F_0 and F are the maximum fluorescent intensity of **1** (or **2**) before and after the addition of analyte, respectively.

Results and discussion

Syntheses and crystal structures

Through two steps reaction involving lanthanide nitrate and the tritopic linker H₃BTB with the help of [RMI]Br, we produced two isostructural complexes, Ln-MOFs [Ln(BTB)H₂O] (Ln = Eu **1**, Tb **2**). To gain some insight into the reaction mechanism and the effect of [RMI]Br, preparations were conducted under varying experiment conditions. Through the investigation of appropriate synthesis conditions, we summarized the following

experiences in this system. (1) For “*First step*”, it is vital to make sure the starting materials dissolve in [RMI]Br thoroughly, in

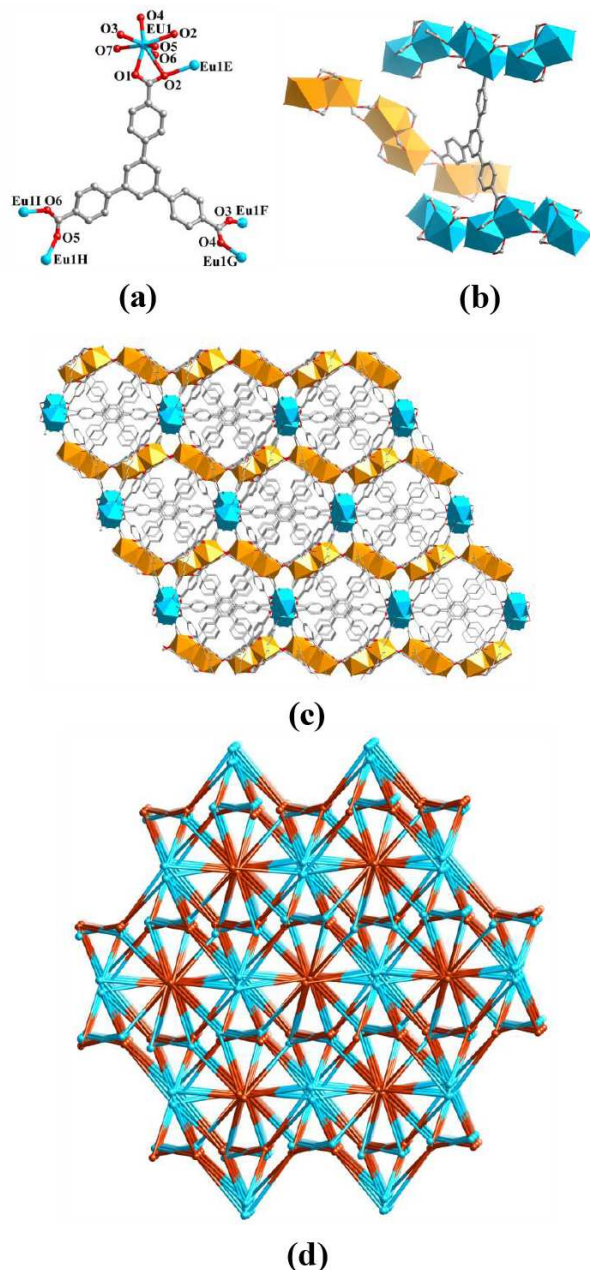


Fig. 1 (a) Representation of the Eu(III) coordination environments and ligands' coordination modes in **1**. Symmetry codes (A) $-x+7/4, y+1/2, -z+5/4$; (B) $-x+9/4, -y+7/4, z-1/2$; (C) $x-1/4, y+1/4, -z+3/2$; (D) $x+1/2, -y+7/4, -z+5/4$; (E) $-x+2, -y+2, -z+1$; (F) $x-1/2, -y+7/4, -z+5/4$; (G) $-x+7/4, y-1/2, -z+5/4$; (H) $-x+9/4, -y+7/4, z+1/2$; (I) $x+1/4, y-1/4, -z+3/2$. (b) View of the rod-shaped Eu(III)-carboxylate SBUs in two separate directions. (c) View of the 3D framework of **1** along [110] direction. (d) Schematic representation of the 6-connected $(4^4.6^7.8^4)(4^8.6^7)$ topology.

order to obtain bulky crystals. When [RMI]Br were directly added into reaction system, only tiny crystals could be obtained in one-pot synthesis process. (2) For “*Second step*”, the reaction solvent only needs DMF-H₂O mixed solvent. Several other

solvents, such as DMF or H₂O or CH₃CN, or CH₃CN-H₂O mixed solvent were attempted, but only fine powder products were obtained. (3) When using LnCl₃·6H₂O instead of Ln(NO₃)₃·6H₂O, small single crystals of [Ln(BTB)H₂O] will be produced in CH₃CN-H₂O mixed solvent, but together with much unspecified impurities. As summarized above, we optimized the reaction conditions after numerous experiments. In a typical synthesis procedure, we firstly dissolve Ln(NO₃)₃·6H₂O and H₃BTB in [RMI]Br, follow with adding DMF-H₂O into reaction system, and perform the reaction at 160 °C for 3 days. This facile procedure can produce [Ln(BTB)H₂O] on a large scale.

Single crystal X-ray analyses and powder X-ray diffraction analyses indicate that the two MOFs are isostructural with orthorhombic crystal system *Fddd* space group, and have noninterpenetrated open 3D frameworks constructed by infinite rod-shaped lanthanide-carboxylate secondary building units (SBUs) and trigonal-planar BTB ligands. Therefore, only the crystal structure details of [Eu(BTB)H₂O] (**1**) will be described herein. The asymmetry unit of complex **1** is composed of one crystallographically unique Eu(III) ion, one BTB ligand and one coordinated water molecule. Each central Eu(III) ion coordinates to eight oxygen atoms from six carboxylate groups of BTB ligands and one terminal water, resulting in a distorted bicaapped triprismatic coordination geometry (Fig. 1a). The Eu–O_{carboxyl} bond lengths fall into the range of 2.299(7)–2.808(8) Å and the Eu–O_{water} bond distance is 2.511(11) Å. The three carboxylate groups in a separate BTB ligand are deprotonated and adopt two types of bridging modes ($(\kappa^1-\kappa^1)-\mu_2$ and $(\kappa^2-\kappa^1)-\mu_2$) with the Eu(III) ions, resulting in the formation of rod-shaped Eu(III)-carboxylate chains passing through the framework in two directions that are almost mutually perpendicular (Fig. 1b). Each infinite Eu(III)-carboxylate chain can be regarded as a SBU, in which the neighboring Eu(III) ions are alternately separated by 4.082 Å and 5.456 Å. These SBUs are sustained by rigid phenyl rings of BTB ligands to construct a 3D coordination framework (Fig. 1c). The effective free volume of **1** was calculated by PLATON analysis as 8.4% of the crystal volume (1611.3 out of the 19157.0 Å³ unit cell volume). Furthermore, topological analysis is carried out to get insight of the structure of complex **1**. As shown in Fig. 1d and S1 in the ESI†, each Eu(III) ion links six BTB ligands, which leads to the presence of a beautiful “butterfly” pattern, thereby the Eu(III) ion can be regarded as a six-connected node. Meanwhile the BTB ligand also can be viewed as a six-connected node. This net can be specified by the Schläfli symbol of $(4^4.6^7.8^4)(4^8.6^7)$ and the vertex symbols for the two nodes (Eu, BTB) being $[4.4.4.3.4.3.6.6.6.4.6.5.6.5.6.6.8.22.8.26.8.28.8.30]$ and $[4.4.4.4.4.4.4.4.6.2.6.2.6.3.6.3.6.3.6.4]$, respectively.

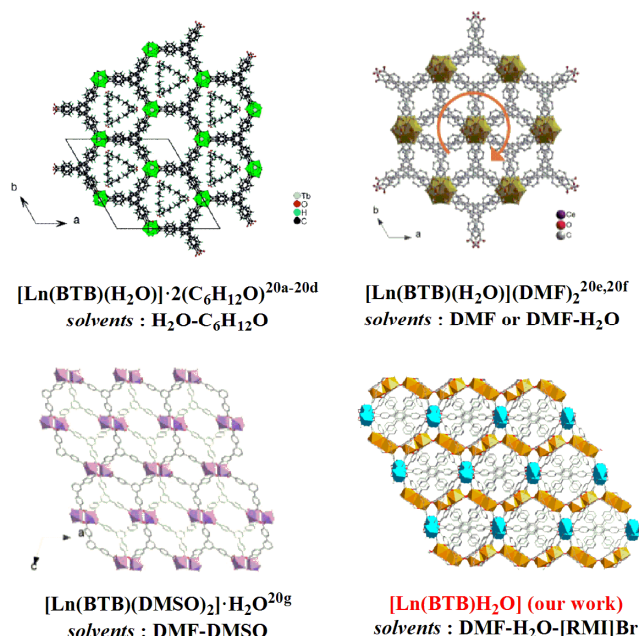
This framework is isostructural with [Ln(TATB)H₂O] (Ln = Y, Eu, Gd, Tb, Dy, Ho, Er) reported by Du,²⁴ where BTB substitutes TATB. The BTB ligand is seriously distorted in order to avoid repulsions between the C–H bonds on the central ring and those on the peripheral rings in **1**,²⁵ while such repulsions are effectively released in [Ln(TATB)H₂O], by introducing a triazine ring into a TATB ligand. The average dihedral angle between the central and peripheral rings of BTB ligand is 14.21° in **1**. However, the TATB ligand is almost planar in [Ln(TATB)H₂O], and the average dihedral angles between the central and

peripheral rings is 9° . The BTB ligands appear in pairs by forming π - π stacking in a staggered arrangement, and the centroid-to-centroid separation of the two central rings in **1** is 3.689 Å, similar to a separation of 3.677 Å in the free H_3BTB complex, but slightly greater than a separation of 3.627 Å in the TATB in $[\text{Ln}(\text{TATB})\text{H}_2\text{O}]$. Additionally, π - π interaction of two equivalent benzene rings of BTB ligands is less favorable than for staggered TATB ligands due to the decreased quadrupole moment.²⁵ Thus, the two central triazine rings of TATB ligands are stacked in such a way that the negatively charged nitrogen atoms are aligned with the positively charged carbon atoms from the other ring to maximize π - π stacking in $[\text{Ln}(\text{TATB})\text{H}_2\text{O}]$, as also observed in MOFs based on TATB ligands.²⁵ In fact, the strongest π - π stacking has been found in $\text{Zn}_6\text{O}(\text{TATB})_4 \cdot (\text{H}^+)_2 \cdot (\text{H}_2\text{O})_5 \cdot (\text{DMSO})_4$ (DMSO = dimethylsulfoxide) reported by Zhou, the distance between the centres of the two triazine rings being only 3.14 Å.²⁵

The Role of ILs

ILs can serve as the solvent, structure-directing agent, charge compensating agent, and can not only influence the crystal structure but also enter the material as a component. Indeed, pioneering studies in this field have proven this by demonstrating that the cation and the anion species can, individually or cooperatively, influence the resulting structures. To date, much of the work on ionothermal synthesis has concentrated on the use of $[\text{RMI}]\text{Br}$ as the solvent. Our group and other group have shown that the addition of small amounts of ILs can change the chemistry of the solvent, which can lead to great differences in the final structure compared to pure hydro/solvothermal condition.¹⁷ The H_3BTB ligand, has already been used by Yaghi and other group with transition-metal and lanthanide cations to produce highly porous MOFs under hydro/solvothermal condition.¹⁸⁻²⁰ As shown in Scheme 1, there have been three types of Ln-MOFs based on H_3BTB ligand: $[\text{Ln}(\text{BTB})(\text{H}_2\text{O})] \cdot 2(\text{C}_6\text{H}_{12}\text{O})$ (denoted MIL-103, $\text{C}_6\text{H}_{12}\text{O}$ = cyclohexanol)^{20a-20d}, $[\text{Ln}(\text{BTB})(\text{H}_2\text{O})](\text{DMF})_2$ ^{20e,20f}, and $[\text{Ln}(\text{BTB})(\text{DMSO})_2] \cdot \text{H}_2\text{O}$ ^{20g}, synthesized in H_2O - $\text{C}_6\text{H}_{12}\text{O}$, DMF, and DMF-DMSO solvent system, respectively. All of the three types of Ln-MOFs present a permanent porosity, with considerable potential void volume (about 50% of the total crystal volume) calculated by PLATON.²⁰ Note that $[\text{Ln}(\text{BTB})(\text{H}_2\text{O})](\text{DMF})_2$ ^{20e,20f} could also be obtained in DMF- H_2O mixed solvent, but only small single crystals would be produced, together with cotton-like impurities. However, when introducing small amount of $[\text{RMI}]\text{Br}$ into DMF- H_2O in our experiments, the crystalline products turned out to be a novel condensed structure $[\text{Ln}(\text{BTB})\text{H}_2\text{O}]$ (**1** and **2**, only 8.4% of potential void volume), with good qualities and high yields especially in $[\text{BMI}]\text{Br}$. Although neither $[\text{RMI}]^+$ cation nor Br^- anion is occluded into the ultimate structure, many tries to synthesize the two complexes (**1** and **2**) under traditional hydro/solvothermal conditions were failure. The $[\text{RMI}]\text{Br}$ may play a important role to direct the formation of non-interpenetrated 3D microporous framework (**1** and **2**). Additionally, there is other evidence for the importance of $[\text{RMI}]\text{Br}$ in complicated crystallization process by comparing the synthesis of the two isostructural framework, $[\text{Ln}(\text{BTB})\text{H}_2\text{O}]$ and $[\text{Ln}(\text{TATB})\text{H}_2\text{O}]$ ²⁴. Repulsions between the C-H bonds on the

central ring and those on the peripheral rings play a key role in controlling the conformation of BTB; the TATB ligand with no C-H bonds on the central ring is not subject to such repulsions. Therefore, TATB is expected to be flatter than BTB in constructing the condensed framework.²⁵ $[\text{Ln}(\text{TATB})\text{H}_2\text{O}]$ ²⁴ can be easily obtained in molecular solvent (DMSO- H_2O), however $[\text{Ln}(\text{BTB})\text{H}_2\text{O}]$ seems not. As mentioned above, H_3BTB ligands react with lanthanide cations probably to give porous Ln-MOFs without the help of $[\text{RMI}]\text{Br}$. The major advantage of ILs in our experiment is the possibility of tuning the solvent properties to match those required by the system under study, making it particularly promising for the synthesis of condensed structure that are inaccessible using traditional synthetic routes.



Scheme 1. The synthetic routes for Ln-MOFs based on H_3BTB .

Thermal and water stability

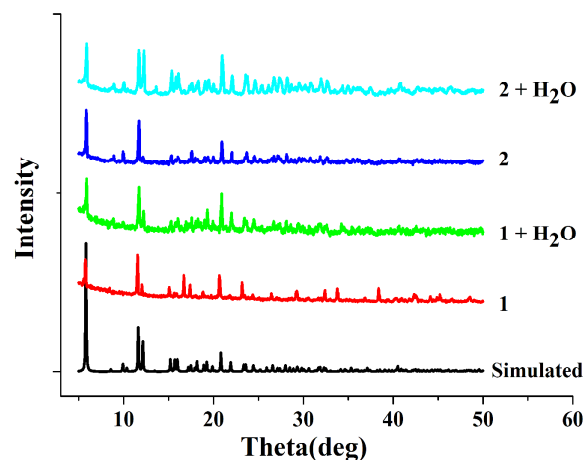


Fig. 2 PXRD patterns of **1** and **2**; the simulated, as-synthesized, and immersed in water for 4 weeks.

Considering practical applications, the robustness and water stabilities of **1** and **2** were firstly investigated. Thermogravimetric analyses (TGA) indicate that **1** and **2** have very high thermal stability and exhibit similar thermal behavior (Fig. S2 in the ESI†). Therefore, only the thermal stability of **1** is discussed in detail. A first weight loss of 3.30 % occurs from 200 to 300 °C, which corresponds to the loss of coordinated water molecule (calcd: 2.97 %). The framework starts to collapse with the loss of BTB ligands from 450 °C. **1** and **2** showed well thermal stability below 500 °C, which attribute to the arrangement of rod-shaped SBUs in two directions tightening the backbone of the ligands and enhancing their resistance to pyrolysis. Besides, when **1** and **2** were soaked in water for several weeks, retention of crystallinity were observed, as were evidenced by PXRD analysis (Fig. 2), affirming the hydrolytic stabilities.

Fluorescent properties

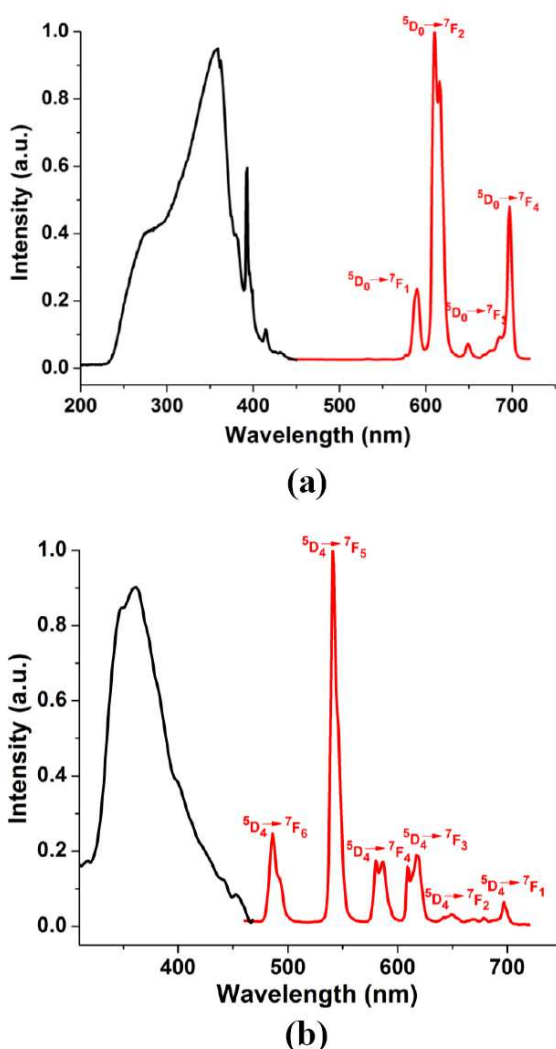


Fig. 3 Solid-state excitation and emission spectra for **1** (a) and **2** (b) at room temperature.

The solid state fluorescence behaviors of **1** and **2** were recorded at room temperature. On the basis of the time-dependent DFT calculation, the H₃BTB has the triplet excited state energy of 23426 cm⁻¹ which is much higher than the ⁵D₀ level of Eu³⁺ (17300 cm⁻¹) and the ⁵D₄ level of Tb³⁺ (20500 cm⁻¹) in order to ensures the occurrence of efficient energy transfer from ligand to metal (Fig. S3-S4 in the ESI†). As shown in Fig. 3, upon excitation at 350 nm, characteristic emissions associated with the 4f–4f transitions of the ⁵D₀ excited state to the low-lying ⁷F_J (*J* = 0, 1, 2, 3, and 4) levels of the Eu(III) ion are observed in the range of 570–720 nm, while those attributed to the ⁵D₄ → ⁷F_J (*J* = 1–6) transitions of the Tb(III) ions appear at 486, 541, 580, 617, 649 and 697 nm, respectively. Note that the ⁵D₀ → ⁷F₂ transition of Eu(III) centered at 610 nm for **1** dominates the whole emission spectrum (Fig. 3a). For **2**, the dominant band of these emissions is attributed to the hypersensitive transition ⁵D₄ → ⁷F₅ of Tb(III) ions (Fig. 3b). We also examined the fluorescent properties of **1** and **2** dispersed in water and common organic solvent. As shown in Fig. S8 and S15 in the ESI†, both of **1** and **2** show the strongest emissions in H₂O, MeCN, and DMF, respectively, and the emission spectra are close to those of solid state sample. The strong emissions and stabilities of **1** and **2** in H₂O suspension indicate potentials to be utilized as nitroaromatic explosives sensors in the aqueous phase.

Detection of nitroaromatic explosives in the aqueous phase

In actuality, the detection of nitroaromatics in an aquatic system is highly desirable for practical applications.¹² The strong emission of **1** and **2** dispersed in water prompted us to explore their application for detection of different nitroaromatics. Benefiting from the stabilities issue in water, the abilities of **1** and **2** to sense trace amounts of nitroaromatics in aqueous medium were investigated. The fine grinding sample **1** (or **2**) was dispersed in 1 mM or saturated aqueous solutions of a series of nitroaromatics. As depicted in Fig. 4, 5, S8 and S13-S15 in the ESI†, the significant quenching of fluorescent intensity of **1** and **2** were observed upon addition of all the selected analytes. Among them, NB, TNP, and 2-NT could thoroughly quench the emission (quenching efficiency > 99%). The two complexes show similar sensitivity orders for different nitroaromatics, that is, for both **1** and **2**, the fluorescence quenching efficiencies of NB, TNP, and 2-NT are significantly higher than those of other nitroaromatics. The order of quenching efficiency for the selected analytes are NB ≈ TNP ≈ 2-NT > 2,4-DNT > 2,6-DNT > TNT > 1,3-DNB ≈ 1,4-DNB for **1**, NB ≈ TNP ≈ 2-NT > 2,4-DNT > TNT > 2,6-DNT > 1,3-DNB ≈ 1,4-DNB for **2**, respectively. This order is nearly in accordance with the trend of electron-withdrawing groups. The fact that NB and 2-NT exhibit the strongest quenching effect can be attributed to their high electron-withdrawing ability. While, the lower reduction potentials of 2,4-DNT, 2,6-DNT, TNT, 1,3-DNB, 1,4-DNB are responsible for their weaker quenching effect. Exceptionally, TNP has the most poor electron-withdrawing ability, but show a high quenching efficiency similar to that of NB and 2-NT (discussed below). In contrast, the emission spectra and fluorescent intensity for **1** (or **2**) dispersed in MeCN, DMF, and even other aromatic compounds, such as BZ, TO, BrBZ, PX, were recorded and compared. As shown in Fig. S8 and S15 in the ESI†, all of these organic solvents display a negligible effect on the emission of **1**

and **2**. Such observations demonstrate that **1** and **2** have selective fluorescence responses to nitroaromatics compared to other non-nitroaromatics.

To examine sensing sensitivity towards nitroaromatics in more detail, a batch of suspensions of **1** (or **2**) with gradually increasing the analytes contents in aquatic system was prepared to monitor the emissive response (Fig. 6, S9-S12 and S16-S19 in the ESI†). The emission response was monitored by fluorescence titration with NB, TNP, and 2-NT. The fluorescence quenching efficiency of **1** and **2** increased drastically with the analytes (NB, TNP, and 2-NT) amount even in the low concentration range and leveled off at high concentration to reach nearly complete quenching (Fig. 7 and S20 in the ESI†). The quenching efficiency can be quantitatively explained by the Stern–Volmer equation: $(F_0/F) = K_{sv}[Q] + 1$, where F_0 and F are the fluorescent intensities before and after addition of the analyte, respectively, K_{sv} is the quenching constant (ppm^{-1}), $[Q]$ is the concentration of the analyte. The SV plots for NB, TNP, and 2-NT were nearly linear at low concentrations, and subsequently deviated from linearity, bending upwards at higher concentrations (Fig. S9-S11 and S16-S18 in the ESI†). The curvature of SV plot may be ascribed to mixed static and dynamics photoinduced electron transfer.²⁶ The calculated K_{sv} values for NB, 2-NT, and TNP were 6.17×10^{-2} , 2.87×10^{-2} , and $6.76 \times 10^{-2} \text{ ppm}^{-1}$ for **1**, and 7.54×10^{-2} , 7.46×10^{-2} , and $3.25 \times 10^{-2} \text{ ppm}^{-1}$ for **2**, respectively, which lie in the normal range for the known MOFs.¹¹ To the best of our knowledge, such highly selective detection of nitroaromatics in the aqueous phase based on a fluorescent MOF is rare.¹²

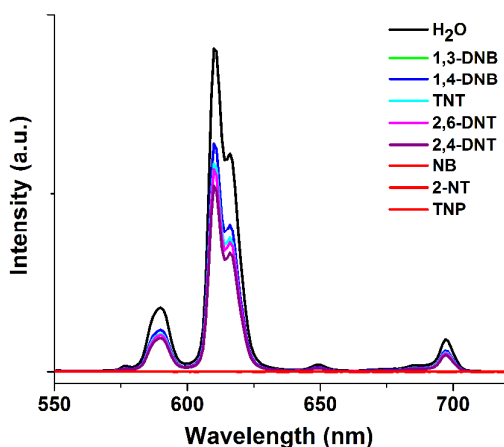


Fig. 4 The emission spectra for **1** dispersed in H_2O and 1 mM or saturated aqueous solutions of the selected analytes at room temperature.

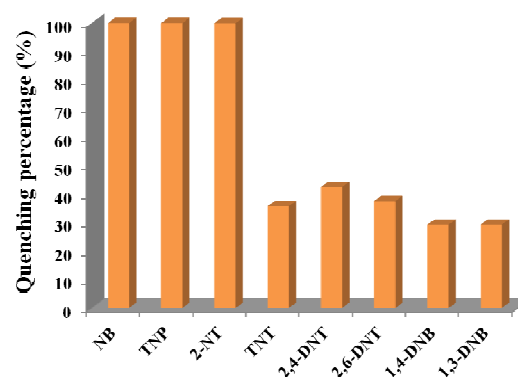


Fig. 5 Quenching efficiency of the fluorescent intensity for **1** dispersed in 1 mM or saturated aqueous solutions of the selected analytes at room temperature. (excited and monitored at 320 nm and 610 nm, respectively).

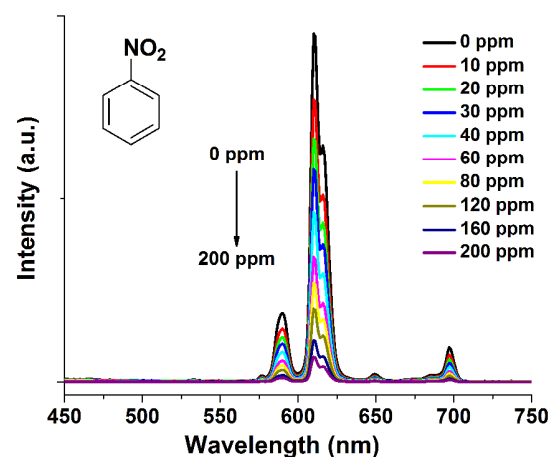


Fig. 6 Fluorescence titration of **1** dispersed in aqueous solution by gradual addition of NB.

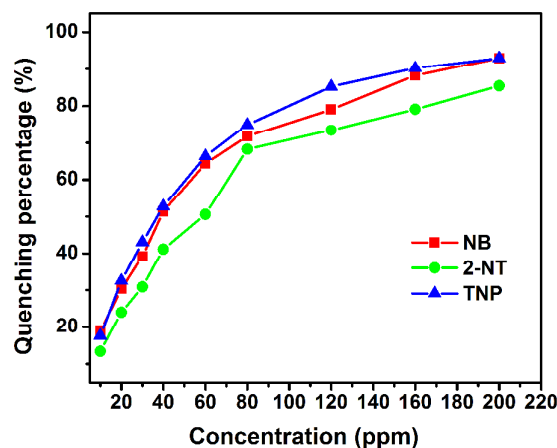


Fig. 7 Quenching efficiency of **1** dispersed in aqueous solutions at different concentrations of NB, 2-NT, and TNP.

50 Mechanism for the nitroaromatic explosives detecting

Encapsulation of nitroaromatics into the pores is ruled out due to the lack of porosity within **1** or **2**. However, the micrometre-sized fine particles of **1** or **2** could be dispersed well in water that enables the analyte molecule to be closely adsorbed on the surface of MOF particles and facilitates possible host–guest interactions.¹¹ Thus, the fluorescence response mechanism in our experiments might be attributed to the photoinduced electron transfer from the excited MOF to the electron deficient analytes adsorbed on the particles surface of **1** and **2**. This mechanism differs from guest-induced fluorescence quenching mechanisms, in which the analytes act as guest molecules that occupy the channels or cages of MOFs.^{9,10,17c} Although all MOFs have extended network structures, they are often characterized by narrow energy bands because of highly localized electronic states. Therefore, they can be regarded as giant “molecules” and the valence-band (VB) and conduction-band (CB) energy levels can be described in a fashion similar to that used for molecular orbitals (MOs).^{10b} In general, the lowest unoccupied MOs (LUMOs) of nitroaromatics are low-lying π^* -type orbitals stabilized by the NO₂ group through conjugation,^{10b,11d} and their energy is below the CB of **1** or **2**. This can force electrons to transfer from the CB of **1** or **2** to the LUMO of nitroaromatics, thus leading to fluorescence quenching upon excitation. Fig. 8 shows the HOMO and LUMO orbital energies of H₃BTB and nitroaromatics, as calculated by density functional theory at the B3LYP/6-31G** level (Table S5 in ESI†). As discussed above, the photoluminescence of **1** or **2** is ligand-centered. The electron rich property of the H₃BTB ligand, which gives a high LUMO energy (-2.00385 eV, higher than the -2.32~ -3.90 eV LUMO energy for the tested nitroaromatics) and facilitates the excited state electron transfer from the framework of **1** or **2** to the analyte molecules, is expected to be responsible for the selective response to nitroaromatics. Additionally, the large optical band gap (ca. 2.7 eV for **1** and 3.2 eV for **2**) indicates that the framework in the excited state is highly reductive, providing an adequate driving force for the electron transfer to the electron deficient analytes^{10a} (Fig. S21–S22 in the ESI†).

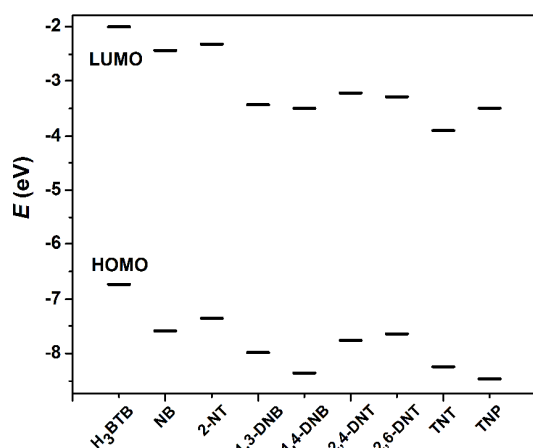


Fig. 8 HOMO and LUMO energies for the selected analytes and the H₃BTB ligand.

However, the correlation between the quenching efficiency and the most poor electron-withdrawing ability of TNP, suggests that the photoinduced electron transfer is not the only mechanism and the long-range energy transfer may also play a key role in such processes.^{12,27} The fluorescence of **1** or **2** results from the antenna effect in which the BTB moieties adsorb the energy and by vibronic coupling between BTB and Ln³⁺, transfer energy to Ln³⁺, leading to the fluorescence of Ln³⁺. The higher quenching efficiency of TNP is attributed to a competition of absorption of the light source energy between TNP and BTB moieties.^{8a} The TNP filter the light adsorbed by BTB moieties, thus decreasing the probability of energy transfer from BTB to Ln³⁺ and subsequently quenching the fluorescence of Ln³⁺. Related research has shown that the incorporation of different substituents on the aromatic moieties of the nitroaromatic explosives can cause a different degree of red shift of the π to π^* transitions of benzene (B band) in the UV-Vis absorption spectrum,^{8a} particularly for TNP, which extends the B band to the wavelength beyond 300 nm (Fig. S23 in the ESI†).¹² As excited, TNP with higher absorbance and thus higher ϵ (molar extinction coefficient) which suggest the absorption spectrum of TNP has a overlap with the emission spectrum of **1** or **2**, is expected to exhibit stronger quenching effect on the fluorescent intensity of **1** or **2** via energy transfer process.^{8a,12} Thus it is clear that TNP can efficiently quench the fluorescence of **1** or **2** via both electron and long-range energy transfer processes, which is in contrast to other nitroaromatics which quench fluorescence by an electron transfer process only.

Conclusion

In summary, two new highly fluorescent Ln-MOFs [Ln(BTB)H₂O] (Ln = Eu **1**, Tb **2**), directed by [RMI]Br ILs based on a rigid nonplanar C₃ symmetric organic ligand (H₃BTB) as an antenna to sensitize Ln³⁺ emission have been successfully synthesized. In addition to helping solubilise the starting materials under the reaction conditions there is evidence that [RMI]Br itself can play a structure directing role and is intimately involved in template ordering in [Ln(BTB)H₂O], even though neither [RMI]⁺ cation nor Br⁻ anion is occluded into the ultimate structure. The excellent hydrolytic stabilities allow the two complexes to be used in an aquatic system, which is highly desirable for practical applications. **1** and **2** both show high selectivity and sensitivity towards the presence of trace amount of nitroaromatic analytes in aqueous phase. It is confirmed that the low porosity and small pore sizes of **1** and **2** exclude the encapsulation of the analytes, which suggests that the fluorescence response mechanism might be attributed to the photoinduced electron transfer from the excited MOF to the electron deficient analytes adsorbed on the particles surface of **1** and **2**. Further analysis demonstrates that TNP can efficiently quench the fluorescences of **1** and **2** via both electron and long range energy transfer processes, while other nitroaromatics quench fluorescence by an electron transfer process only.

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Notes and references

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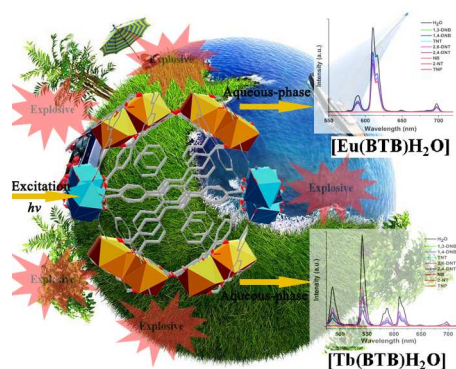
† Electronic Supplementary Information (ESI) available: [Structure figure, TG plot, excited state calculation, fluorescence spectra, details of detecting of the analytes, diffuse reflectance spectra, crystal data, selected bond lengths and angles, approximate sizes of the analytes, HOMO and LUMO energies calculated for H₃BTB and the analytes.]. See DOI: 10.1039/b000000x/

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Ionic liquids directed syntheses of water-stable Eu- and Tb-organic-frameworks for aqueous-phase detection of nitroaromatic explosives

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