High-efficient liquid exfoliation of 2D metal-organic framework using deep-eutectic solvents

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1. Introduction

Since the discovery of graphene, two-dimensional (2D) nanomaterials [1-6], such as boron nitride, metal hydroxides, transition metal chalcogenides, and black phosphorus, have attracted much attention due to their unique electronic structure and fascinating properties. However, 2D materials mentioned above are mostly inorganic compounds with simple composition and lack of structural diversity. Metal-organic frameworks (MOFs) nanosheet comprising organic linkers and metallic nodes, as a new kind of 2D nanomaterials, appeals increasing interest recently [7-13]. Due to the ultrathin thickness, numerous structural possibilities, easy access to active sites and large surface areas, 2D MOF nanosheets show promising applications in molecular sieving [14,15], energy storage and conversion [16,17], catalysis [9,18-21], and luminescent sensing [22,23]. Although there are multitudinous 2D MOF structures, only a few studies on ultrathin 2D MOF nanosheets have been reported owing to the poor stability and the limitations of production. It is more difficult for 2D MOF exfoliation than traditional 2D materials, because hydrogen bonds, \( \pi-\pi \) stacking, multiple interactions between the wrinkle surface all result in the interlayer interactions not always weaker than the intralayer coordination bonds of layered 2D MOFs. Therefore, developing new strategies for ultrathin MOF nanosheet construction is of great significance.

Similar to other 2D materials preparation, both top-down exfoliation and bottom-up assembly can be adopted to synthesis 2D MOF nanosheets [24]. Especially, “top-down” approaches, for example, liquid-phase sonication exfoliation [25,26], ball-milling [27,28] and chemical intercalation [29], are readily achieved and scalable production pathway. Solvent-mediated sonication exfoliation of bulk layered MOFs into 2D nanosheet is very attractive for its general applicability and accessibility. Solvents play important roles during exfoliation. The good wettability, suitable Hasen solubility parameter and surface tension, intercalation, strong interactions and stabilization effects of solvents all contribute significantly for bulk MOFs stripping ultrasonically. Unfortunately, solvents used for layered MOFs peeling off, for example N,N-Dimethylformamide, tetrahydrofuran, hexane and acetone, are generally volatile, toxic or not eco-friendly, and not efficient enough [30]. Therefore, approaches to exfoliate layered MOFs in a more efficient and
Ionic liquids with a melting point lower than 100 °C are highly demanded. Deep eutectic solvent (DES), constructed from H-bond donor and acceptor via hydrogen bonding, is a kind of green solvents similar to environment-friendly manner are highly demanded. Compared with ionic liquids which are efficient green solvents for 2D materials preparation, DES are considered as more easily available and cost-effectively green solvents. Considering the surface tensions of DES based on ethylene glycol or glycerol around 40–47 mJ m⁻², DES has already been used for 2D material construction under sonication, such as graphene [35-37] and metal hydroxides [59]. The adjustable composition, low vapor pressure, suitable surface tension and abundant hydrogen interactions endow DES great potential to produce 2D MOF nanosheet with crystal integrality and high production by ultrasonic exfoliation. Nevertheless, there is still no report for MOF nanosheet preparation in DES.

Chemical sensor is an effective method for trace pollutant determination in water. MOFs are good candidates for metal cations and anions sensing due to their tunable topological structures and high porosity [38-40]. Particularly, lanthanide based MOFs (Ln-MOFs) exhibit brilliant performance as luminescent probes owing to their special 4f electronic configurations [41,42]. However, the high coordination numbers and flexible coordination geometry of lanthanide made the desired Ln-MOFs design and synthesize challenging. Moreover, the current used Ln-MOFs are mainly in bulk-size which limits their interactions with the analytes. With large lateral size and ultrathin thickness, 2D Ln-MOF nanosheet is in favor of more accessible active sites on their surface and beneficial to realize highly sensitive luminescent sensing. Post-synthetic modification (PSM) provides convenient opportunities to prepare 2D Ln-MOFs as luminescent sensors. In this work, bulk MOFs named as MAMS-1 was successfully exfoliated into layered nanosheets (MAMS-1-NS). PSM was utilized as a facile yet versatile approach to fabricate a 2D luminescent Ln-MOF by encapsulating Eu³⁺ cations into MAMS-1-NS. The obtained Eu³⁺@MAMS-1-NS exhibits multi-responsive behavior towards Hg²⁺, Fe³⁺ and Cr₂O₇²⁻, MnO₄⁻ with high quenching efficiency.

2. Experimental section

2.1. Bulk MAMS-1 crystals synthesis

MAMS-1 was synthesized as previously reported [43]. Briefly, 0.34 mmol 5-tert-Butyl-1,3-benzenedicarboxylic acid (H₅(bbdc)) and 0.51 mmol Ni(NO₃)₂·6H₂O were dissolved in 7.5 mL H₂O/ethylene glycol (4:1 v/v,) and sealed in an autoclave. The reaction proceeded at 210 °C for 24 h and light-green crystals were obtained.

2.2. Ultrasonic exfoliation in DES

Firstly, DES was prepared by heating the mixture of choline chloride (ChCl) and ethylene glycol (EG) with a molar ration 1:2 at 80 °C. Then, the MAMS-1 crystals were dispersed in DES with the help of surfactants. The concentration of MAMS-1 dispersion is 3 mg/g in DES. Surfactants such as PVP, SDS and CTAB are added into DES with a concentration of 0.5 mg g⁻¹. Finally, the dispersion was ultrasonically treated in an ultrasonic processor for 60 min. After centrifugation at 5,000 r.p.m. for 30 min, the colloidal MAMS-1 nanosheet (MAMS-1-NS) suspension was collected. MAMS-1-NS in solid state was obtained after a 15,000 r.p.m centrifugation and vacuum drying. Controlled experiment was done without surfactants at the same sonication conditions. Moreover, MAMS-1 crystals dispersed in DES with PVP under mechanical agitation for an hour was also investigated to certify the function of sonication.

2.3. Preparation of Eu³⁺@MAMS-1-NS

Eu³⁺@MAMS-1-NS was synthesized by soaking 100 mg MAMS-1-NS into 10 mL Eu(NO₃)₃·6H₂O (0.2 mmol ml⁻¹) ethanol solution for 48 h. The resulting Eu³⁺@MAMS-1-NS was obtained after centrifugation and washing with ethanol for several times. Eu³⁺@MAMS-1-NS suspension used for luminescent sensing was prepared by introducing 1 mg Eu³⁺@MAMS-1-NS power into 10 mL ethanol under ultrasonication.

2.4. Luminescence sensing of Eu³⁺@MAMS-1-NS

The luminescent sensing of Eu³⁺@MAMS-1-NS was explored by treating 3 mL MOF suspension (0.1 mg/ml) with 30 μL aqueous solution of M(NO₃)₂ (10 mM; M = Na⁺, Ag⁺, Mg²⁺, Co²⁺, Ca²⁺, Ni²⁺, Zn²⁺, Pb²⁺, Cd²⁺, Ca²⁺, Cr³⁺ and Fe³⁺) or KyX (0.1 mM; X = Br⁻, Cl⁻, NO₃⁻, SO₄²⁻, CH₃COO⁻, ClO₄⁻, F⁻, I⁻, SO₃²⁻, Cr₂O₇²⁻ and MnO₄⁻) at room temperature. The mixtures were then used for luminescence measurements. Quinine sulphate (0.1 M in H₂SO₄) was used as reference for relative photoluminescence quantum yield measurement. The absorbance of Eu³⁺@MAMS-1-NS dispersion was detected with the same procedure for quantum yield calculation. The fluorescence lifetime is determined by time-resolved fluorescence.

2.5. Characterization

A Nicolet 6700 FTIR spectrometer is used for FTIR spectra detection in the range 4000–400 cm⁻¹. PXRD patterns were collected from 5° to
50° (2θ) with a scanning rate 4° min⁻¹ on an X-ray powder diffractometer (Rigaku MiniFlex 600). Transmission electron microscope (TEM, JEM-2100plus) and scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy-dispersive X-ray spectrometer are applied to characterize the morphology of sensors used in this work. Excitation and emission spectra were taken on a Cary Eclipse spectrofluorimeter. The atomic force microscopy (AFM, MuLtimode 8) is carried out using a tapping-mode. X-ray photoelectron spectroscopy (XPS) is recorded on an ESCALab220i-XL electron spectrometer with 300 W Al Kα radiation.

3. Results and discussion

3.1. Exfoliation of bulk MAMS-1

A layered 2D MOF named as MAMS-1 is a hydrothermal stable molecular sieve with an interlayer distance 1.9 nm [44]. Herein, we conducted the first study on bulk MAMS-1 exfoliation in DES. The preparation procedure of MAMS-1-NS is illustrated in Scheme 1. DES was selected as an appropriate solvent for liquid exfoliation. Conventional DES composed of ChCl and EG with a molar ratio 1:2 was certified to be effective. With the help of sonication and surfactants, bulk MAMS-1 was exfoliated. Upon exposing layered MAMS-1 to an acoustic cavitation process, single or few-layer MAMS-1-NS can be produced, attributing to the high energy supplied via bubbles creation and collapse under sonication in solvents. Without sonication, MAMS-1-NS cannot be obtained (Fig. S2). Sonication is essential and leads to mechanical deformation of bulk MAMS-1 at the edge, followed by sequential insertion of ions or molecules from DES solution. This process was eco-friendly without volatile organic solvents participation.

Before exfoliation, bulk MAMS-1 with obvious lamellar structure can be observed from SEM and TEM images in Fig. 1(A). The bulk MAMS-1 presents a rectangular morphology with the length 50 μm and width 1.5 μm. After stripping, nanosheets were obtained and a colloidal suspension with good dispersion stability can be prepared. Due to light scattering, Tyndall effect can be observable (the insert of Fig. 1(B)). From the SEM and TEM images in Fig. 1(B), bulk MAMS-1 chunks have disappeared and curly nanosheets presented. Ultrasonic cavitation remarkably reduced the thicknesses along the c-axis of MAMS-1-NS during the exfoliations. Inevitably, the MOF size along the plane direction was also diminished under ultrasonication. XRD patterns of MAMS-1-NS presented in Fig. 1(C) showed no obvious peak position changes compared with the original MAMS-1. The main diffraction peaks are observed at 8.28°, 10.56°, 14.07°, 18.18°, and 28.17°. However, the peak intensity of (0 1 1) located at 8.28° become weaker in MAMS-1-NS, indicating that MAMS-1 stacks along the (0 1 1) direction and MAMS-1-NS was successfully exfoliated from bulk MAMS-1 via ultrasonication. Additionally, the relative peak intensities of I(0 1 3)/I(0 1 1) and I(0 1 5)/I(0 1 1) for MAMS-1-NS (0.26, 0.30) are noticeable greater than those of MAMS-1 (0.17, 0.14). It is concluded that more lattice plane were exposed, such as (0 1 3) and (0 1 5) shown in Fig. 1(C), which may offer abundant active sites and be beneficial to ions transmission [45].

The morphologies and surface topographies of finely dispersed MAMS-1-NS were further characterized by AFM. MAMS-1-NS was deposited onto a silica substrate for AFM observation. AFM images revealed flaky MAMS-1-NS with several lamellas were fully exfoliated (Fig. 2). MAMS-1-NS obtained exhibit relatively large lateral dimensions, some of which are up to 5 × 1 μm². Their thicknesses are
typically around 4 nm corresponding to the thickness of two elementary host layers. The nanometre-sized thickness accompanying with broad lateral dimension distinctly certified the successful exfoliation. Bulk MAMS-1 crystals composed of 2D layers via weak van der Waals stacking, are deliberately broken under sonication in DES here. Accordingly, bulk MAMS-1 could be efficiently exfoliated into ultrathin nanosheets with about two-layer overlapped stacks in a facile and green manner. The successful exfoliation may be attributed to the ultrasonication, befitting surface tension of solvents, hydrogen bonding and hydrophobic interactions between DES and surface ligands of MAMS-1, and the stabilization of surfactants [46].

Surface tension of solvents plays an important role during the ultrasound-assisted exfoliation of 2D materials [47]. Using water and glycerol as probe liquids, the surface energy of MAMS-1 was determined 43 mJ m⁻² (Surface energy Determination of MAMS-1 in supporting information). The reported surface tension of DES composed of ChCl/EG (1:2) is 48 mN m⁻¹ [48], and a little larger than MAMS-1. After the introduction of surfactants, the surface tension of DES decreased and was closer to the MAMS-1 surface energy. Different surfactants such as PVP, SDS, and CTAB were investigated in this work. MAMS-1 can be peeled in DES without surfactants under ultrasonication with only 23% efficiency. With the addition of surfactants, the exfoliation efficiencies of MAMS-1 were enhanced to 73%, 80% and 75% in PVP, SDS, and CTAB solutions, which are much higher than pure DES. It can be attributed to surface tension suitability for DES solution after surfactant introduction. With a surfactant PVP, SDS and CTAB concentration 0.5 mg g⁻¹ in DES, the surface tensions of solvents are 46 mN m⁻¹, 39 mN m⁻¹ and 34 mN m⁻¹ respectively. Obviously, the highest efficiency was achieved in SDS solution which can be explained by the best matched surface tension with MAMS-1. Therefore, surface tension compatibility is conducive to the improvement of exfoliation efficiency.

Furthermore, the obtained MAMS-1-NS assisted without or with surfactants was studied by SEM in Fig. 3. After ultrasonic treatment, the original rectangular bulk MAMS-1 was broken and MAMS-1-NS with a thickness in nanometers can be observed. The lateral dimension of MAMS-1-NS is about several micrometers. However, there are still some swollen MAMS-1 appeared in Fig. 3. Obviously, PVP exhibits the most effective role in assisting the stripping and dispersion of MAMS-1-NS. A stable MAMS-1-NS dispersion with a high concentration of 2.2 mg g⁻¹ could be generated within an hour and no obvious precipitation can be observed after standing more than one month. Non-ionic surfactant tends to exhibit better performance than ionic ones. It has been reported that the higher molecular weight of PVP than SDS and CTAB results in stronger steric repulsion effect and better suspending ability for 2D nanosheets [49].

3.2. Luminescence and sensing properties

MAMS-1-NS is composed of a hydrophilic octanickel cluster layer sandwiched by two hydrophobic carboxylate layers with a 2D porous structure.
structure [43], providing a platform for post-modification and functionalization. Therefore, MAMS-1-NS is a good candidate for luminescent sensing. Herein, a simple post-synthetic pathway was adopted for luminescent Eu$^{3+}$-doped MAMS-1-NS preparation. XRD patterns of the as-synthesized Eu$^{3+}$@MAMS-1-NS showed in Fig. S3 are in good agreement with that of the original MAMS-1-NS, suggesting that the crystal structure still remains unchanged after Eu$^{3+}$ incorporation. The supported Eu$^{3+}$ on MAMS-1-NS can be directly observed by the SEM element mapping shown in Fig. 4. The morphology of MAMS-1-NS was well preserved after Eu$^{3+}$ adsorption as revealed in Fig. 4(A). Eu$^{3+}$ was dispersed uniformly on MAMS-1-NS (Fig. 4(B)).

XPS analysis proves that the Eu$^{3+}$ ions were successfully coordinated with MAMS-1-NS. The peak of Eu 3d$^5$ at 1135.05 eV observed in Fig. 5(A) confirmed the presence of Eu$^{3+}$ in MAMS-1-NS. The peak of O 1s is broaden and binding energy moved from 531.34 to 531.76 eV after Eu$^{3+}$ introduction. These changes imply the successful coordination between free carboxylic acid and Eu$^{3+}$ (Fig. 5(B)) [50]. The highly porous feature and exposed active surface containing uncoordinated carboxyl groups of MAMS-1-NS were proved to be suitable platforms for Ln(III) ions encapsulation to form novel Ln-doped luminescent materials.

Successful doping Eu$^{3+}$ ion onto MAMS-1-NS was further certified by the photoluminescence study. Due to the π-π transition of ligands, MAMS-1-NS displays weak luminescence with a wide band centered around 450 nm when it is excited by 295 nm (Fig. S4). After the integration of Eu$^{3+}$ ion, the ligand centered emissions of MAMS-1-NS were remarkably depressed. The excitation and emission spectroscopy of Eu$^{3+}$@MAMS-1-NS was demonstrated in Fig. 6(A). As excited at 290 nm, the characteristic emission bands of Eu$^{3+}$ at 562, 594, 616, 650, and 700 nm can be observed, which can be attributed to $^5D_0 \rightarrow ^7F_j$ ($J = 0–4$) transitions of Eu$^{3+}$ ions [51]. There is a direct correlation between transitions and the inversion symmetry around the Eu$^{3+}$ ion. Magnetic dipole transition from $^5D_0$ to $^7F_1$ suggests an inversion location. Conversely, the electric dipole transition from $^5D_0$ to $^7F_2$ reveals Eu$^{3+}$ ion in the noninversion site [52]. The intensity proportion between $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ of Eu$^{3+}$@MAMS-1-NS was up to 3 and proved the Eu$^{3+}$ ions low-symmetry coordination site locations [53]. The reduced ligand centered emission and the strong luminescent peaks of Eu$^{3+}$@MAMS-1-NS demonstrate a so-called “antenna effect” occurs and energy transfer from ligands to Eu$^{3+}$ ions within the framework has happened. Therefore, MAMS-1-NS is an efficient scaffold for lanthanide sensitization. The photophysical behaviors of Eu$^{3+}$@MAMS-1-NS were also studied. To evaluate the luminescent efficiency, relative photoluminescence quantum yield referred to quinine sulfate (54%) was calculated and an 8.8% quantum yield achieved. The exciton recombination dynamic was investigated by time-resolved PL spectra. The fluorescent lifetime value was calculated through fitting with the decay curve (Fig. 6(B)). Eu$^{3+}$@MAMS-1-NS has an average lifetime 3.73 ns.

Based on the excellent luminescence of Eu$^{3+}$@MAMS-1-NS, we...
examine the feasibility of Eu$^{3+}$@MAMS-1-NS as a fluorescent-based sensor for cations and anions in water systems. The as-prepared Eu$^{3+}$@MAMS-1-NS suspension of 0.1 mg/mL was used for luminescence detection with various metal ions (Ag$^{+}$, Ca$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Mg$^{2+}$, Na$^+$, Ni$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, and Hg$^{2+}$, 0.1 mM) and different anions (Br$^-$, CH$_3$COO$^-$, Cl$^-$, ClO$_4^-$, F$^-$, I$^-$, NO$_3^-$, SO$_4^{2-}$, SO$_3^{2-}$, Cr$_2$O$_7^{2-}$, and MnO$_4^-$) respectively. As shown in Fig. 7 (A) and (B), under excitation at 290 nm, various metal ions and anions have markedly different effects on the luminescence of Eu$^{3+}$ ions. The Mg$^{2+}$, Na$^+$ ions have little influence in the luminescence intensity of Eu$^{3+}$, while Ag$^{+}$, Ca$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, and Cr$^{3+}$ ions could weakly decrease the Eu$^{3+}$ emission intensity. However, the luminescence intensity at 616 nm is remarkably restrained with a quenching efficiency up to 90.2% and 96.1% when Fe$^{3+}$ and Hg$^{2+}$ are involved respectively, indicating that Eu$^{3+}$@MAMS-1-NS can be a promising luminescent sensor for detecting Fe$^{3+}$ and Hg$^{2+}$ ions. Furthermore, the effects of Fe$^{3+}$ and Hg$^{2+}$ respectively mixed with other metal ions (Ag$^{+}$, Ca$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Mg$^{2+}$, Na$^+$, Ni$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, and Cr$^{3+}$ ions) on the emission of Eu$^{3+}$@MAMS-1-NS were investigated. Although different metal ions were introduced, the quenching effects of Fe$^{3+}$ and Hg$^{2+}$ on the emission intensity of Eu$^{3+}$@MAMS-1-NS were almost undisturbed (Fig. 7 C and D). Therefore, Eu$^{3+}$@MAMS-1-NS is an ideal luminescent probe for Fe$^{3+}$ and Hg$^{2+}$ detecting.

Fluorescence titration experiments were performed by the gradual addition of concentrated Fe$^{3+}$ and Hg$^{2+}$ into the Eu$^{3+}$@MAMS-1-NS dispersion. As shown in Fig. 8 A and B, the emission intensity of Eu$^{3+}$@MAMS-1-NS at 616 nm obviously decreased with the increasing Fe$^{3+}$ and Hg$^{2+}$ concentration. With Fe$^{3+}$ concentration 100 µM and Hg$^{2+}$ 3 µM, the emission of Eu$^{3+}$@MAMS-1-NS was almost completely quenched. The relationships between luminescence intensity and the concentration of Fe$^{3+}$ and Hg$^{2+}$ were studied and the results were showed in Fig. 8 (C) and (D). For Fe$^{3+}$ concentrations within 10 µM, the calculated detection limit (LOD) of 0.40 µM is obtained at a signal-to-noise ratio for 10 times. The legal provision of Fe$^{3+}$ ions in drinking water (no more than 5.4 µM) is covered in our detection range [54]. For Hg$^{2+}$ concentrations within 1.0 µM, the detection limit is 38.16 nM. The Health Organization (WHO) prescribed maximum permissible level of mercury concentration in drinking water is 190 nM [55]. Therefore, Eu$^{3+}$@MAMS-1-NS exhibit good-performances in Fe$^{3+}$ and Hg$^{2+}$ sensing.

Furthermore, the quenching efficiency was rationalized by Stern-Volmer equation quantitatively [56]:

$$I_0/I = 1 + K_{sv}[M]$$

(1)

where $I_0$ and $I$ are the luminescence intensity of Eu$^{3+}$@MAMS-1-NS suspension without and with metal ion addition. $K_{sv}$ represents the quenching constant, [M] is the metal ion concentration. Good linear correlations are observed for the plots of $I_0/I$ vs. [Fe$^{3+}$] and [Hg$^{2+}$] over the concentration range from 0 to 45 and 1.6 to 2.8 µM (the insert of Fig. 8A and B). The $K_{sv}$ of Fe$^{3+}$ and Hg$^{2+}$ were calculated to be 1.05 × 10$^3$ M$^{-1}$ ($R^2 = 0.993$) and 5.78 × 10$^6$ M$^{-1}$ ($R^2 = 0.992$). The linear variation at the low concentration region is mainly ascribed to the static quenching [57]. Low detection limits (0.40 and 0.038 µM) and strong quenching constants (1.05 × 10$^3$ and 5.78 × 10$^6$ L mol$^{-1}$) denote that Eu$^{3+}$@MAMS-1-NS is a promising fluorescent sensor for the practical detection of Fe$^{3+}$ and Hg$^{2+}$.

The fluorescence responses of Eu$^{3+}$@MAMS-1-NS towards typical halide anions (F$^-$, Cl$^-$, Br$^-$ and I$^-$) and inorganic acid radicals (CH$_3$COO$^-$, ClO$_4^-$, NO$_3^-$, SO$_4^{2-}$, SO$_3^{2-}$, Cr$_2$O$_7^{2-}$ and MnO$_4^-$) were also explored. As illustrated in Fig. 5B, Br$^-$, Cl$^-$, ClO$_4^-$, F$^-$, and NO$_3^-$ have
negligible effects on Eu$^{3+}$@MAMS-1-NS luminescence intensity; CH$_3$COO$^-$, I$^-$, SO$_4^{2-}$, and SO$_3^{2-}$ ions can weaken the luminescence intensity. However, the fluorescence intensities of Eu$^{3+}$@MAMS-1-NS towards Cr$_2$O$_7^{2-}$ and MnO$_4^-$ were sharply depressed with a quenching efficiency up to 83.4% and 91.5%. Anti-interference experiments showed in Fig. 9 (A) and (B) indicating the good sensing selectivity for Cr$_2$O$_7^{2-}$ and MnO$_4^-$ ions. The detection limits obtained from Fig. 9 (C) and (D) for Cr$_2$O$_7^{2-}$ and MnO$_4^-$ ions were 0.33 μM (in the range of 0 to 10 μM) and 0.088 μM (in the range of 0 to 2.0 μM) respectively. The $K_q$ of Cr$_2$O$_7^{2-}$ and MnO$_4^-$ were calculated to be $1.55 \times 10^5$ M$^{-1}$ ($R^2 = 0.995$) and $4.49 \times 10^3$ M$^{-1}$ ($R^2 = 0.995$) (Fig. 9 E and F). Consequently, Eu$^{3+}$@MAMS-1-NS shows highly selectivity and sensitivity for Cr$_2$O$_7^{2-}$ and MnO$_4^-$ ion detection.

As a comparison, the sensing ability of bulk Eu$^{3+}$@MAMS-1 was also studied (Fig. 10). The detection limits of bulk Eu$^{3+}$@MAMS-1 for Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$ and MnO$_4^-$ sensing were 0.87 μM, 0.11 μM, 0.49 μM and 0.20 μM respectively (Fig. S5). Obvious enhancements for ion detection can be observed after the bulk MAMS-1 delaminated into nanosheets. The $K_{SV}$ of bulk Eu$^{3+}$@MAMS-1 are $4.75 \times 10^4$ M$^{-1}$, $1.32 \times 10^6$ M$^{-1}$, $7.57 \times 10^4$ M$^{-1}$ and $2.14 \times 10^6$ M$^{-1}$ for Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$ and MnO$_4^-$ respectively (the insert of Fig. 10). Therefore, the nanosheet morphology is much more sensitive than the bulk ones. Furthermore, the comparison of detection limit (LOD) and $K_{SV}$ value was summarized in Table S1 for different ion sensing using Eu-MOF-based fluorescent materials. Eu$^{3+}$@MAMS-1-NS demonstrates higher sensitivity and selectivity for ion sensing than most previously reported Eu-MOFs and has the ability to simultaneously detect a variety of cations and anions. The nanosheet morphology of Eu$^{3+}$@MAMS-1 endows this fluorescent-based sensor with highly accessible active sites on the surface and facilitates the close contact between ions and Eu$^{3+}$@MAMS-1. Thus 2D Eu$^{3+}$@MAMS-1-NS exhibits a much lower detection limit and higher sensitivity compared with bulky MOFs.

3.3. Sensing mechanism

To gain deep insight into the luminescence quenching effect induced by Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$ and MnO$_4^-$ ions, further characterizations including PXRD patterns and UV–visible absorption spectra were carried out. The powder XRD of Eu$^{3+}$@MAMS-1-NS after soaking in Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$ and MnO$_4^-$ solutions remained unchanged (Fig. S6), indicating its good stability as luminescent detectors and no skeletal collapse during the fluorescence quenching.

The UV–vis absorption spectra of Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$ and MnO$_4^-$ ions show a maximum overlap with the excitation spectrum of Eu$^{3+}$@MAMS-1-NS between 250 and 350 nm (Fig. 11), clearly indicating a competitive absorption for the light source energy between Eu$^{3+}$@MAMS-1-NS and Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$, MnO$_4^-$.

Thus, energy transfer from ligand to Eu$^{3+}$ is hindered on account of the competition light absorption between the Eu$^{3+}$@MAMS-1-NS and the quencher ions, leading to the prominent fluorescence quenching [58]. As a consequence, the efficient energy transfer allows Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$, MnO$_4^-$ to have a much higher fluorescence quenching effect compared with other tested cations and anions.

4. Conclusions

In conclusion, we have prepared 2D MOF nanosheets via an efficient
top-down exfoliation pathway in DES under sonication. The suitable surface tension, abundant hydrogen bonding and hydrophobic interactions endow DES great efficiency to MAMS-1 stripping. The obtained MAMS-1-NS was doped with Eu$^{3+}$ by a PSM method and showed relative selectivity and high sensitivity to Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$, and MnO$_4^-$ in solution due to its highly accessible active sites on the surface. According to the quenching response of Eu$^{3+}$@MAMS-1-NS induced by ions, lower LODs (0.40 μM, 0.038 μM, 0.33 μM and 0.088 μM for Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$, and MnO$_4^-$) and larger quenching constants (1.05 × 10$^5$ M$^{-1}$, 5.78 × 10$^6$ M$^{-1}$, 1.55 × 10$^5$ M$^{-1}$, and 4.49 × 10$^5$ M$^{-1}$ for Fe$^{3+}$, Hg$^{2+}$, Cr$_2$O$_7^{2-}$, and MnO$_4^-$) are achieved compared the bulk Eu$^{3+}$@MAMS-1. This interesting work provides a good example of designing Ln$^{III}$-MOFs nanosheets with excellent multiple-responsive fluorescence-sensing abilities.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Appendix A. Supplementary data

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Fig. 10. Luminescent intensity at 616 nm of Eu\(^{3+}\)@MAMS-1-NS treated with 0.1 × 10\(^{-3}\) M various cations (A) and anions (B), and the luminescent spectra of Eu\(^{3+}\)@MAMS-1-NS in the presence of Fe\(^{3+}\) (C), Hg\(^{2+}\) (D), Cr\(_2\)O\(_7^{2-}\) (E) and MnO\(_4^{-}\) (F) ions with different concentrations. Insets: the linear correlation for the plot of I/I\(_0\) vs concentration of Fe\(^{3+}\), Hg\(^{2+}\), Cr\(_2\)O\(_7^{2-}\) and MnO\(_4^{-}\) ions, respectively.

Fig. 11. (A) The UV spectra of metal ions in water and the fluorescence excitation spectra of Eu\(^{3+}\)@MAMS-1-NS dispersion; (B) The UV spectra of anions in water and the fluorescence excitation spectra of Eu\(^{3+}\)@MAMS-1-NS dispersion.
coordination polymer with HER electrocatalytic activity, Ultrason. Sonochem. 70 (2021), 105292.

27. L. P. Yang, T. Xu, S. Liu, J. Tong, R. Chou, H. B. Liu, Exfoliating polyoxometalate-encapsulating metal-organic framework into two-dimensional nanosheets for superior oxidative desulfurization, ChemCatChem 10 (23) (2018) 3590-3596.

28. M. Wang, H. Shi, P. Zhang, Z. Liao, M. Wang, H. Zhong, F. Schwotzer, A.S. Nia, E. Zechec, S. Zhou, S. Kaskel, R. Dong, X. Feng, Phthalocyanine-based 2D conjugated metal-organic framework nanosheets for high-performance micro-supercapacitors, Adv. Funct. Mater. 30 (2020) 2002656.

29. Y. Ding, Y. Chen, X. Zhang, L. Zou, D. Jiang, H. Xu, H. Zhou, Controlled intercalation and chemical exfoliation of layered metal-organic frameworks using a chemically labile intercalating agent, J. Am. Chem. Soc. 139 (2017) 9136-9139.

30. M. Zhao, Y. Huang, Y. Peng, Z. Huang, Q. Ma, H. Zhang, Two-dimensional metal-organic framework nanosheet synthesis and applications, Chem. Soc. Rev. 47 (16) (2018) 6267-6295.

31. H. Qin, X. Hu, J. Wang, H. Cheng, L. Chen, Z. Qi, Overview of acidic deep eutectic solvents on synthesis, properties and applications, Green Energy Environ. 5 (1) (2020) 8-21.

32. C. Florindo, L.C. Branco, L.M. Marruco, Quest for green-solvent design: from hydrophilic to hydrophobic (deep) eutectic solvents, ChemSusChem 12 (2019) 1549-1559.

33. B.S. Singh, H.R. Lobo, D.V. Pinjari, K.J. Jarag, A.B. Pandit, G.S. Shankarling, Ultrasonic and deep eutectic solvent (DES): a novel blend of techniques for rapid and energy efficient synthesis of o xoazoles, Ultrason. Sonochem. 20 (2013) 267-293.

34. M. Francisco, A. van den Bruijnhorst, M.C. Koon, Low-transition-temperature mixtures (LTTMs): a new generation of designer solvents, Angew. Chem. Int. Ed. 52 (11) (2013) 3074-3085.

35. A.M. Abdellaker, H.V. Patten, Z. Li, Y. Chen, I.A. Kinloch, Electrochemical exfoliation of graphite in quaternary ammonium-based deep eutectic solvents: a route for the mass production of graphene, Nanoscale 7 (2015) 11386-11392.

36. A.M. Abdellaker, I.A. Kinloch, Mechanochemical exfoliation of 2D crystals in deep eutectic solvents, ACS Energy Lett. 4 (8) (2019) 4645-4677.

37. M.H. Chakrabarti, N.S.A. Manan, N.P. Brand, R.C. Maher, F.S. Mjalli, I.A. Kinloch, Atomically precise graphene etch stops for three dimensional integrated circuits, ACS Nano 13 (6) (2019) 6925.

38. Zande, A.M. Abdelkader, H.V. Patten, Z. Li, Y. Chen, I.A. Kinloch, Controlling rotation of two-dimensional material flakes, ACS Nano 13 (6) (2019) 6952-6963.

39. B. Wang, J. Jocozu, M. Zhang, M. Ye, S. Yan, H. Jin, S. Wang, Z. Zou, Z. Lin, The charge carrier dynamics, efficiency and stability of two-dimensional material-based perovskite solar cells, Chem. Soc. Rev. 48 (18) (2019) 4854-4891.

40. C. Vaitsis, G. Sourkouni, C. Argirusis, Metal organic frameworks (MOFs) and their derivatives for electrochemical energy storage and catalysis, Chem. Soc. Rev. 47 (2018) 3085-3103.

41. C. Huang, G. Liu, X. Chen, Z. Xue, K. Liu, X. Qiao, X. Li, L. Lu, L. Zhang, Z. Lin, T. Wang, A metal-organic framework nanosheet-assembled film with high permeability and stability, Adv. Funct. Mater. 30 (2020) 1903180.

42. C. Xu, G. Zhao, Y. Chen, Y. Liu, Q. Zhou, J. Chen, J. Zhu, W. Sun, W. Huang, S. X. Dou, Hybrid 2D dual-metal-organic frameworks for enhanced water oxidation catalysis, Adv. Funct. Mater. 28 (2018) 1801554.

43. Y. Wang, M. Zhao, J. Ping, B.O. Chen, X. Cao, Y. Huang, T. Tan, M. Su, W. Yu, Y. Lu, J. Tian, Q. Yan, Y. Qiu, H. Zhang, Biinspired design of ultrafast 2D bimetallic metal-organic framework nanosheets used as biomimetic enzymes, Adv. Mater. 28 (2016) 4149-4155.

44. H. Zhu, M. Zhao, S. Han, Z. Li, Y. Zang, C. Tan, Q. Qu, L. Chen, J. Xiang, X. Zhang, Z. Zhang, B. Li, B. Chen, Y. Hong, Growth of Au nanoparticles on 2D metalloporphyrinic metal-organic framework nanosheets used as biomimetic catalysts for cascade reactions, Adv. Mater. 29 (2017) 1701022.

45. D. Feng, T. Lei, M.R. Lukatayya, J. Park, Z. Huang, M. Lee, I. Shaw, S. Chen, A. V. Yulokenvko, A. Kulkarni, J. Xu, K. Fredrickson, J.R. Tor, X. Yu, C. Zuo, B. Hao, Robust and conductive two-dimensional metal-organic frameworks with exceptionally high volumetric and areal capacitance, Nat. Energy 3 (1) (2018) 30-36.

46. Z. Zhao, Y. Wang, J. Dong, C. He, H. Yin, P. Pan, K. Zhao, X. Zhang, C. Gao, L. Zhang, J. Li, J. Wang, J. Zhang, A.M. Khattak, N.A. Khan, Z. Wei, J. Zhang, S. Liu, H. Zhao, Z. Tang, Ultrathin metal-organic framework nanosheets for electrocatalytic oxygen evolution, Nat. Energy 1 (2016) 1-10.

47. L. Cheng, G. Liu, W. Jin, Recent progress in two-dimensional material membranes for gas separation, Acta Phys.-Chim. Sin. 35 (2019) 1090-1098.

48. H. Zhu, D. Liu, The synthetic strategies of metal-organic framework membranes, films and 2D MOFs and their applications in devices, J. Mater. Chem. A 7 (37) (2019) 21004-21025.

49. K. Zhao, W. Zhu, S. Liu, X. Wei, G. Ye, Y. Su, Z. He, Two-dimensional metal-organic frameworks and their derivatives for electrochemical energy storage and conversion, Adv. Sci. (2020) 2001652.

50. B. Liu, R. Yin, X. Xu, L. Zhang, W. Shi, X. Cao, Structural engineering of low-dimensional metal-organic frameworks: synthesis, properties, and applications, Adv. Sci. 6 (2019) 1802273.

51. Y. Zhao, Z. Yang, Y. Zeng, L. Lin, Y. Sun, J. Ren, X. Qiao, Two-dimensional metal-organic framework/enzyme hybrid nanocatalyst as a benign and self-activated cascade reagent for in vivo wound healing, ACS Nano 13 (2019) 5222-5230.

52. J. Ran, J. Qu, H. Zhang, T. Wen, H. Wang, S. Chen, L. Song, X. Zhang, L. Jing, R. Zheng, S. Qiao, 2D metal organic framework nanosheet: a universal platform promoting highly efficient visible-light-induced hydrogen production, Adv. Energy Mater. 9 (2019) 1803402.

53. X. Zhang, L. Chang, Z. Yang, Y. Shi, C. Long, J. Han, B. Zhang, X. Qiu, G. Li, L. Tang, Facile synthesis of ultrathin metal-organic framework nanosheets for Lewis acid catalysis, Nano Res. 12 (2) (2019) 437-440.

54. Y. Wang, L. Feng, J. Pang, J. Li, N. Huang, G.S. Day, L. Cheng, H.F. Drake, Y. Wang, C. Lollar, J. Qin, G. Tu, S. Yuan, H. Zhou, Photocatalyst-anchorred 2D MOF nanosheets as highly efficient and accessible catalysts toward amine combustion, Adv. Sci. 6 (2019) 1802059.

55. R.A. Natour, Z.K. Ali, A. Assoud, M. Hamedeh, Two-dimensional metal-organic framework nanosheets as a dual ratiometric and turn-on/off luminescent probe, Inorg. Chem. 58 (16) (2019) 10202-10219.

56. X. Hu, J. Gao, X. Qian, J. Wang, H. He, Y. Cui, Yu. Yang, Z. Wang, Q. Gao, Metal-organic framework nanosheets for fast-response and highly sensitive luminescent sensing of Fe2+, J. Mater. Chem. A 4 (28) (2016) 10900-10905.

57. J. Liu, R. Li, Study of ultrasound-assisted exfoliation for preparing graphite-molybdenum disulfide nanosheets, Ultrason. Sonochem. 63 (2020) 104923.

58. W. Pang, B. Zhao, X-Q. Tan, C. Tang, Z. Zhang, J. Huang, Exfoliation of metal-organic frameworks into efficient single-layer metal-organic nanosheets and electrocatalysts by the synergistic action of host-guest interactions and sonication, Nanoscale 12 (2020) 3623-3629.

59. N. Contreras-Pareda, F. Moghiz, J. Basilea, H. Zhang, J. Janczak, S. Solomonnejad, B. Dong, D. Ruiz-Molina, Ultrasound-assisted exfoliation of a layered 2D...
X. Mi, D. Sheng, Yu’e Yu, Y. Wang, L. Zhao, J. Lu, Y. Li, D. Li, J. Dou, J. Duan, S. Wang, Tunable light emission and multiresponsive luminescent sensitivities in aqueous solutions of two series of lanthanide metal-organic frameworks based on structurally related ligands, ACS Appl. Mater. Inter. 11 (8) (2019) 7914–7926.

S. Mirlohi, A.M. Dietrich, S.E. Duncan, Age-associated variation in sensory perception of iron in drinking water and the potential for overexposure in the human population, Environ. Sci. Technol. 45 (15) (2011) 6575–6583.

C. Li, Q. Niu, J. Wang, T. Wei, T. Li, J. Chen, X. Qin, Q. Yang, Bithiophene-based fluorescent sensor for highly sensitive and ultrarapid detection of Hg$^{2+}$ in water, seafood, urine and live cells, Spectroc. Acta Pt. A-Molec. Biomolec. Spectr. 233 (2020), 118208.

S.W. Thomas, G.D. Joly, T.M. Swager, Chemical sensors based on amplifying fluorescent conjugated polymers, Chem. Rev. 107 (4) (2007) 1339–1386.

G. Li, G. Liu, Y. Li, L. Hou, Y. Wang, Z. Zhu, Uncommon pyrazoyl-carboxyl bifunctional ligand-based microporous lanthanide systems: sorption and luminescent sensing properties, Inorg. Chem. 55 (2016) 3952–3959.

S. Xu, J. Shi, B. Ding, Z. Liu, X. Wang, X. Zhao, E. Yang, A heterometallic sodium(i)-europium(iii)-organic layer exhibiting dual-responsive luminescent sensing for nitrofuran antibiotics, Cr$_2$O$_7^{2-}$ and MnO$_4$ anions, Dalton Trans. 48 (2019) 1823–1834.

X. Ge, Ionothermal synthesis of cobalt iron layered doublehydroxides (LDHs) with expanded interlayerspacing as advanced electrochemical materials, J. Mater. Chem. A 2 (2014) 17066–17076.