**Eu$^{3+}$ functionalized robust membranes based on the post-synthetic copolymerization of a metal–organic framework and ethyl methacrylate†**

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Metal–organic frameworks (MOFs) are recognized as a class of promising crystalline materials. However, their subsequent processing and shaping still remain a challenge, and one emerging strategy is to hybridize MOFs with flexible polymers. Herein, by utilizing a simple and cost-effective post-synthetic polymerization method, under mild conditions, MOF particles with olefin bonds are covalently linked to polymer chains. Moreover, photoactive europium ions are also introduced into this system during the polymerization process. Importantly, the resulting MOF-based membrane (MOF-Eu$^{3+}$@PEMA) is uniform, showing great structural and fluorescence stability against strict conditions (aqueous solutions with pH 0.98–13.11). Besides, given its good luminescence properties, the membrane is employed for the identification of common volatile organic compounds and a selective response to toluene was achieved. This work accelerates the practical applications of MOF-based membranes and enriches the methods for MOF modification.

### Introduction

As a type of well-defined crystalline material, metal–organic frameworks (MOFs) consist of metal ions or clusters and bridging organic ligands. Benefiting from their high porosity, desirability, adjustability, and multiple host–guest interactions related to both the organic and inorganic parts, MOFs have become an increasingly important platform with potential applications in numerous fields, including gas storage and separation, catalysis, magnetic materials, sensing, and so on. Despite the above-mentioned advantages, on account of their crystalline nature closely arising from their inorganic moieties, it is often difficult to realize the processing and molding of fragile MOFs without destroying their structure. Moreover, the metal–ligand bonds in MOFs are usually not strong enough and could be easily attacked and broken, thereby reducing the structural stability of MOFs, and this greatly limits their practical applications. Therefore, the improvement of the processability and structural stability of MOFs is necessary and highly significant.

Polymers are one of the preferred "candidates" for the construction of composite materials, which can provide diverse desired attributes such as easy modification and processing, low cost, chemical stability, and good mechanical properties. Nevertheless, polymer chains, under most circumstances, are randomly entangled in the bulk state, and thus their available properties usually depend on the average behaviors of most disordered chains. Fabricating composites of MOFs and polymers can be a good choice to eliminate such defects, because their combination might lead to better performances than that of the individual components: first, the regular and adjustable open channels in MOFs facilitate the specific assembly of polymers; and second, the functional polymers can not only improve the processability, but also bring diverse potential unexplored properties.

Among these, the PSP method has been gaining efforts have been made to study the hybridization of powder-form MOFs and polymers. So far, several approaches have been applied for the creation of their composites, such as polymerization in nanochannels of MOFs, introduction of polymer chains into nanochannels of MOFs, and use of post-synthetic polymer-tethered ligands (post-synthetic polymerization, PSP) and MOF-based mixed matrix membranes (MMMs, with MOF particles as fillers scattered in a polymer matrix). Among these, the PSP method has been gaining significant attention of scientific researchers in correlative...
areas; since it is capable of achieving a covalent connection between MOF crystals and polymer chains, the resulting MOF–polymer composites often possess good stability and conformity.\textsuperscript{16,26,32,41} Even so, as far as we know, the existing MOF-based membranes are mostly obtained by physically dispersing MOF particles in the polymer or introducing polymer chains into the MOF pores; explorations involving PSP on MOFs are still rare.\textsuperscript{16-18,22,41} Thus, additional studies are needed in this area.

In this work, apart from MOFs and polymers, known for their unique eye-catching luminescence characteristics (narrowband emission, high color purity, and long lifetime),\textsuperscript{32,42} photoactive lanthanide ions were also added to produce a material integrating the advantages of all three. Specifically, a facile and mild PSP method was presented for the fabrication of a luminescent membrane: the almost unstudied Cd-centered MOFs with polymerizable groups $\{[\text{Cd}_2(\text{fma})_2(\text{phen})_2]_n, \text{MOF}1\}$ and $\{[\text{Cd}(\text{fma})(\text{bipy})_2(\text{H}_2\text{O})]_n, \text{MOF}2\}$ were employed for copolymerization with organic monomers (ethyl methacrylate), meanwhile, lanthanide ions (Eu\textsuperscript{3+} or Tb\textsuperscript{3+}) were involved in the entire process. Importantly, the resulting uniform membrane with excellent luminescence properties retains good structural and fluorescence stability under harsh conditions. Furthermore, on the basis of an “on–off” fluorescence change, the distinction of toluene from other common volatile organic solvents can be achieved with this membrane, and the possible sensing mechanism is analyzed. This attempt provides a new strategy for the fabrication of luminescent membranes comprising MOFs, polymers, and lanthanide ions (Fig. 1).

**Experimental section**

**Materials and reagents**

Eu(NO$_3$)$_3$·6H$_2$O and Tb(NO$_3$)$_3$·6H$_2$O were prepared by dissolving the corresponding oxides into excess concentrated hydrogen nitrate with continuous magnetic stirring, followed by evaporation and crystallization several times. All the other related chemicals are of at least analytical grade, commercially available and utilized directly without further purification. Cd(\(\text{CH}_2\text{COO})_2\cdot2\text{H}_2\text{O}, \text{fumaric acid (fma), phenanthroline (phen), 2,2’-bipyridine (bipy), benzoyl peroxide, ethyl methacrylate, and NaOH were produced by Sigma-Aldrich. Rare earth oxides, and all the organic solvents, including acetone, acetonitrile, methanol, tetrahydrofuran, and toluene, were purchased from Aladdin Chemistry Co. (Shanghai, China). Absolute ethanol (95%) and deionized water were used for all the experiments.

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**Preparation of membranes**

Preparation of the MOF-Ln\textsuperscript{3+}@PEMA membrane. 5 mL ethyl methacrylate, a specific amount of MOF powder (3.5 wt% of ethyl methacrylate), Ln(NO$_3$)$_3$·6H$_2$O (0.8 wt% of ethyl methacrylate) and 0.5 mL ethanol (for better dispersion of MOF powders in ethyl methacrylate and polymerization) were mixed.
in a 50 mL centrifuge tube; after sonication at room temperature for 20 minutes, dibenzoyl peroxide (1 wt% with respect to the total weight of two monomers, as the initiator) was added into the suspension and sonicated for another 5 minutes. Then, it was heated to 75 °C in a water bath with continuous magnetic stirring and kept for a while until the fluid became uniform and viscous. Then, the resulting material was dripped into a Teflon mold (1 cm × 1 cm × 1.5 mm or 3 cm × 3 cm × 1 mm), and allowed to set for about 6 hours, and a robust, flexible, and homogeneous membrane was formed. In addition, the conditions for the fabrication of Ln\(^{3+}\)@PEMA are the same as those for MOF-Ln\(^{3+}\)@PEMA except that the MOF is removed (MOF = MOF1, MOF2; Ln\(^{3+}\) = Eu\(^{3+}\), Tb\(^{3+}\), EMA = ethyl methacrylate).

**Fluorescence properties of membranes.** The excitation and emission spectra were collected directly from the membranes of suitable size. In addition, the fluorescence recognition of the MOF1-Eu\(^{3+}\)@PEMA membrane towards common volatile organic compounds was also explored: the as-synthesized membrane was shredded into proper size and then placed into a 10 ml centrifuge tube with 50 μL volatile organic compounds (note that the membrane and organic compounds cannot be in direct contact); after 30 minutes of interaction at 50 °C, these membranes were taken out and their fluorescence spectra were collected.

**Results and discussion**

**Characterization of MOFs and membranes**

As shown in Fig. S1,† the powder X-ray diffraction (PXRD) patterns of as-synthesized MOF1 and MOF2 are highly consistent with the simulated conditions, proving the successful preparation of MOF1 and MOF2. Notably, based on the previous work of our group,\(^36\) there are olefinic bonds in MOF1 and MOF2 (demonstrated in Fig. S2 and S3†), which could offer interaction sites for their post-synthetic copolymerization with other polymerizable substances. In this work, MOF powders and Ln(NO\(_3\))\(_3\)·6H\(_2\)O were added into ethyl methacrylate and then sonicated to form suspensions, taking dibenzoyl peroxide as the heat-initiator; on heating in a water bath under continuous magnetic stirring, membranes with good shape could be prepared, and all the conditions involved in the polymerization reaction were mild. What’s more, as can be seen from Fig. 2(a), the PXRD profile of MOF1-Eu\(^{3+}\)@PEMA powder collected by digesting the membrane with CH\(_2\)Cl\(_2\) matches well with the simulated one, and more importantly, the MOF1-Eu\(^{3+}\)@PEMA membrane also retains the characteristic XRD peaks of both MOF1 and Eu\(^{3+}\)@PEMA, confirming that the polymerization process does not destroy the topology and crystallinity of MOF1.

The occurrence of copolymerization between MOF1 and PEMA can be proved by Fourier transform infrared (FTIR) spectroscopy (Fig. 2(b)). As shown in Fig. 2(b), the newly appearing absorption band at 1720 cm\(^{-1}\) could be ascribed to the carboxylate along with EMA; meanwhile, after polymerization, the characteristic band associated with C=C bonds observed at 1678 cm\(^{-1}\) disappeared, revealing that the polymerization here is relatively thorough and efficient, which could be further confirmed by the \(^1\)H NMR spectrum (Fig. S5†). The as-prepared MOF1-Eu\(^{3+}\)@PEMA membrane integrates the 1H signals of both PEMA and ligands in MOF1. Moreover, as illustrated in the scanning electron microscopy (SEM) images of the membranes (Fig. 3(a) and (b)), apparently, the as-prepared membrane is uniform, and there are no voids at the interface, showing that this copolymerization method is suitable and can improve the chemical and physical interactions at the interface between the MOF particles and polymers.\(^17,22\) The images in Fig. 3(c) and (d) display the good flexibility and fluorescence emission of the obtained membranes.

**Luminescence properties of MOFs and membranes**

The fluorescence emission and excitation spectra of MOF1 and MOF2 in the solid state were initially recorded at room temperature. As revealed in Fig. S6,† both MOF1 and MOF2 exhibit a broad band in their excitation and emission spectra, which is regarded as a result of the π to π* electron transition in the ligands of the corresponding MOFs. With the same excitation...
and emission scan slits, it can be seen in Fig. S7† that the fluorescence emission of MOF1-PEMA is stronger than that of MOF2-PEMA; therefore, selecting MOF1-PEMA as the matrix material, we further introduced photoactive lanthanide ions. Fig. S8† shows that the energy transfer from the ligands in MOF1 to Eu³⁺ is much better than that to Tb³⁺, and thus MOF1-Eu³⁺@PEMA exhibits stronger emission than MOF1-Tb³⁺@PEMA; based on this, we further studied the luminescence properties of MOF1-Eu³⁺@PEMA and tried to develop it as a fluorescent probe for the identification of volatile organic compounds.

By keeping the width of the scan slit at a constant value, interestingly, as we can see in Fig. 4, pure PEMA can hardly emit fluorescence, and MOF1 alone glows very weakly; however, the polymerization process between MOF and EMA monomers enhanced the fluorescence, in other words, the hybrid material resulting from the copolymerization of MOF and PEMA shows a stronger luminescence. Particularly, with the introduction of Eu³⁺, it is worth mentioning that the luminescence is greatly strengthened, indicating the efficient energy transfer from the ligand to Eu³⁺ (antenna effect), and thus, apart from the original peaks belonging to the ligands of MOF1, five characteristic narrow peaks from Eu³⁺ appeared at 579, 592, 616, 651, and 701 nm separately, which could be ascribed to its typical "⁵D₀ → ⁷F₉ (J = 0–4) transitions. Apparently, the emission peak at 616 nm is the strongest, originating from the "⁵D₀ → ⁷F₂ transition. Hence, in pursuit of better sensitivity, 616 nm was selected as the emission wavelength for the subsequent lifetime measurement experiment.

As revealed in Fig. S9,† by fitting the data with a biexponential curve, the lifetime of typical Eu³⁺ emission at 616 nm is calculated as 882 ms with χ² = 1.131, much bigger than the microsecond level lifetime of MOF1-PEMA in Fig. S10.†

Stability is one of the most important indicators for the evaluation of MOF-based materials; moreover, since the metal–ligand bonds in MOFs are usually weak and could be easily attacked by water molecules, the structural stability of these materials in water is particularly critical. Herein, to observe the stability variation of MOF1 after the post-synthetic polymerization with ethyl methacrylate, we immersed MOF1 powders and the MOF1-Eu³⁺@PEMA membrane in water for 24 h and collected their PXRD patterns. The low match of PXRD peaks between the experimental situations and the simulated ones in Fig. S11† illustrates that the presence of water molecules may change the topological structure of MOF1 crystals. However, as can be seen in Fig. S12,† after 24 hour immersion in water, a strong acid or a strong alkali, the main PXRD features of MOF1-Eu³⁺@PEMA can be still well maintained, indicating its excellent and superior structural stability over MOF1 powders alone. More importantly, MOF1-Eu³⁺@PEMA shows wonderful fluorescence stability over a wide pH range (0.98–13.11), which is shown in Fig. 5: after soaking in a variety of aqueous solutions with different pH values for 24 hours separately, no matter whether the solution is highly acidic, alkaline, or neutral, the membranes exhibit very similar emission intensities.

Besides, we explored the fluorescence change of the MOF1-Eu³⁺@PEMA membrane with time, as clearly shown in Fig. S13.† For 1 month after the preparation of the membrane, the emission of MOF1-Eu³⁺@PEMA remained almost
unchanged from the initial state, revealing its extraordinary fluorescence stability.

Responses of MOF1-Eu$^{3+}@$PEMA to volatile organic compounds

Inspired by the excellent luminescence properties and excellent material stability of the MOF1-Eu$^{3+}@$PEMA membrane, we investigated its fluorescence behaviors with volatile organic compounds (toluene, acetone, acetonitrile, methanol, ethanol, and tetrahydrofuran). Significantly, it can be found that the MOF1-Eu$^{3+}@$PEMA membrane shows special luminescence response to toluene. As revealed in Fig. 6, if we take the fluorescence emission of the MOF1-Eu$^{3+}@$PEMA membrane without treatment as a reference standard, among all the common volatile organic compounds tested in this experiment, only toluene caused a remarkable quenching effect on the luminescence of the MOF1-Eu$^{3+}@$PEMA membrane stemming from the characteristic $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$, while other volatile organic compounds can slightly increase or reduce the fluorescence emission of the MOF1-Eu$^{3+}@$PEMA membrane, indicating the membrane’s good selectivity for toluene. With regard to the remarkably decreased fluorescence of the MOF1-Eu$^{3+}@$PEMA membrane caused by toluene vapor, we speculate the order of solubility parameters of the constituent materials and the analytes can be responsible. The solubility parameters for toluene, acetone, acetonitrile, methanol, ethanol, and tetrahydrofuran are 18.0, 20.0, 24.3, 30.2, 25.9, and 18.8 $J^{1/2} cm^{-3/2}$ respectively, while for polyethyl methacrylate it is about 16.2–18.6 $J^{1/2} cm^{-3/2}$. According to previous reports, the closer the solubility parameters between different substances are, the easier it is to dissolve and permeate each other. This mutual dissolution disrupts the energy transfer of the membrane’s components. Consequently, the luminescence of the MOF1-Eu$^{3+}@$PEMA membrane is weakened. Additionally, the outspread π-rich system in MOF1 leads to the membrane’s higher adsorption of toluene, thereby changing the fluorescence; the strong π–π interactions between toluene and the phenanthroline ligand in MOF1 play a role in impeding the emission of MOF1-Eu$^{3+}@$PEMA.

The fluorescence lifetime can be used to confirm whether the fluorescence quenching is dynamic or static: dynamic quenching corresponds to an obvious change in the lifetime, while static quenching shows small influence on this, and it...
rather gives rise to a shift of the excitation wavelength.\textsuperscript{20,42,53,54} Hence, to better clarify the possible response mechanism, the decay curves and excitation spectra of the MOF1-Eu\textsuperscript{3+}@PEMA membrane before and after exposure to toluene vapor were recorded as well. As revealed in Fig. S14 and S15,† after exposure to gaseous toluene at 50 °C for 30 minutes, there is almost no change in both lifetime and excitation wavelength; instead, this fluorescence quenching induced by toluene is rather gives rise to a shift of the excitation wavelength.\textsuperscript{20,42,53,54}

Conclusions

In summary, by means of facile and cost-effective post-synthetic polymerization, based on polymerizable MOF particles and ethyl methacrylate, a novel uniform membrane with good material properties was fabricated. Moreover, we studied its fluorescence properties and explored its responses to common volatile organic compounds. It is worth mentioning that the MOF1-Eu\textsuperscript{3+}@PEMA membrane exhibits excellent structural and luminescence stability in aqueous solutions with a wide range of pH values (0.98–13.11). Significantly, in contrast to the matrix of pure PEMA, the hybrid membrane composed of the Cd-centered MOF and ethyl methacrylate can sensitize the fluorescence emission of Eu\textsuperscript{3+} more effectively. Besides, the MOF1-Eu\textsuperscript{3+}@PEMA membrane shows the capacity of recognizing toluene from other typical volatile organic compounds. This work provides a simple and efficient method for the preparation of luminescent polymer membranes, which can further enrich approaches for MOF modification and expand its applications.

Conflicts of interest

There are no conflicts to declare.

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