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Anionic porous metal–organic framework with novel 5-connected *vbk* topology for rapid adsorption of dyes and tunable white light emission†

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A novel porous metal–organic framework, $\{[Zn_2(L)\cdot H_2O]\cdot 3H_2O\cdot 3DMAc\cdot NH_2(CH_3)_2\}_n$ (Zn(II)–MOF), was synthesized under solvothermal conditions using a flexible multicarboxylic acid (H_5L = 3,5-bis(1-methoxy-3,5-benzene dicarboxylic acid)benzoic acid). Zn(II)–MOF contains 1D nanotubular channels of 13.8 Å × 16.4 Å and exhibits a rare 5-connected *vbk* net with a Schläfli symbol of $\{4^5.6^5\}$ topology. Notably, Zn(II)–MOF can adsorb toluidine blue fast and effectively, and trap lanthanide ions such as Eu^{3+} and Tb^{3+} to sensitize their emissions in the solid state through a Ln^{3+}-exchanged approach. Furthermore, we successfully obtained white light emitting materials.

Introduction

Recently, metal–organic frameworks (MOFs) have met with great interest owing to their enormous variety of interesting molecular topologies and a wide range of potential applications as functional materials.[1] A key feature in MOFs is their porosity, which plays a significant role in the functional properties, typically in guest species recognition and adsorption.[2] Most of the functionalities derive from the ability of MOFs to recognize specific guest substrates through elusive host–guest interactions. Furthermore, the highly regular channel structures and controllable pore sizes of MOFs permit their applications in adsorption of guest molecules/ions, such as dyes or lanthanide ions.

With the development of the dyeing and finishing industry, dye effluent is emerging as an environmentally challenging issue worldwide, particularly in China.[3] Many dyes are considered to be toxic and even carcinogenic, and most toxic dyestuffs are stable to light and oxidants, which make them difficult to degrade.[4] Although several techniques, such as biological treatments, membrane processes, advanced oxidation processes, electrochemical techniques, and adsorption procedures,[5] have been proposed, materials containing nanometer sized pores and channels are currently receiving a considerable amount of attention because of their adsorbing applications. Although a host of applications that utilize the capability of MOFs for physical absorption have been explored, work about rapid dye adsorption of MOFs has been rarely reported.[2g–m]

White-light-emitting materials deserve particular attention due to their potential applications in solid-state lighting (SSL), full-color displays, and backlights.[6] White emission should ideally be composed of two (blue and yellow) or three (blue, green, and red) primary colors and cover the whole visible range from 400 to 700 nm, and the emitters should have the ability to emit primary colors simultaneously and be comparable in intensity to produce white light and the pure colors separately in a tunable way.[7] Different approaches have been reported to obtain efficient white-light-emitting materials. They mainly focus on metal-doped or hybrid inorganic materials,[8] nanomaterials,[9] organic molecules,[10] and metal complexes.[11] In the photo- and electroluminescence fields, lanthanide-containing materials, which exhibit excellent sharp-emission luminescence properties with suitable sensitization, have attracted much interest and have been effectively used in designing white-light emitting materials.[12] However, the design and synthesis of hetero-lanthanide MOFs is very hard due to the inherent difficulty of synthesis of organic ligands with specific recognition sites required by the different lanthanide cations. So, with judiciously chosen red, green and blue-emissive ions incorporated in a suitable host, it is possible to obtain luminescent materials which emit across the entire visible spectrum with high color purity.[13] However, as to the white-light-emitting materials study of MOFs, there are few reports about the encapsulation of lanthanide ions to generate white light emission through a Ln^{3+}-exchanged approach.

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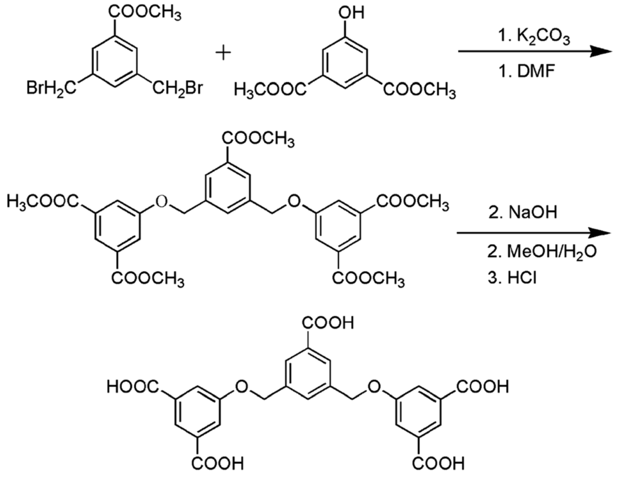
Based on the above consideration, we have been developing a program for the preparation of porous MOFs. The MOF built from a bulky ligand which enables the formation of large channels can serve as a host for adsorbing dyes effectively and an antenna for generating luminescent lanthanide MOFs. In this contribution, we present a novel porous metal–organic framework $\{[Zn_2(L)\cdot H_2O]\cdot 3H_2O\cdot 3DMAc\cdot NH_2(CH_3)_2\}_n$ (Zn(II)–MOF), which is generated from H_5L (3,5-bis(1-methoxy-3,5-benzene dicarboxylic acid)benzoic acid) and $ZnCl_2$ under solvothermal conditions. Zn(II)–MOF is anionic, and dimethylammonium cations reside in its 1D pores. Furthermore, we can replace the dimethylammonium cations with specific cations in a post synthetic fashion.[14] Thus, we successfully obtained multi-functional MOF materials which can adsorb toluidine blue fast and effectively, and we also obtained white-light emitting materials through trapping of Eu^{3+} and Tb^{3+} ions into the pores of the Zn(II)–MOF material.



Scheme 1 The synthesis of ligand H_5L.

Experimental

Materials and physical measurements

All reagents and solvents employed in the present work were of analytical grade as obtained from commercial sources and used without further purification. Elemental analysis for C, H, and N 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 Nicolet NEXUS 470-FTIR spectrometer. Thermogravimetric analysis (TGA) was performed on an SDT 2960 thermal analyzer under air from room temperature to 800 °C with a heating rate of 20 °C min^{-1}. Data for Zn(II)–MOF were collected using the MX1 beamline at the Australian Synchrotron operating at 15.995 keV (λ = 0.71073 Å) for the 100 K structure. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer. UV-visible absorption spectra were recorded on a TU-1900 double-beam UV-Vis spectrophotometer. Inductively coupled plasma spectroscopy (ICP) was performed on a Thermo ICAP 6500 DUO spectrometer. The Commission International de I'Eclairage (CIE) color coordinates were calculated on the basis of the international CIE standards.[15]

Preparation of 3,5-bis(1-methoxy-3,5-benzene dicarboxylic acid)benzoic acid (H_5L)

The ligand was prepared by the reaction of methyl 3,5-bis(bromomethyl)benzoate[16] with dimethyl-5-hydroxy-benzene-1,3-dioate[17] (Scheme 1). A mixture of methyl 3,5-bis(bromomethyl)-benzoate (0.96 g, 3 mmol), dimethyl-5-hydroxy-benzene-1,3-dioate (1.79 g, 8.5 mmol), K_2CO_3 (1.80 g, 13 mmol) and DMF (50 mL) were placed in a 100 mL round-bottom flask and the reaction completed after the solution was stirred at 50 °C for 48 hours under a N_2 atmosphere. The product mixture was poured into H_2O (100 mL), and the aqueous solution was extracted by CH_2Cl_2 (2 × 100 mL). The combined CH_2Cl_2 layer was washed with saturated $NaHCO_3$ solution (3 × 100 mL), dried over $MgSO_4$, filtered and evaporated on a rotary evaporator to give a 3,5-bis(1-methoxy-3,5-benzene dicarboxylic acid)benzoic acid dimethyl ester. Then, the product and NaOH (3.6 g, 0.09 mol) were dissolved in 60 mL of methanol and 60 mL of water and refluxed overnight. The methanol was removed by distillation under reduced pressure and the resulting aqueous solution was acidified to pH $\sim$ 2.0 by 6 M HCl solution. A white solid was precipitated and filtered. Next the solid was dried under vacuum overnight. Yield: 1.22 g, 86%. Elemental analysis (%): calcd for $C_{25}H_{18}O_{12}$: C, 58.83; H, 3.55; O, 37.62. Found: C, 58.73; H, 3.61; O, 37.66. ^1H NMR (300 MHz, DMSO-d_6): δ 8.10 (s, 2H), 8.03 (d, 2H), 7.88 (s, 1H), 7.77 (s, 4H), 5.35 (m, 4H). IR (KBr, cm^{-1}): 3443(s), 1693(vs), 1596(vs), 1465(m), 1418(s), 1301(s), 1264(m), 1127(m), 1072(m), 1042(w), 883(w), 775(s), 728(m), 488(w).

Preparation of $\{[Zn_2(L)\cdot H_2O]\cdot 3H_2O\cdot 3DMAc\cdot NH_2(CH_3)_2\}_n$ (Zn(II)–MOF)

A mixture of H_5L (0.0153 g, 0.03 mmol), $ZnCl_2$ (0.0272 g, 0.2 mmol), and DMAc–methanol (1/1.5) (DMAc = *N*,*N*′-dimethylacetamide) was stirred for 10 min in air at room temperature. Then the mixture was transferred and sealed in a Teflon-lined stainless steel vessel (18 mL) and heated at 90 °C for 3 days. After the mixture was cooled to room temperature at 4 °C h^{-1}, colorless crystals of Zn(II)–MOF were obtained (57.2% yield based on H_5L). Elemental analysis (%): calcd for $C_{39}H_{56}O_{19}N_4Zn_2$: C, 46.12; H, 5.56; N, 5.52. Found: C, 46.18; H, 5.96; N, 5.61. IR (KBr, cm^{-1}): 3426(s), 1622(vs), 1578(vs), 1455(m), 1403(s), 1364(s), 1262(m), 1126(m), 1036(m), 963(w), 889(w), 780(s), 726(m), 594(w).

Experimental details for dye adsorption

Freshly prepared Zn(II)–MOF (30 mg) was immersed for 30 min in 3 mL DMAc solutions with different toluidine blue concentrations (10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} M).

Encapsulation of lanthanide(III) cations in Zn(II)–MOF

Soakage of Zn(II)–MOF in DMAc solutions of lanthanide hydrochloride. Freshly prepared Zn(II)–MOF (30 mg) was soaked in DMAc solutions (3 mL) of hydrochloride of Eu^{3+} and Tb^{3+}, respectively. After one day of soakage at 50 °C, the crystals were washed with DMAc to remove residual lanthanide(III) cations on the surface.

Soakage of Zn(II)–MOF in DMAc solutions of europium(III)/terbium(III) hydrochloride with different Eu^{3+}/Tb^{3+} ratios. Freshly prepared Zn(II)–MOF (30 mg) was soaked in DMAc solutions (3 mL) of lanthanide hydrochloride with different molar ratios of Eu^{3+}/Tb^{3+}. After one day of soakage at 50 °C, the crystals were washed with DMAc to remove residual lanthanide(III) cations on the surface.

X-ray crystallography

Single-crystal X-ray diffraction data of Zn(II)–MOF was conducted on the MX1 beamline at the Australian Synchrotron operating at 15.995 keV ($\lambda = 0.71073$ Å) for the 100 K structure. The sample was mounted on a 0.1 mm cryo-loop using viscous oil and the temperature was maintained using an open-flow N_2 cryostream. Data were collected from a single phi scan using the Bluice interface program.[18] Initial data processing was carried out using XDS.[19] The structure was solved by direct methods with SHELXS-97 (ref. 20) and refined with the full-matrix least-squares technique using the SHELXL-97 (ref. 21) program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ligand were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of solvent molecules and thereby to produce a set of solvent-free diffraction intensities. The structure was then refined again using the data generated. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data, data collection parameters, and refinement statistics for Zn(II)–MOF are listed in Table S1.† Relevant bond distances and bond angles for Zn(II)–MOF are given in Table S2.†

Results and discussion

Synthesis and crystal structure

The reactions of $ZnCl_2$ and H_5L in a mixed solvent system of DMAc–methanol at 90 °C for 72 h produced colourless crystals of Zn(II)–MOF. A single crystal X-ray diffraction study reveals that Zn(II)–MOF crystallizes in monoclinic space group $P2_1/c$ and has a non-interpenetrated three-dimensional framework. As shown in Fig. 1, the asymmetric unit of Zn(II)–MOF consists of two Zn(II) cations, one L^{5-} anion, one coordinated water molecule, three free water molecules, three free DMAc molecules, and one free dimethylammonium cation ($Me_2NH_2^+$) which results from the hydrolysis of DMAc under the reaction condition.[22] The five carboxylate groups of the L^{5-} ligand bind the metal ions *via* the μ_8-η^1:η^1:η^1:η^0:η^1:η^1:η^1:η^1:η^1:η^0 mode as depicted in Fig. S1.† The Zn1 center adopts a distorted tetrahedral geometry surrounded by four oxygen atoms from four distinct L^{5-} ligands, while the ZnO_5 pentacoordination in Zn2 is provided by four carboxylate oxygen atoms from four separate L^{5-} ligands (Zn–O = 1.901(3)–2.079(5) Å) and one coordinated water molecule (Zn–O1W = 2.172(6) Å). The two Zn(II) ions are held together by three bis-bidentate carboxylate groups from three different L^{5-} ligands, forming a triple lamella "paddle-wheel" secondary building unit (SBU) (Fig. S2†). In the crystal structure of Zn(II)–MOF, these SBUs are connected together through L^{5-} ligands to give a 3D structure (Fig. 2), which contains two different kinds of channels along the *b*-axis: smaller quadrilateral channels of 7.7 Å × 5.4 Å (measured between opposite atoms) and larger quadrilateral channels of 13.8 Å × 16.4 Å (measured between opposite atoms) in size, as shown in Fig. 3. Both ends of the L^{5-} ligands are linked together with the binuclear SBUs to form the larger channel, while only one end of the L^{5-} ligands connect the binuclear SBUs to form the smaller 1D channel. The total solvent accessible volume calculated using PLATON is 68.1% of the unit cell volume.

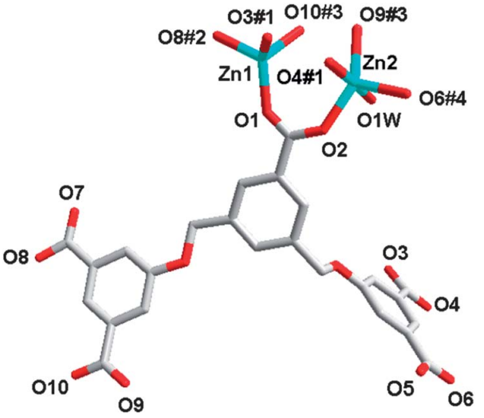


Fig. 1 Coordination environment of the Zn(II) center in Zn(II)–MOF. Symmetry code: #1 x, $1.5 - y$, $0.5 + z$; #2 $-x$, $1 - y$, $1 - z$; #3 x, $1 + y + 2$, $1 + z$; #4 $1 - x$, $0.5 + y$, $0.5 - z$ (all of the H atoms and solvent molecules are omitted for clarity).

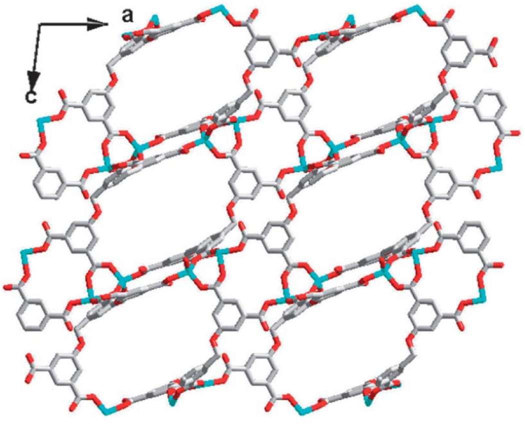


Fig. 2 Three-dimensional network structure of Zn(II)–MOF.

A better insight into the nature of the intricate framework can be achieved by the application of a topological approach, reducing multidimensional structures to simple nodes and

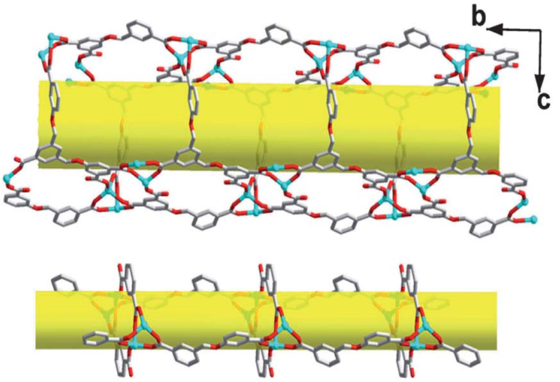


Fig. 3 Representation of the two kinds of quadrilateral nanotube-like channels of Zn(II)–MOF viewed along the *a*-axis.

connection nets. If the paddle-wheel cluster (which bonds to five separate L^{5-} ligands) is considered as a five-connecting node, and the L^{5-} ligand is also considered as a five-connecting node, the structure displays the unusual 3D 5-connected *vbk* net (both nodes are topologically equivalent) with the point (Schläfli) symbol of $\{4^5.6^5\}$ calculated with TOPOS[23] (Fig. 4). To the best of our knowledge, only a few examples of frameworks with 5-connected networks have been reported to date.[24]

Thermogravimetric analysis

The thermal stability of Zn(II)–MOF was examined by thermogravimetric analysis (TGA) in the temperature range of 30–800 °C with a heating rate of 10 °C min^{-1} under an air atmosphere, as shown in Fig. S4.† The curve exhibits three major losses in the temperature range of 30–510 °C, the weight loss of 5.35% during the first step between 30 and 98 °C corresponds to the loss of three lattice H_2O (calculated 5.32%), and the weight loss of 32.13% during the second step between 98 and 230 °C corresponds to the loss of three guest DMAc molecules, one free dimethylammonium cation and one coordinated H_2O molecule (calculated 32.04%). Decomposition of Zn(II)–MOF began above 230 °C. The residue was ZnO (experimental: 16.31% and calculated: 16.03%).

Host–guest system

Single-crystal X-ray diffraction revealed that the framework of Zn(II)–MOF is anionic, with dimethylammonium cations and DMAc molecules residing in the 1D channels. The solvent molecules could not be removed completely by solvent exchange and subsequent drying in vacuum. Furthermore, gas sorption measurements gave low sorption values, though this technique can be of limited value in demonstrating porosity in certain systems.[25] Thus, to further probe the permanent porosity and accessibility of Zn(II)–MOF, the dye-adsorptions were measured with a range of different dyes.[26] When immersed into DMAc solutions of toluidine blue (TB), methylene blue (MB), and rhodamine 6G (R6G) at different times at room temperature, respectively, Zn(II)–MOF presents different adsorption behaviors toward these dyes as monitored by UV-Vis absorption spectroscopy (Fig. 5, S5 and S6†), in the order of TB > MB > R6G, which could be mainly ascribed to the anionic nature of the framework of Zn(II)–MOF. Their molecular structures are shown in Fig. S7.† It is noteworthy that the solution color of TB decreased in the process with the increased time and nearly disappeared after 30 min, and the corresponding absorbance of the solution almost decreased to zero. It is also worth mentioning that when the mixtures are shaken adsorption is instantaneous. These adsorption phenomenon clearly show that Zn(II)–MOF possesses rapid adsorption of organic dye TB molecules.

Exposure of Zn(II)–MOF to a solution of TB in DMAc (3 mL, 10^{-3} M) indicated that Zn(II)–MOF adsorbs TB quickly. TB belongs to the class of thiazine dyes, and it exhibits strong absorption in the visible region. Fig. 6 shows the fluorescence spectra for TB@Zn(II)–MOF. Obviously, the strongest emission peak for TB@Zn(II)–MOF is at 704 nm with the excitation peak at 640 nm at room temperature, which is similar to the previous

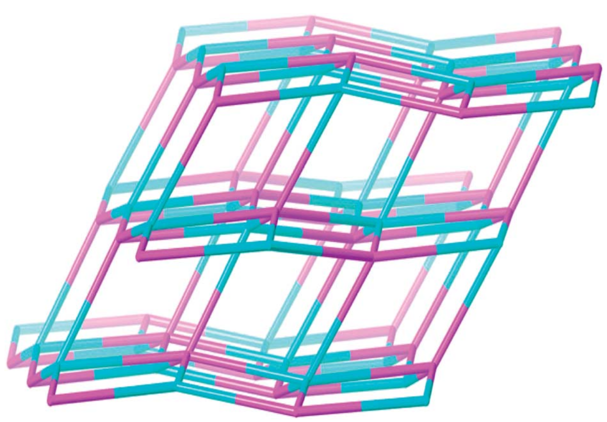


Fig. 4 Novel 5-connected network with $\{4^5.6^5\}$ topology of Zn(II)–MOF (the purple nodes represent the Zn paddle-wheel SBUs, the light blue nodes represent the L^{5-} ligands).

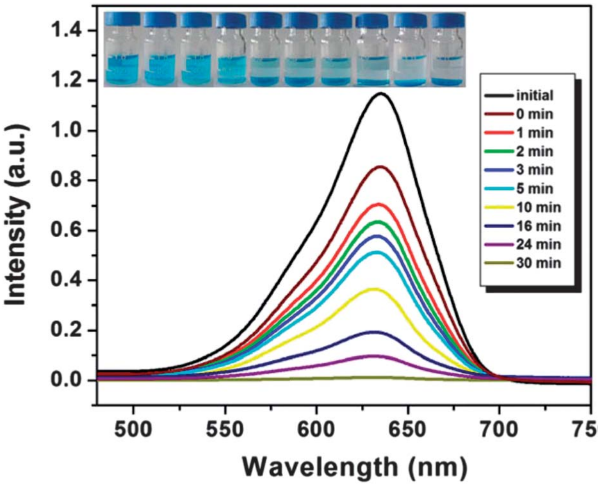


Fig. 5 UV-Vis spectra of the original and Zn(II)–MOF treated (30 mg) organic dye TB (5.0×10^{-5} M, 2 mL) solution at various times. The insets are photos of the corresponding solutions at various times.

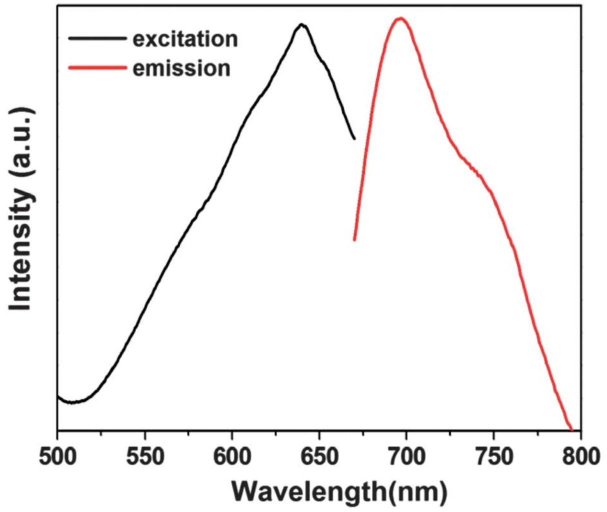


Fig. 6 Fluorescence spectra of TB@Zn(II)–MOF at room temperature.

results obtained on TB-doped materials.[27] Furthermore, TB@Zn(II)–MOF can also be obtained by immersing Zn(II)–MOF in solutions of TB in DMAc with different concentrations (10^{-4}, 10^{-5}, and 10^{-6} M) for 30 min. We can see that the emission peaks present a blue shift (703 nm, 680 nm, and 657 nm, respectively) when the concentration of the TB solution used to prepare TB@Zn(II)–MOF is decreased from 10^{-3} to 10^{-6} M (Fig. S8†), which implies that the TB in the crystals is present as free monomer molecules and shows fine fluorescence properties.[28] The PXRD patterns of dye-included MOFs are virtually the same as the pristine Zn(II)–MOF (Fig. S3†), indicating that the structural integrity and open channels of the porous Zn(II)–MOF are maintained after exposure to the solution.

Zn(II)–MOF was then placed into an apparatus to filter DMAc solutions of TB (Fig. 7a). The much decreased color of the outflow compared with original solution shows successfully removal of TB from the DMAc solution. Furthermore, Zn(II)–MOF exhibits the highest efficiency and it maintains a filter efficiency of 100% for TB until a critical concentration of 120 mL g^{-1} (Fig. 5b and inset). After that the efficiency drops rapidly due to the penetration of dye molecules.

Luminescence properties

As mentioned above, the porous Zn(II)–MOF contains quadrilateral-like channels (dimensions *ca.* 13.8 Å × 16.4 Å) and dimethylammonium cations reside in its 1D pores, which makes it suitable for the trapping of different Ln^{3+} cationic species into the host framework to form a heterometallic host–guest system, and sensitize their emissions to exhibit mono- or dual-emission. Lanthanide(III) ions were introduced into the pores of Zn(II)–MOF, by soaking the samples in DMAc solutions (3 mL) of hydrochloride salts of Eu^{3+} or Tb^{3+} (0.1 mmol) (0.470Eu^{3+}@Zn(II)–MOF, 0.470Tb^{3+}@Zn(II)–MOF). The doped amounts of the lanthanide ions were confirmed by inductively coupled plasma spectroscopy (ICP). The PXRD patterns of the Eu^{3+}, Tb^{3+} loaded samples confirmed that the structure of Zn(II)–MOF was maintained upon the lanthanide ion adsorption (Fig. S3†). Upon excitation with a standard laboratory UV lamp (365 nm), the europium and terbium loaded samples emitted their respective red and green colors, which can be readily observed by the naked eye as a qualitative indication of lanthanide sensitization. The excitation and emission spectra measured at room temperature for the powder samples of H_5L and Zn(II)–MOF are displayed in Fig. 8. The free H_5L ligand exhibits a strong emission at 419 nm presumably due to π–π* transitions under 366 nm UV light excitation. Zn(II)–MOF exhibits more enhanced blue light emission and shifts slightly to 424 nm with the excitation at 359 nm. The 0.470Eu^{3+}@Zn(II)–MOF exhibits the characteristic transitions of Eu^{3+} excited at 359 nm, which are assigned to the transitions between the first excited state ($^5D_0$) and the ground multiplet (^7F_J, $J = 0$–4) for Eu^{3+} at 578, 591, 615, 649 and 698 nm (Fig. 8c). The quantum yield of 0.470Eu^{3+}@Zn(II)–MOF is 5%. Similarly, the 0.470Tb^{3+}@Zn(II)–MOF displays additional characteristic transitions of Tb^{3+} excited at 359 nm, which are attributed to the transitions between the first excited state ($^5D_4$) and the ground multiplet (^7F_J, $J = 6$–3) at 488, 542, 582 and 620 nm for Tb^{3+}

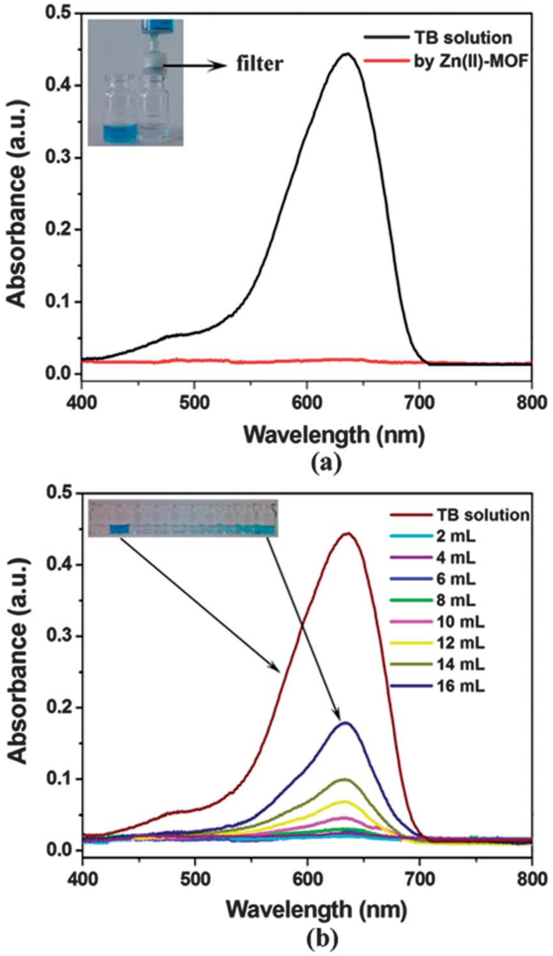


Fig. 7 (a) UV-Vis spectra and images of (a) the original (3.0×10^{-5} M) and filtered TB solution with Zn(II)–MOF. (b) Filtrate collected at different filter amounts of TB DMAc solution. The amount of adsorbent was 50 mg.

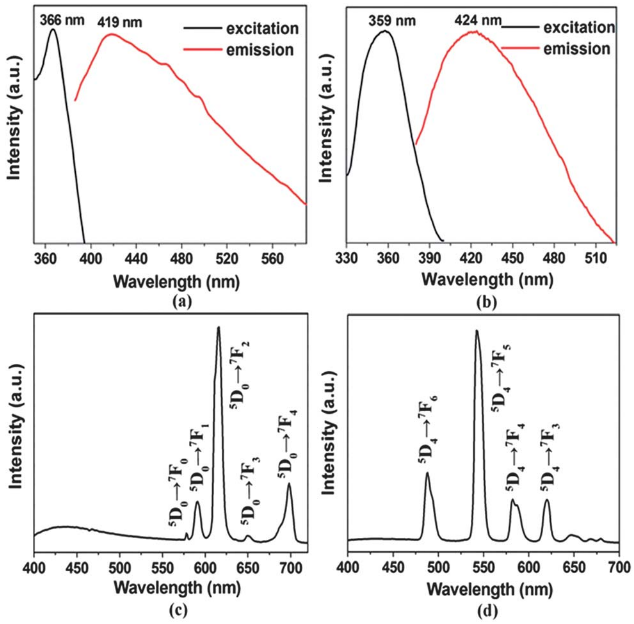


Fig. 8 (a) Excitation and emission spectra of the H_5L ligand. (b) Excitation and emission spectra of Zn(II)–MOF. (c) Emission spectra of Eu^{3+}@Zn(II)–MOF excitation at 359 nm. (d) Emission spectra of Tb^{3+}@Zn(II)–MOF excitation at 359 nm.

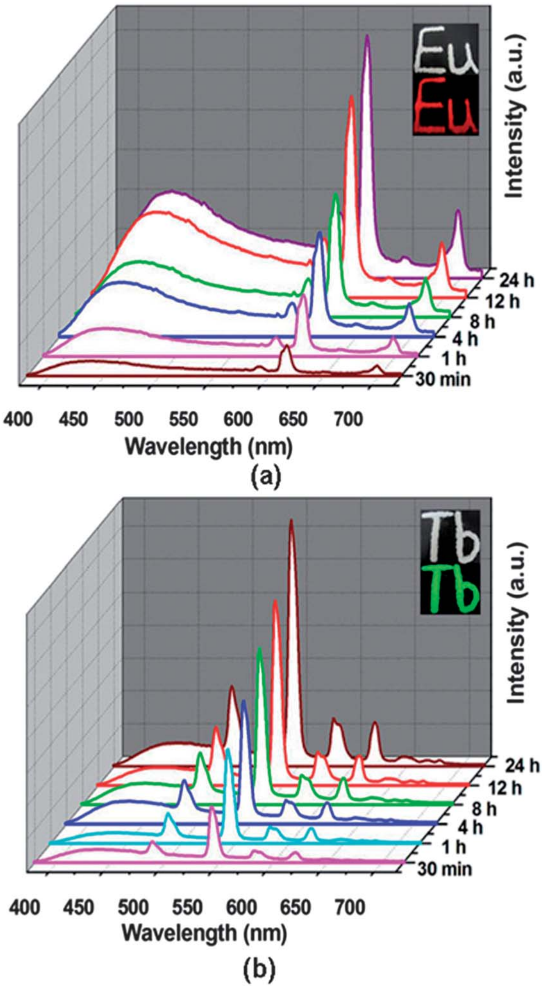


Fig. 9 The emission spectra for Zn(II)–MOF in DMAc solution of Eu^{3+} (a) and Tb^{3+} (b) at 0.5 h, 1 h, 4 h, 8 h, 12 h and 24 h and photographs showing the crystals of Eu^{3+}@Zn(II)–MOF and Tb^{3+}@Zn(II)–MOF with natural light (inset, top) and 365 nm laboratory UV light (inset, bottom).

(Fig. 8d). The quantum yield of 0.470Tb^{3+}@Zn(II)–MOF is 17%. We can see that the intensity of the ligand nearly disappears. These results suggest that the energy transfer from Zn(II)–MOF to the lanthanide centers is very effective when the Eu^{3+} or Tb^{3+} emitters are brought into the Zn(II)–MOF. The luminescent lifetimes of 0.470Eu^{3+}@Zn(II)–MOF and 0.470Tb^{3+}@Zn(II)–MOF were measured and found to be 1.1022 ns and 2.4648 ns, respectively, and they have shown much shorter lifetimes compared with other strong fluorescence materials.[29] Despite this limitation, the doped materials displayed strong luminescence which can be easily observed by the naked eye and a high quantum yield.

In order to investigate the Eu^{3+} and Tb^{3+} adsorption processes, fresh samples of Zn(II)–MOF with the same quality (30 mg) were immersed in 3 mL DMAc solution with 0.1 mmol Ln^{3+} for different times (0, 0.5 h, 1 h, 4 h, 8 h, 12 h, 24 h), respectively. This adsorption process was then monitored by photoinduced emission spectra. The emission monitoring indicated that with the increase of immersion time, the entry of Eu^{3+} or Tb^{3+} ions into the Zn(II)–MOF host framework led to a distinct increase of the emission intensity as the guest loading increased. Upon excitation with a standard UV lamp (λ_{ex} = 365 nm), Eu^{3+}@Zn(II)–MOF and Tb^{3+}@Zn(II)–MOF emit their corresponding red and green emission (Fig. 9), which can be readily observed by the naked eye as a qualitative indication of lanthanide sensitization.

As expected, when the amount of Eu^{3+} or Tb^{3+} introduced into Zn(II)–MOF increases, the corresponding emissions increase gradually. We can see that the Eu^{3+}-exchanged materials generate tunable colors from blue, blue-red, red, red-yellow, and the Tb^{3+}-exchanged materials generate tunable colors from blue to blue-green, green, green-yellow. The corresponding CIE chromaticity photographs of the tunable colors generated from the doped Eu^{3+}@Zn(II)–MOF and Tb^{3+}@Zn(II)–MOF excited under 359 nm are shown in Fig. S9.†

It is expected that trapping two kinds of lanthanide ions into porous MOFs for developing compounds with tunable luminescent properties is a promising approach. Notably, developing high performance white-light emitting compounds has attracted much attention due to their important applications in general lighting sources. Recently, significant efforts have been made towards the design and synthesis of hetero-lanthanide-based materials.[30] However, f–f hybrid coordination compounds are very hard to prepare selectively. A new approach *via* a simple cation exchange based on porous MOFs[31] perhaps could provide an alternative way to access to white-light emitting materials.

The tunable colors from the doped Eu^{3+}@Zn(II)–MOF and Tb^{3+}@Zn(II)–MOF provided the basis for us to compensate the blue color from Zn(II)–MOF, green color from Tb^{3+} and red color from Eu^{3+} in the co-doped $x$$Eu^{3+}$/$y$$Tb^{3+}$@Zn(II)–MOF by adjusting

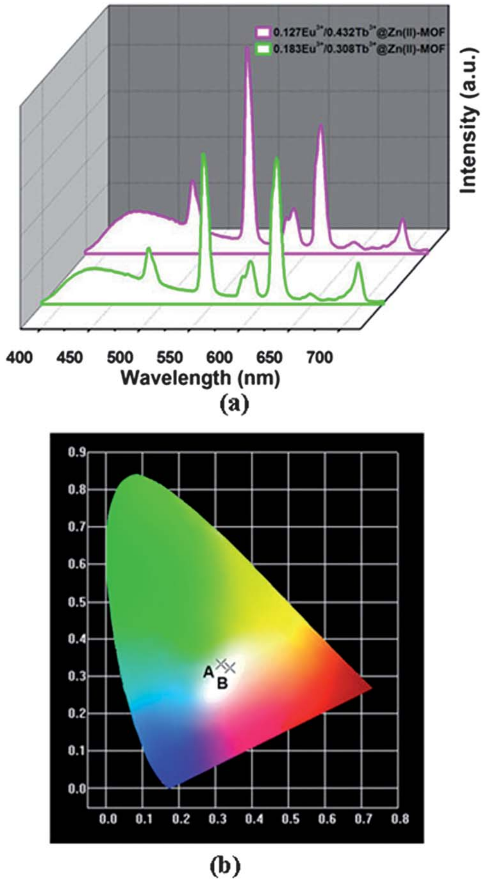


Fig. 10 (a) Emission spectra of $0.183\mathrm{Eu}^{3+}/0.408\mathrm{Tb}^{3+}$@Zn(II)–MOF and $0.127\mathrm{Eu}^{3+}/0.432\mathrm{Tb}^{3+}$@Zn(II)–MOF excitation at 359 nm. (b) CIE chromaticity diagram for the $x\mathrm{Eu}^{3+}/y\mathrm{Tb}^{3+}$@Zn(II)–MOF monitored under 359 nm ((A) $x = 0.127$, $y = 0.432$ and (B) $x = 0.183$, $y = 0.408$).

different amounts of the doped Eu^{3+} and Tb^{3+} ions. A series of Ln^{3+}-exchanged materials with different guest Ln^{3+} ratios were obtained. The PXRD patterns on the resulted heterometallic materials are identical to that of Zn(II)–MOF, so the framework is stable during the different lanthanide species adsorption (Fig. S3†). The emission spectra of these loaded samples excited at 359 nm are listed in Fig. S10.† The emission spectra of the Ln^{3+}-exchanged materials exhibit characteristic emissions of the Eu^{3+} and Tb^{3+} and the blue emission of the Zn(II)–MOF. We can see that the emission spectra of Tb^{3+} exhibits significant decrease along with the decrease of Tb^{3+} concentration, while the emission spectrum of Eu^{3+} is largely enhanced along with the increase of Eu^{3+} concentration and these results herein confirms that energy transfer does occur from Tb^{3+} to Eu^{3+} when the two kinds of lanthanide species co-exist in the Zn(II)–MOF.[2b] Such multiband emissions from the heterolanthanide doped Zn(II)–MOF might be a barcoded luminescent material.[32] When the emission intensities at 434, 543, and 616 nm can be compensated, white light emission can be readily produced. Accordingly, the best combination of Eu^{3+} and Tb^{3+} concentration in the Ln^{3+}-exchanged materials for white light emission is $0.127\mathrm{Eu}^{3+}/0.432\mathrm{Tb}^{3+}$@Zn(II)–MOF (the quantum yield is $\eta = 7\%$) and $0.183\mathrm{Eu}^{3+}/0.408\mathrm{Tb}^{3+}$@Zn(II)–MOF (the quantum yield is $\eta = 8\%$) with the corresponding CIE coordinates being (0.312, 0.335) and (0.339, 0.327), respectively; both are very close to the coordinates for pure white-light (0.333, 0.333), according to the 1931 CIE coordinate diagram (Fig. 10).

Conclusion

In conclusion, we have successfully synthesized an anionic porous metal–organic framework, $\{[\mathrm{Zn_2(L)\cdot H_2O}]\cdot 3\mathrm{H_2O}\cdot 3\mathrm{DMAc}\cdot \mathrm{NH_2(CH_3)_2}\}_n$ (Zn(II)–MOF), with large 1D nanotubular channels of 13.8 Å × 16.4 Å and a rare 5-connected *vbk* net $\{4^5.6^5\}$ topology, constructed from "paddle-wheel" secondary building units. The MOF was also shown to readily and quickly adsorb toluidine blue dye molecules. In addition, white light emitting materials were obtained based on the porous Zn(II)–MOF by a cation exchanged approach. It is believed that these results will further facilitate the exploration of such MOFs as new types of functional materials for applications in fields such as environmental issues and optical materials. Further investigations in this domain are underway.

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