

## Supporting Information

### **A microporous anionic metal–organic framework for aqueous encapsulation and highly reversible sensitization of emitting Tb<sup>3+</sup> ion**

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**Materials and Measurements.** All reagents and solvents were commercially available and were used without further purification. The solutions were prepared with 18 mΩ•cm ultrapure water. All glassware was cleaned prior to use by sequential washing in 1M HCl and 1M HNO<sub>3</sub>, followed by a thorough rinsing with ultrapure water. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400-4000 cm<sup>-1</sup> region. Photoluminescence analyses were performed on an Edinburgh FLS55 luminescence spectrometer. Elemental analyses (C, H and N) were performed with a Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5°C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). An Axis ultra spectrometer was selected to measure X-ray photoelectron spectroscopy (XPS).

**Crystallography.** The diffraction data was collected at 296(2) K for Me<sub>2</sub>NH<sub>2</sub>@MOF-1, with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scanwidth of 0.3° and Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were carried out utilizing

SADABS routine.<sup>[1]</sup> The structures were solved by direct methods and refined using the SHELXTL 97 software.<sup>[2]</sup> Atoms were located from iterative examination of difference Fmaps following least squares refinements of the earlier models. All the atoms except hydrogen atoms, which were fixed at calculated positions and refined by using a riding mode, were refined anisotropically until full convergence was achieved. It was necessary to constrain or restrain a number of bond lengths and angles in the structure in order to get a stable refinement and chemically reasonable model. The microporous framework was occupied by extremely electron density, which could be assigned to be free solvent molecules. Because these guest solvents in the crystal are highly disordered and impossible to refine using conventional discrete-atom models, the SQUEEZE subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered solvent molecules, and sets of solvent-free diffraction intensities were produced. The free solvent molecules for Me<sub>2</sub>NH<sub>2</sub>@MOF-1 were determined by combining single crystal structures, elemental microanalysis and TGA data. The crystallographic data and selected bond lengths and angles for Me<sub>2</sub>NH<sub>2</sub>@MOF-1 are listed in Table S2 and Table S3, respectively. CCDC: 1557752 contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC) via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Synthesis of [H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>][KZn<sub>2</sub>(bpyp)(dcba)<sub>2</sub>]·DMF·1.5H<sub>2</sub>O (Me<sub>2</sub>NH<sub>2</sub>@MOF-1).** A mixture of bpyp (23.35 mg, 0.10 mmol), H<sub>3</sub>dcba (48.36 mg, 0.10 mmol) and Zn(CH<sub>3</sub>COOH)<sub>2</sub>·2H<sub>2</sub>O (66.36 mg, 0.25 mmol) was dissolved in DMF (2.0 mL) in a screw-capped vial. After three drops of KOH (0.01M.) and 1.0 mL water were added to the mixture, the vial was

capped and placed in an oven at 105 °C for 7 days. The resulting single crystals were washed with DMF and dried in air to give Me<sub>2</sub>NH<sub>2</sub>@MOF-1. Yield: 65%. Elemental analysis calcd (%) for C<sub>62</sub>H<sub>51</sub>Zn<sub>2</sub>KN<sub>5</sub>O<sub>13.5</sub>: C, 59.55; H, 4.17; N, 5.59. Found: C, 61.11; H, 4.24; N, 5.62%. IR (KBr, cm<sup>-1</sup>; see Fig S8): 3448(m), 2946(w), 2485(w), 1941(w), 1667(m), 1605(s), 1408(w), 1368(s), 1193(m), 1005(m), 774(s), 586(w), 445(w).

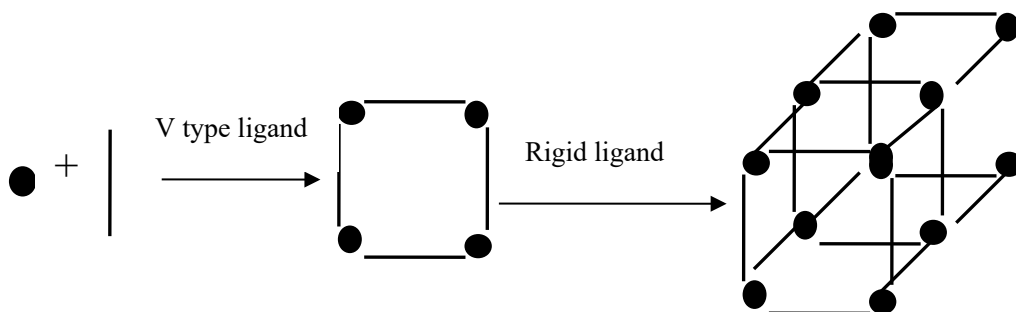
### **Preparation of Ln<sup>3+</sup>@MOF-1 (Ln<sup>3+</sup> = Sm<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, or Dy<sup>3+</sup>) and Na<sup>+</sup>@MOF-1.**

**Ln<sup>3+</sup>@MOF-1:** The Me<sub>2</sub>NH<sub>2</sub>@MOF-1 material was soaked in 5 ml the Ln<sup>3+</sup> nitrate solution (Sm<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, or Dy<sup>3+</sup>), held for 24 h, then refreshed the Ln<sup>3+</sup> nitrate solution, repeated the procedure in total of 14 times; After cation exchange was completed, the materials were thoroughly washed with pure water for several times until no characteristic emission was observed upon excitation, and then dried in air.

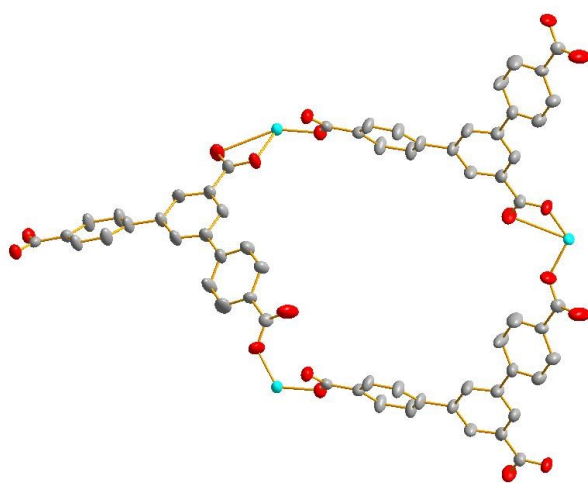
**Na<sup>+</sup>@MOF-1:** The Tb<sup>3+</sup>@MOF-1 material was soaked in 5 ml a saturated solution of NaCl in H<sub>2</sub>O, held for 12 h, then refreshed the saturated solution, repeated the procedure in total of 12 times; After cation exchange was completed, the materials were thoroughly washed with pure water for several times, and then dried in air.

### **References**

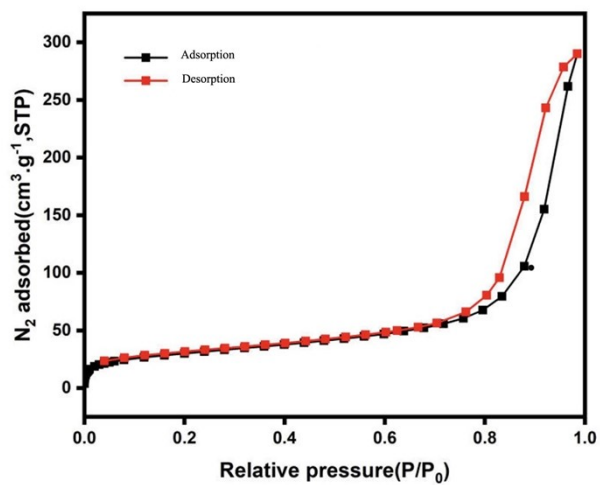
- [1] Bruker. SADABS, SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, **2002**.
- [2] G. M. Sheldrick, SHELXL-97, program for the refinement of the crystal structures. University of Göttingen, Germany, **1997**.



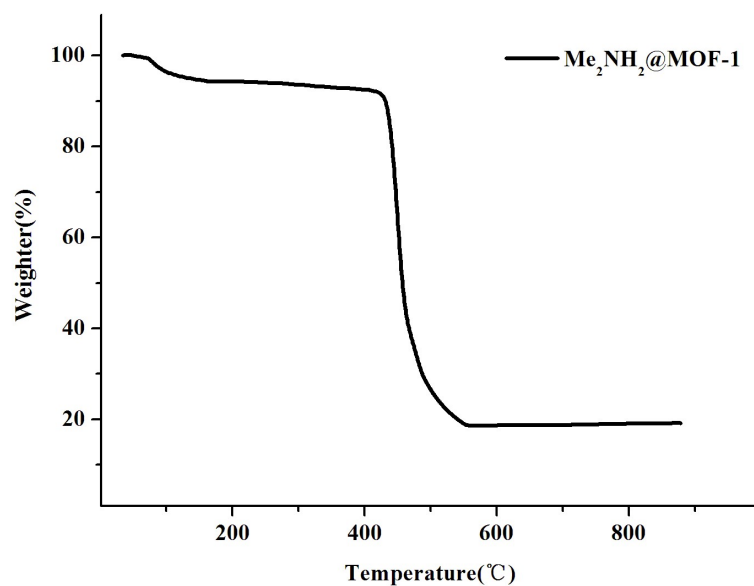
**Scheme S1** The microporus formation



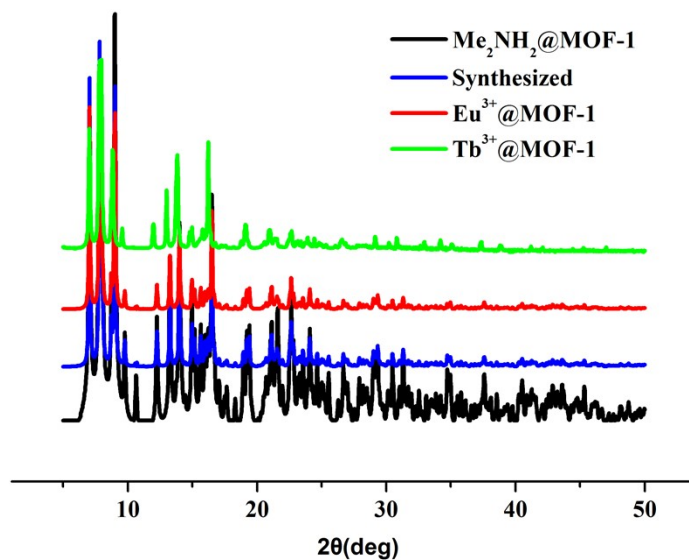
**Fig S1** The dcba ligand is connected to the zinc atom to form sub-molecules.



**Fig S2** View of the BET surface area of **1**.

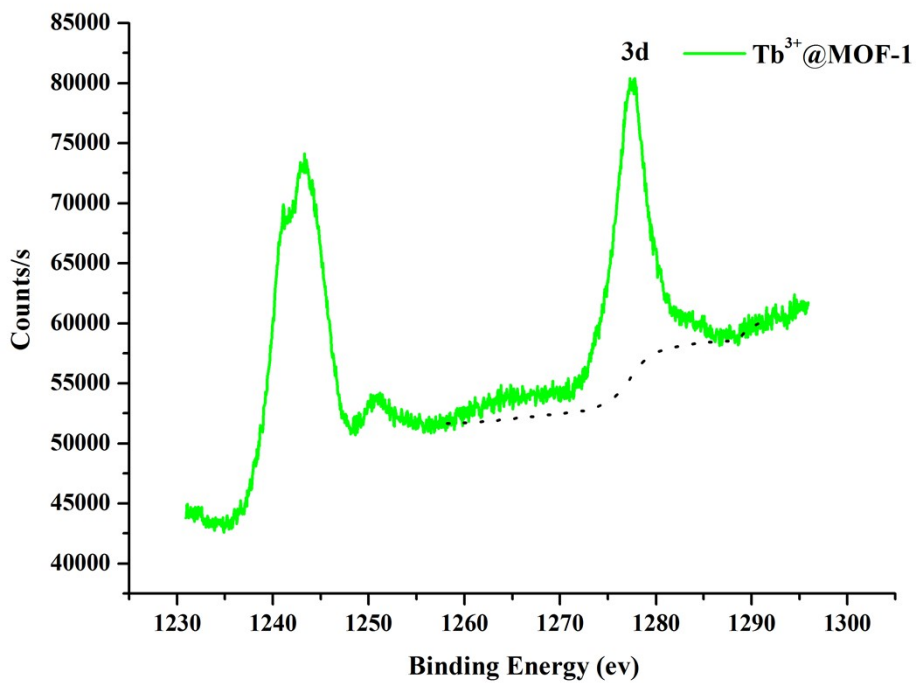
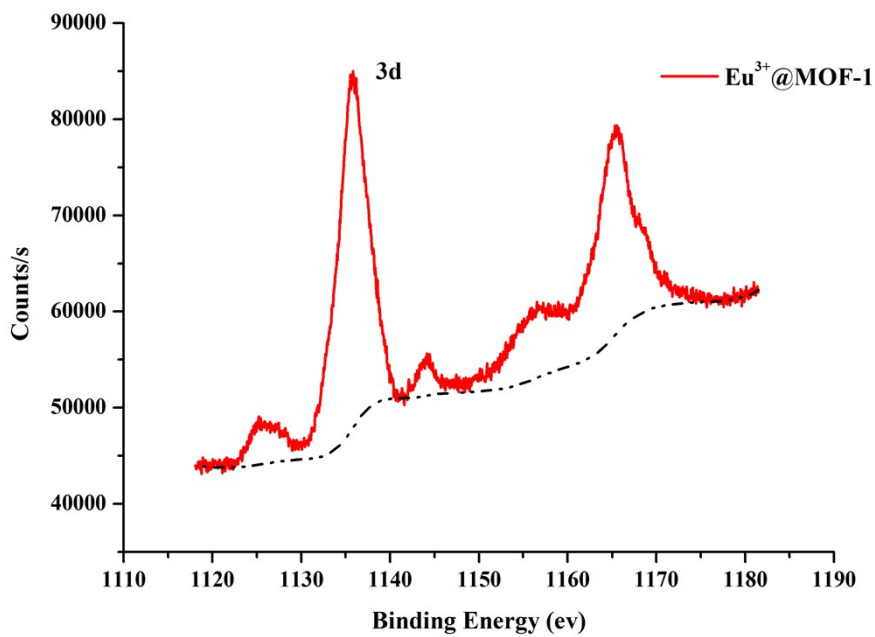


**Fig S3** TGA plot of  $\text{Me}_2\text{NH}_2@\text{MOF-1}$  under  $\text{N}_2$  environment. Thermogravimetric analysis (TGA) reveals that  $\text{Me}_2\text{NH}_2@\text{MOF-1}$  can be stable up to  $400^\circ\text{C}$ . In the temperature range  $70\text{--}160^\circ\text{C}$ , there is loss of DMF and  $\text{H}_2\text{O}$  molecules (found = 8.1%, calcd = 8.0%).



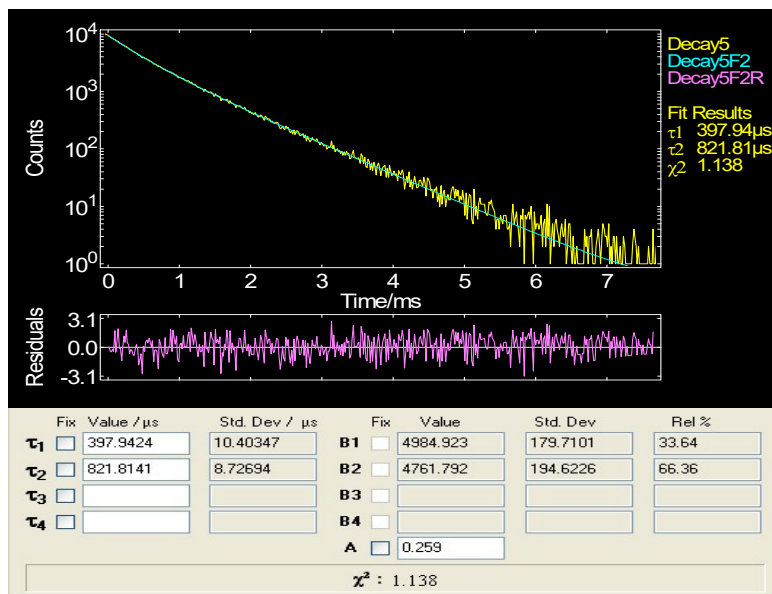
**Fig S4** The XRPD patterns at room temperature.

The X-ray powder diffraction (XRPD) patterns were checked at room temperature, although minor differences can be seen in the positions, intensities, and widths of some peaks, which indicates that  $\text{Me}_2\text{NH}_2@\text{MOF-1}$  were obtained as a single phase and the porous frameworks of  $\text{Eu}^{3+}@\text{MOF-1}$  and  $\text{Tb}^{3+}@\text{MOF-1}$  were almost unchanged.

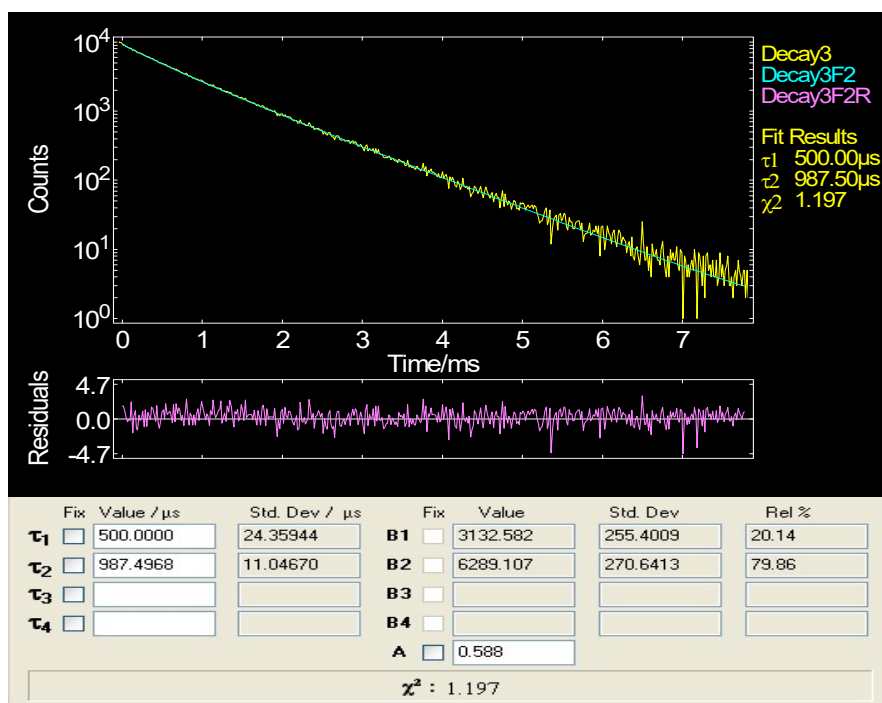


**Fig S5** The X-ray photoelectron spectroscopy (XPS) experiment on Eu<sup>3+</sup>@MOF-1 and Tb<sup>3+</sup>@MOF-1 showed that the interaction between Eu<sup>3+</sup>/Tb<sup>3+</sup> and framework.

**Eu<sup>3+</sup>@MOF-1:**

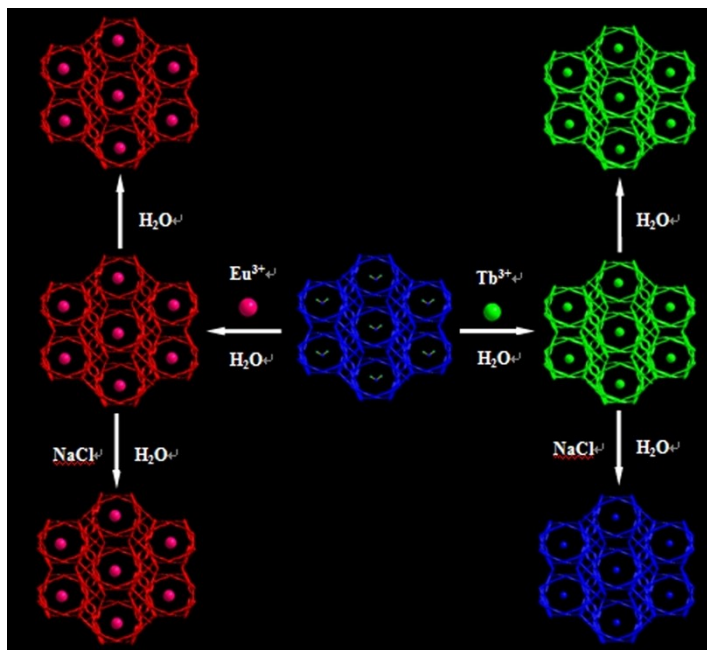


### Tb<sup>3+</sup>@MOF-1:

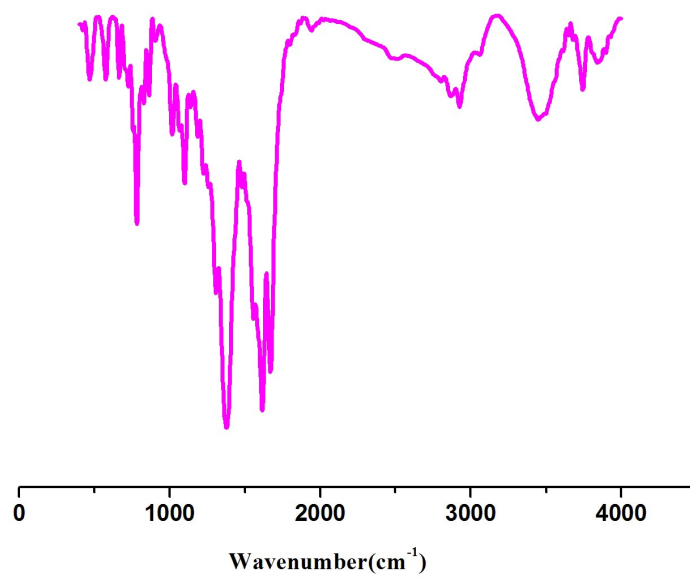


**Fig S6** Eu<sup>3+</sup>@MOF-1 and Tb<sup>3+</sup>@MOF-1 luminescence lifetimes at room temperature.

The lifetime at 618 nm emission of Eu<sup>3+</sup>@MOF-1 shows 398  $\mu$ s (33.64%) / 822  $\mu$ s (66.36 %),  $\chi^2 = 1.138$  and the lifetime at 538 nm emission of Tb<sup>3+</sup>@MOF-1 shows 500  $\mu$ s (20.14%) / 987  $\mu$ s (79.86 %),  $\chi^2 = 1.197$ . The observation indicates that Eu<sup>3+</sup>@MOF-1 and Tb<sup>3+</sup>@MOF-1 may be the excellent candidate for potential photoactive material.



**Fig S7**  $Tb^{3+}$  can be exchanged reversibly, and  $Eu^{3+}$  is an irreversible exchange.





**Fig S8** The IR patterns of **Me<sub>2</sub>NH<sub>2</sub>@MOF-1**.

Sl. No.	Cations	Number of Cations per Formula Unit	Exchange of Cations with [Me <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup> per Formula Unit
1	Sm <sup>3+</sup>	0.225	0.675
2	Eu <sup>3+</sup>	0.293	0.879
3	Tb <sup>3+</sup>	0.268	0.804
4	Dy <sup>3+</sup>	0.250	0.750

**Table S1:** ICP-MS data for cation exchange**Table S2** Selected crystallographic data for **Me<sub>2</sub>NH<sub>2</sub>@MOF-1**

Compound	<b>Me<sub>2</sub>NH<sub>2</sub>@MOF-1</b>
Empirical formula	C <sub>62</sub> H <sub>51</sub> Zn <sub>2</sub> KN <sub>5</sub> O <sub>13.5</sub>
Formula mass	1251
Crystal system	Monoclinic
Space group	C 2/C
<i>a</i> [Å]	13.347(2)
<i>b</i> [Å]	22.155(4)
<i>c</i> [Å]	25.424(4)
<i>α</i> (°)	90
<i>β</i> (°)	99.205
<i>γ</i> (°)	90
<i>V</i> [Å <sup>3</sup> ]	7421
<i>Z</i>	4
T <sub>min</sub> , T <sub>max</sub>	0.622, 0.746
<i>μ</i> [mm <sup>-1</sup> ]	0.697
<i>F</i> [000]	2392
Reflections collected	4968
Final <i>R</i> <sup>[a]</sup> indices [I>2σ(I)]	<i>R</i> <sub>1</sub> = 0.0712 <i>wR</i> <sub>2</sub> = 0.2465

$$[a] R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}$$

**Table S3.** Selected bond lengths (Å) and angles (°) of Me<sub>2</sub>NH<sub>2</sub>@MOF-1

<b>Me<sub>2</sub>NH<sub>2</sub>@MOF-1</b>			
Zn(1)-O(1)	1.9559	Zn(1)-N(1)	2.0689
Zn(1)-O(3)	1.9071	Zn(1)-O(6)	2.7691
Zn(1)-O(5)	1.9546	K(1)-O(2)	2.7446
K(1)-O(4)	2.7502	K(1)-O(2A)	2.6172
K(1)-O(4A)	2.6744	O(1)-Zn(1)-N(1)	93.133
O(1)-Zn(1)- O(3)	123.731	O(1)-Zn(1)- O(6)	153.510
O(1)-Zn(1)- O(5)	105.512	N(1)-Zn(1)-O(3)	102.007
N(1)-Zn(1)-O(6)	84.112	N(1)-Zn(1)-O(5)	109.896
O(3)-Zn(1)-O(6)	82.449	O(3)-Zn(1)-O(5)	118.694
O(5)-Zn(1)-O(6)	51.916	O(2)- K(1)- O(4)	79.214
O(2)- K(1)- O(2A)	172.108	O(2)- K(1)- O(4A)	97.791
O(4)- K(1)- O(2A)	99.041	O(4)- K(1)- O(4A)	171.906
O(2A)-K(1)- O(4A)	82.895		

[a] Symmetry codes: A 1.5-x, 0.5-y, -z