Electronic Supporting Information (ESI)

A new anionic metal-organic framework showing tunable emission by lanthanide(III) doping and high selective CO_2 adsorption properties

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Contents

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1. Infrared (IR) spectra.

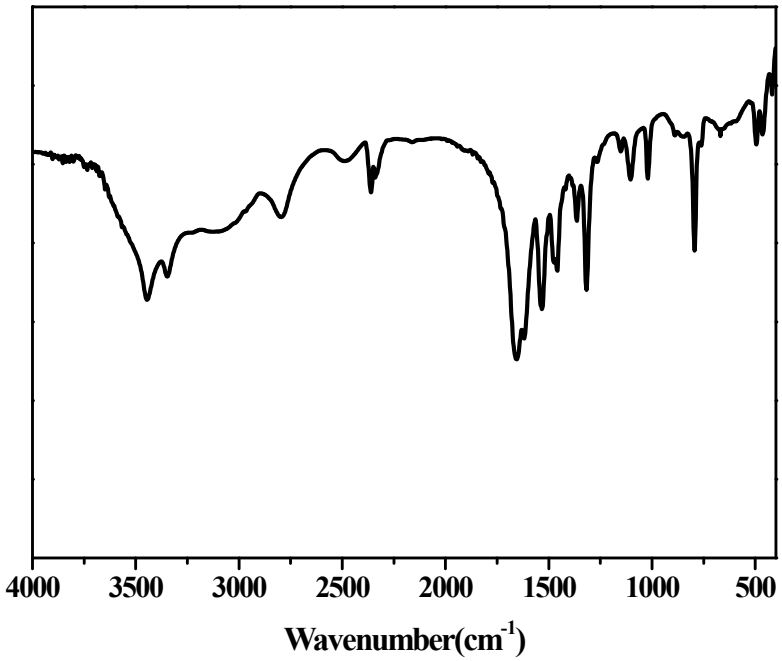

Fig. S1 IR spectrum of **1**.

2. Thermogravimetric anlysis (TGA).

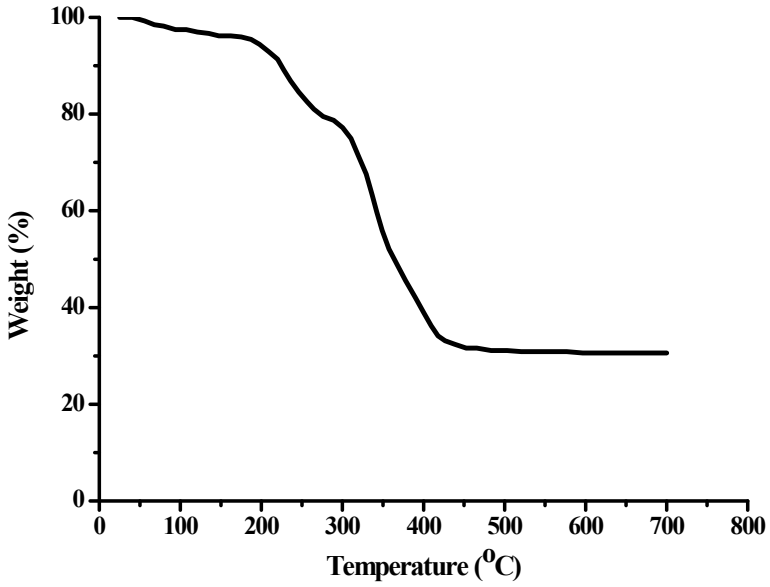

Fig. S2 Thermogravimetric curve of **1**.

3. Additional structure figures.

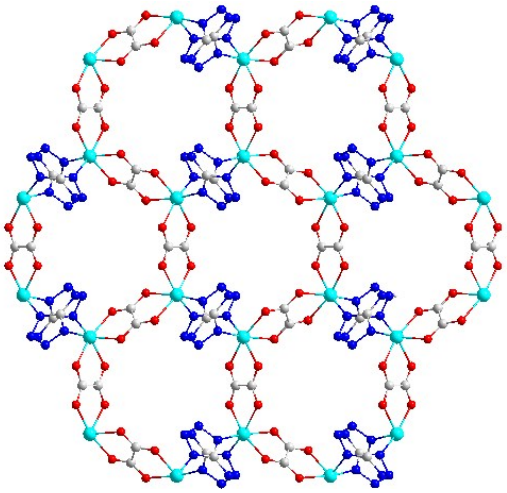

Fig. S3 The shape of the pore along *c*-axis.

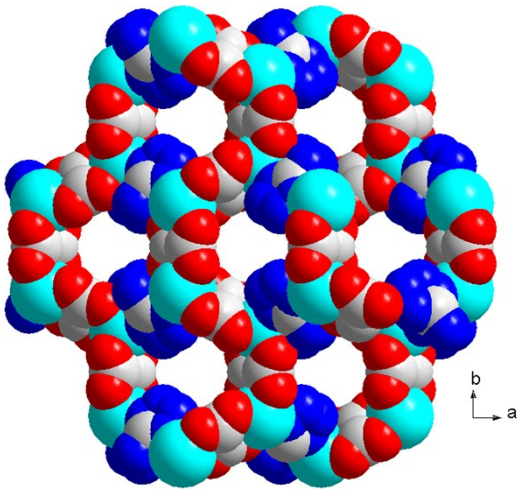

Fig. S4 Space-filling representation of the 3D open framework along *c*-axis.

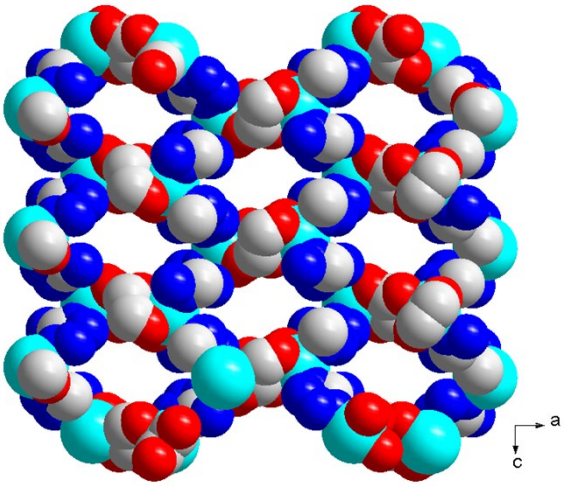

Fig. S5 Space-filling representation of the 3D open framework along *b*-axis.

4. PXRD patterns.

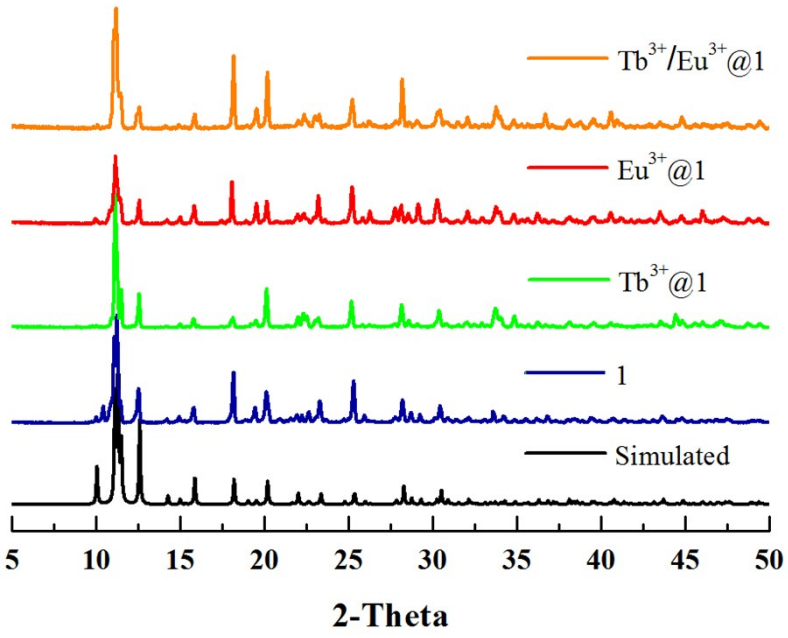

Fig. S6 PXRD patterns of the simulated **1**, as-synthesized **1**, **Tb^{3+}@1**, **Eu^{3+}@1** and **Tb^{3+}/Eu^{3+}@1** samples.

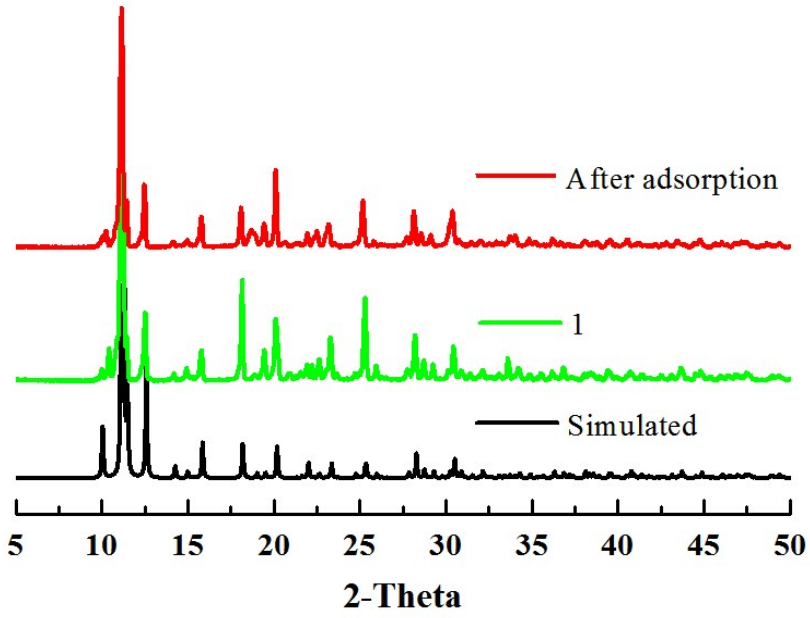

Fig. S7 The PXRD patterns of **1**: the simulated pattern based on X-ray single-crystal data (black), the as-synthesized (green) and the pattern after gas adsorption measurements (red).

5. Table S1 Selected bond distances and angles.

Table S1 Selected bond distances (Å) and angles (°) of **1**.

Complex **1**			
N(1)-Zn(1)	2.101(4)	N(4)-Zn(1)#3	2.103(4)
O(1)-Zn(1)	2.094(3)	O(2)-Zn(1)	2.208(3)
O(3)-Zn(1)	2.188(3)	O(4)-Zn(1)#2	2.108(3)
O(1)-Zn(1)-N(1)	100.34(14)	O(1)-Zn(1)-N(4)#4	88.32(14)
N(1)-Zn(1)-N(4)#4	94.05(15)	O(1)-Zn(1)-O(4)#2	165.49(13)
N(1)-Zn(1)-O(4)#2	91.94(13)	N(4)#4-Zn(1)-O(4)#2	98.56(14)
O(1)-Zn(1)-O(3)	90.45(12)	N(1)-Zn(1)-O(3)	168.28(13)
N(4)#4-Zn(1)-O(3)	90.81(14)	O(4)#2-Zn(1)-O(3)	76.77(12)
O(1)-Zn(1)-O(2)	77.11(12)	N(1)-Zn(1)-O(2)	90.79(14)
N(4)#4-Zn(1)-O(2)	165.26(14)	O(4)#2-Zn(1)-O(2)	95.17(12)
O(3)-Zn(1)-O(2)	87.13(13)		

Symmetry codes: #2: -x, -y, -z + 2; #4: -x + 1/2, -y, z + 1/2.

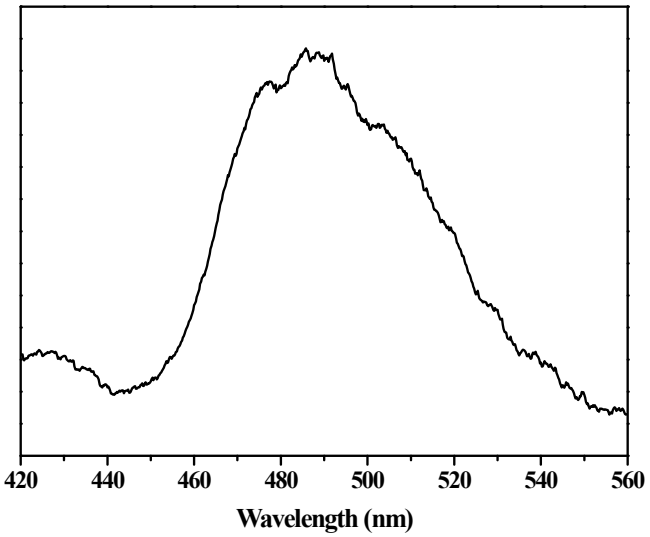

Fig. S8 Solid-state emission spectra of Hatz.

6. Gas adsorption measurements.

Samples of complex **1** and **Eu^{3+}@1** were treated with supercritical CO_2 in a Tousimis™ Samdri® PVT-30 critical point dryer. Prior to drying, the samples were soaked in absolute ethanol to exchange the occluded solvent for C_2H_5OH for 72 h. Then the ethanol-containing samples were placed inside the dryer and the ethanol was exchanged with CO_2 (liquid) over a period of 6 hrs according to literature.[S1] During this time the liquid CO_2 was vented under positive pressure for five minutes each hour. The processed samples were loaded in sample tubes and activated under high vacuum at 50 °C for **1**. Degassed samples were used for gas sorption measurements. Gas adsorption measurements were performed using an ASAP 2020 Surface Area and Porous analyzer.

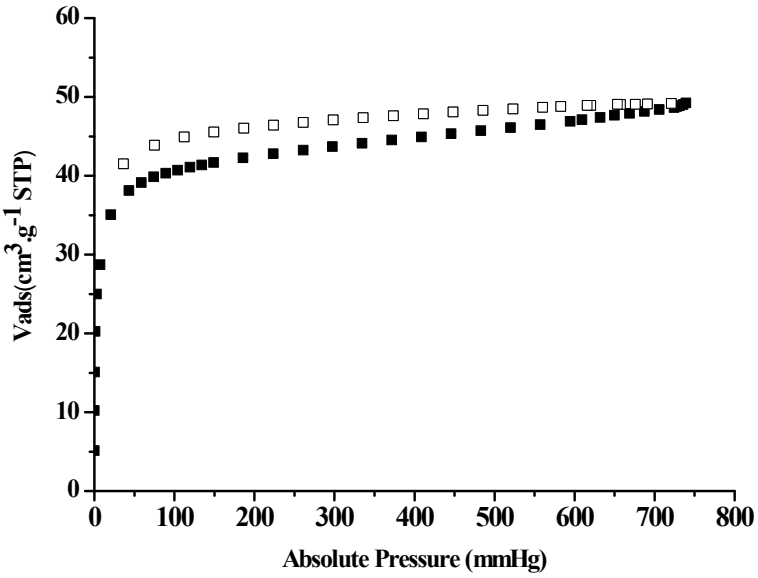

Fig. S9 Gas adsorption isotherms of CO_2 in **1** at 195 K (adsorption and desorption branches are shown with closed and open symbols, respectively).

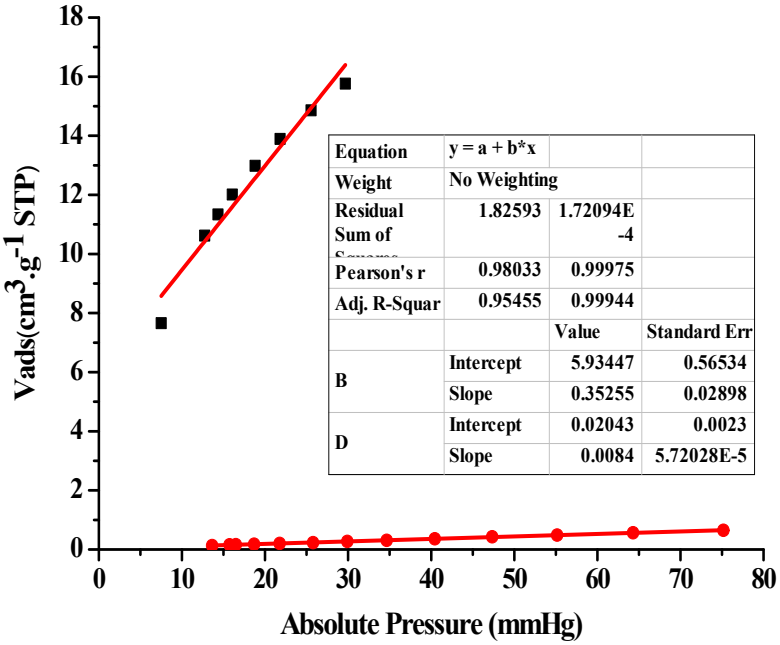

Fig. S10 The fitting initial slopes for CO_2 and CH_4 isotherms of **1** at 273 K.

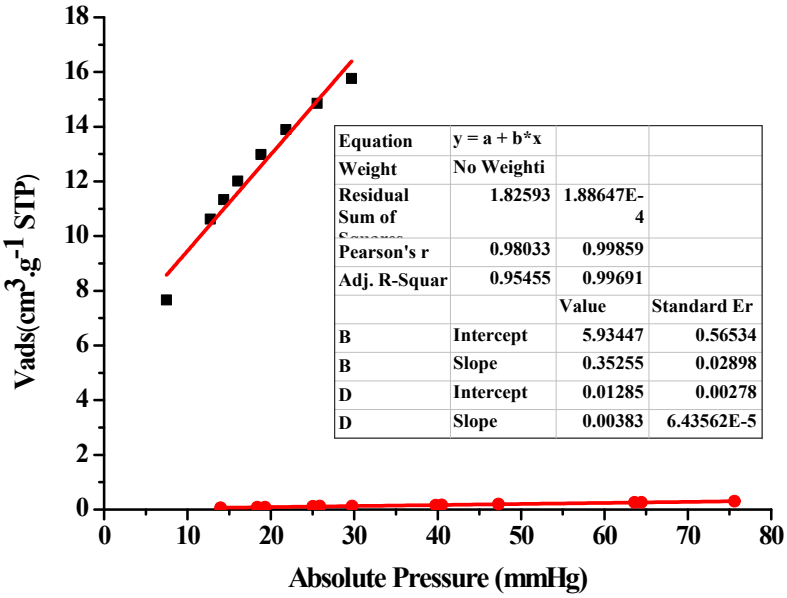

Fig. S11 The fitting initial slopes for CO_2 and N_2 isotherms of **1**at 273 K.

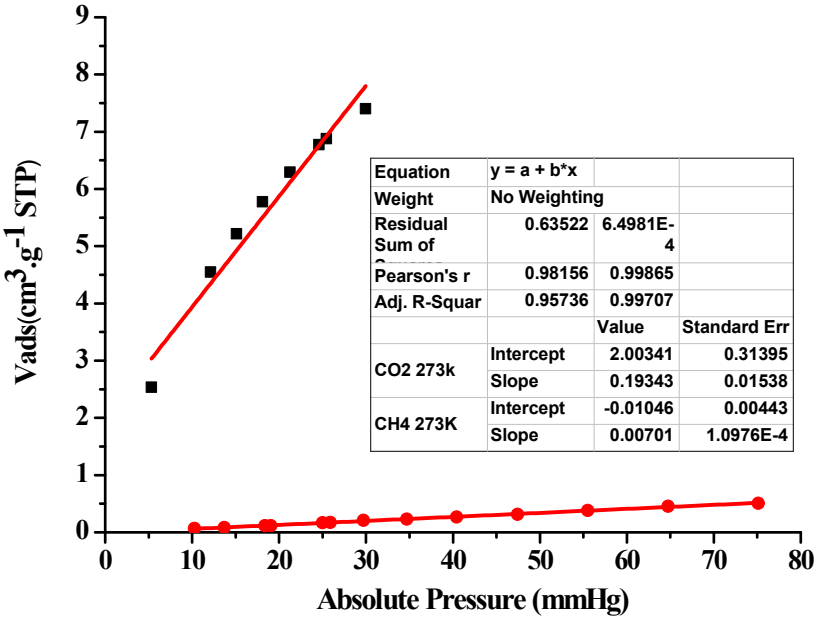

Fig. S12 The fitting initial slopes for CO_2 and CH_4 isotherms of **Eu^{3+}@1** at 273 K.

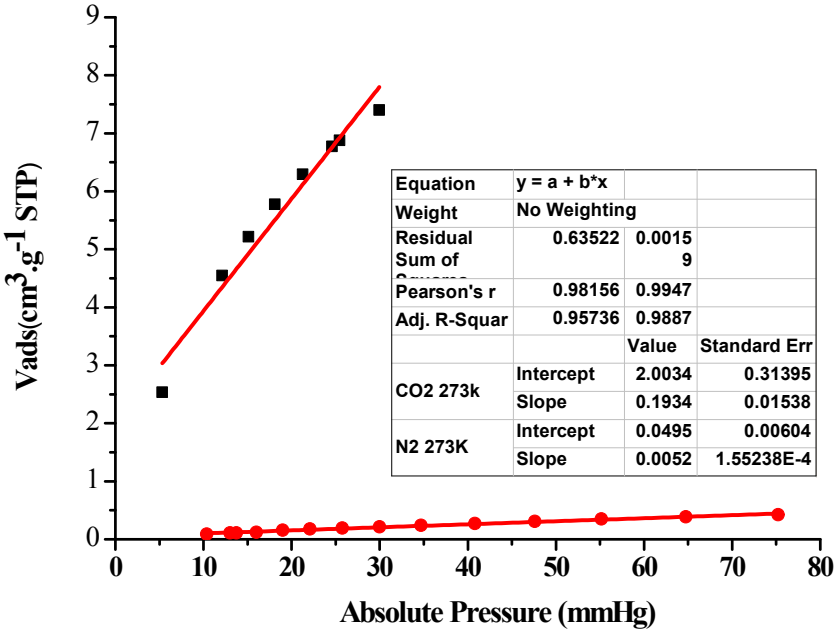

Fig. S13 The fitting initial slopes for CO_2 and N_2 isotherms of **Eu^{3+}@1** at 273 K.

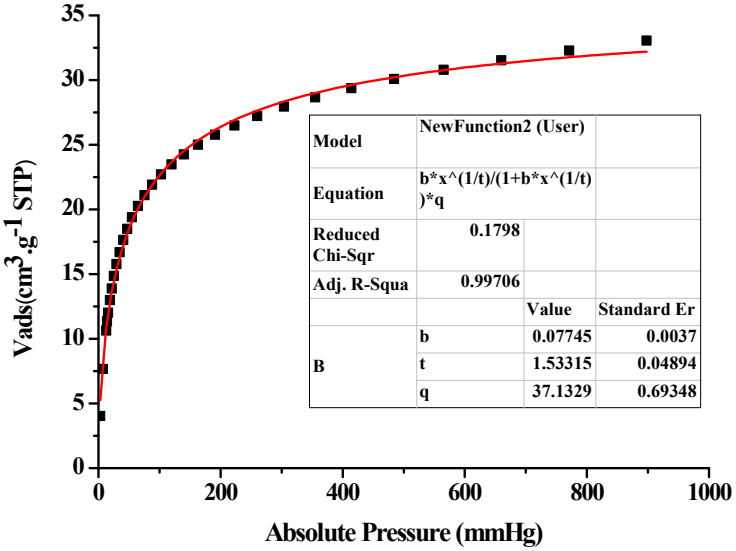

Fig. S14 CO_2 adsorption isotherm for **1** fitted by the Clausius-Clapeyron equation at 273 K.

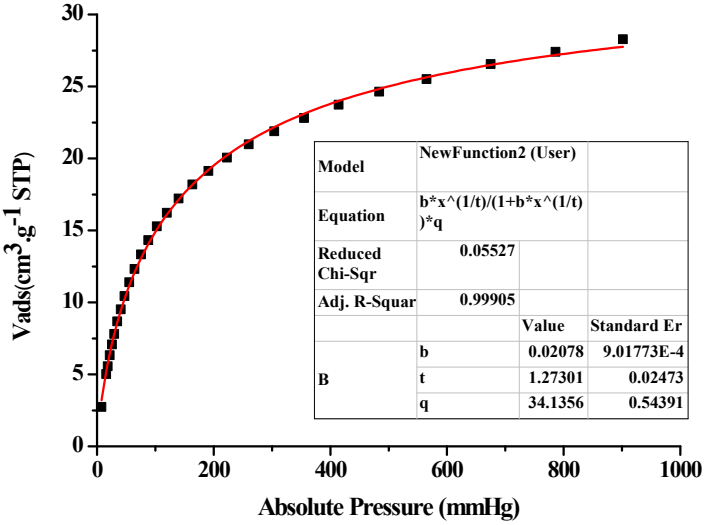

Fig. S15 CO_2 adsorption isotherm for **1** fitted by the Clausius-Clapeyron equation at 298 K.

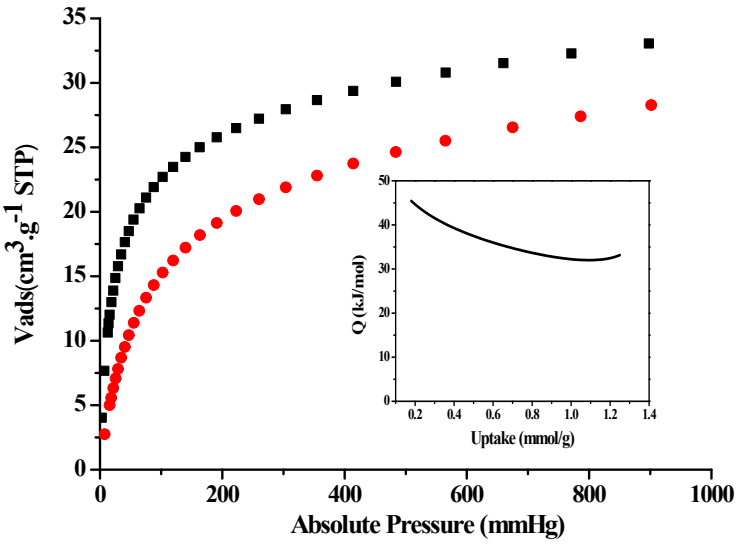

Fig. S16 Gas adsorption isotherms of CO_2 at 273 K and 298 K for **1**. Inset shows the adsorption heat (Q_{st}) depending on gas uptake.

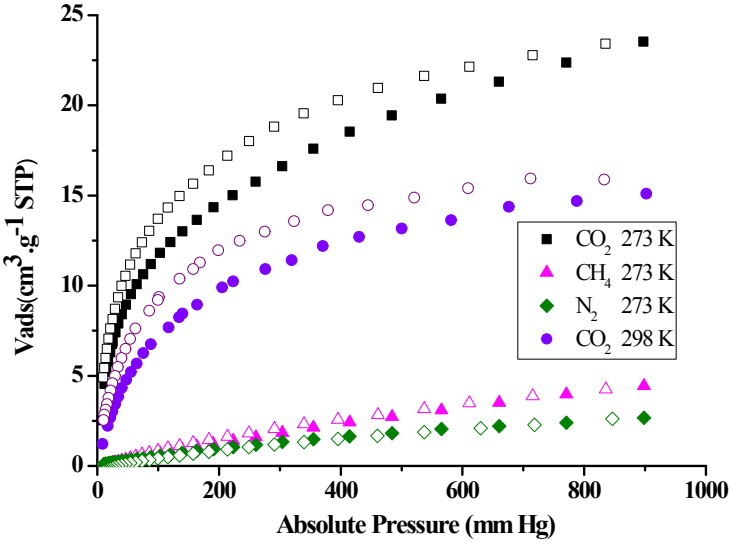

Fig. S17 Gas adsorption isotherms of CO_2, CH_4 and N_2 at 273 K and CO_2 at 298 K for **Eu^{3+}@1**.

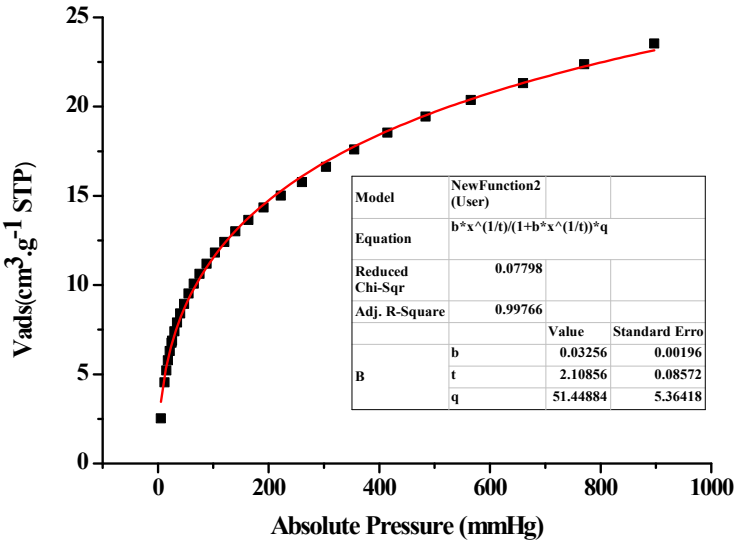

Fig. S18 CO_2 adsorption isotherm for **Eu^{3+}@1** fitted by the Clausius-Clapeyron equation at 273 K.

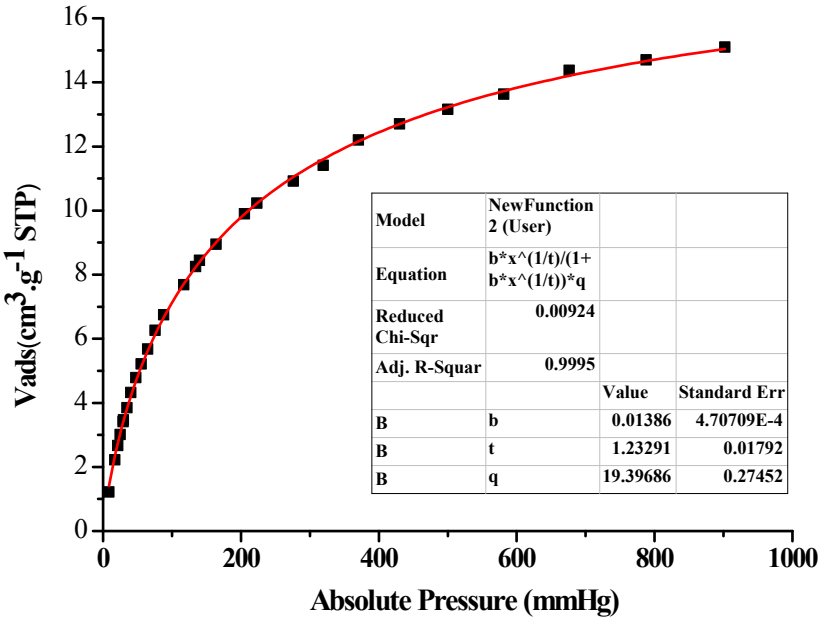

Fig. S19 CO_2 adsorption isotherm for **Eu^{3+}@1** fitted by the Clausius-Clapeyron equation at 298 K.

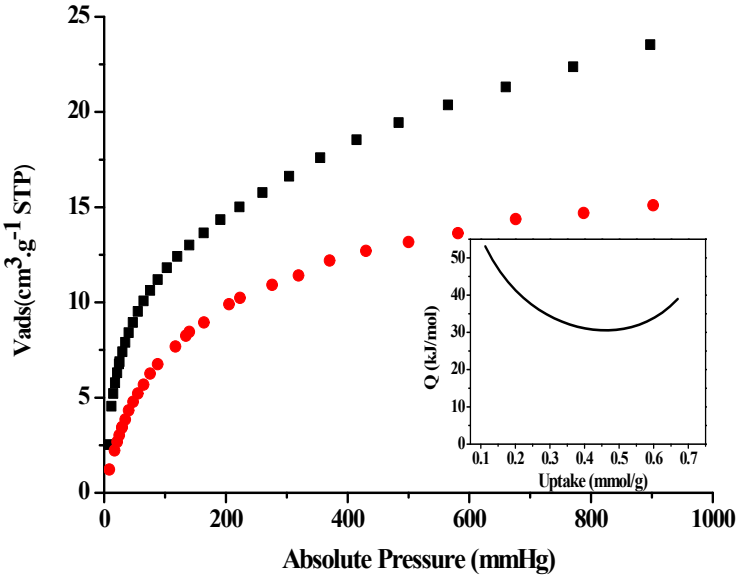

Fig. S20 Gas adsorption isotherms of CO_2 at 273 K and 298 K for **Eu^{3+}@1**. Inset shows the adsorption heat (Q_{st}) depending on gas uptake.

References.

S1 A. P. Nelson, O. K. Farha, K. L. Mulfort, J. T. Hupp, *J. Am. Chem. Soc.*, 2009, **131**, 458.