A Robust Multifunctional Eu_6-Cluster Based Framework for Gas Separation and Recognition of Small Molecules and Heavy Metal Ions

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Supporting Information

Table S1. Crystal data of **Eu-SPFF** (CCDC number: 1912826)

Identification code	**Eu-SPFF**
Empirical formula	$C_{159}H_{116}Eu_6F_{12}O_{38}$
Formula weight	3774.27
Temperature	100.01(10) K
Wavelength	1.54184 Å
Crystal system	Cubic
Space group	*Pm*-3*m*
Unit cell dimensions	a = 19.4694(2) Å
Volume	7380.0(2) $Å^3$
Z	1
Density (calculated)	0.849 g/cm^3
Absorption coefficient	0.397 mm^{-1}
F(000)	1860
Theta range for data collection	4.5280 to 69.1140°.
Completeness to theta = 67.684°	98 %
Max. and min. transmission	1.00000 and 0.847
Goodness-of-fit on F^2	1.391
Final R indices [I>2sigma(I)]	R1 = 0.0940, wR2 = 0.2826
R indices (all data)	R1 = 0.0984, wR2 = 0.2909
Largest diff. peak and hole	4.485 and -5.215 $e.Å^{-3}$

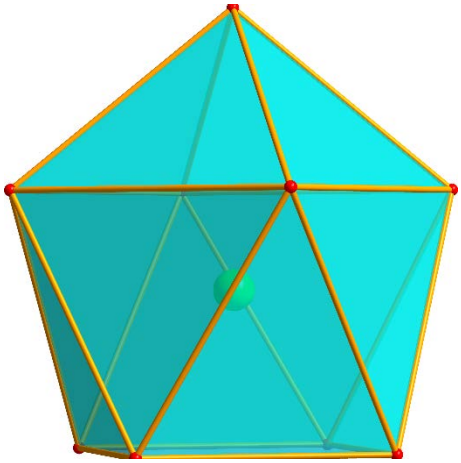

Figure S1. The mono-capped square antiprism coordination geometry of Eu(III).

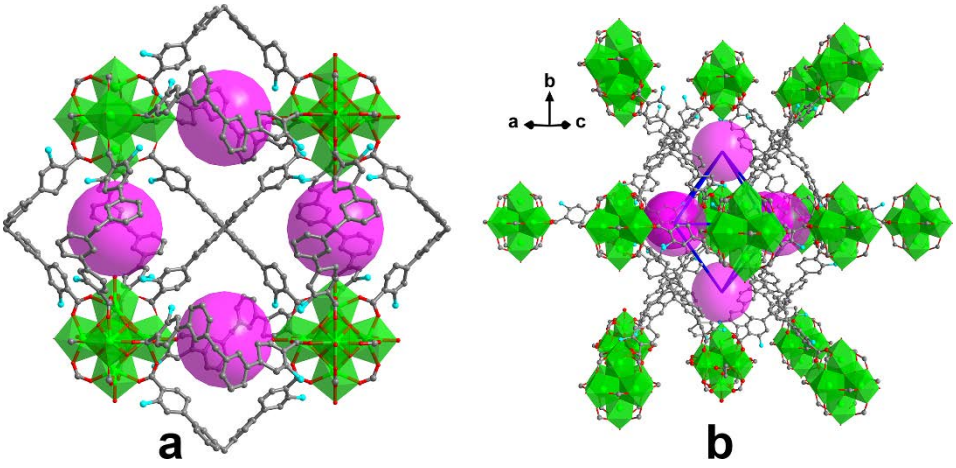

Figure S2. Coordination environment of (a) ligand and (b) Eu_6 cluster.

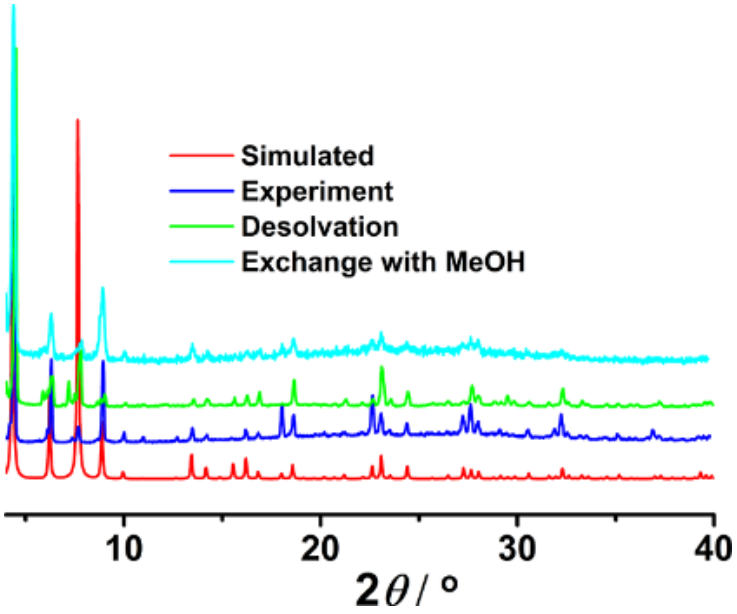

Figure S3. The PXRD patterns of **Eu-SPFF** (from bottom to top: simulated, as-synthesized, after exchange with MeOH and after desolvation).

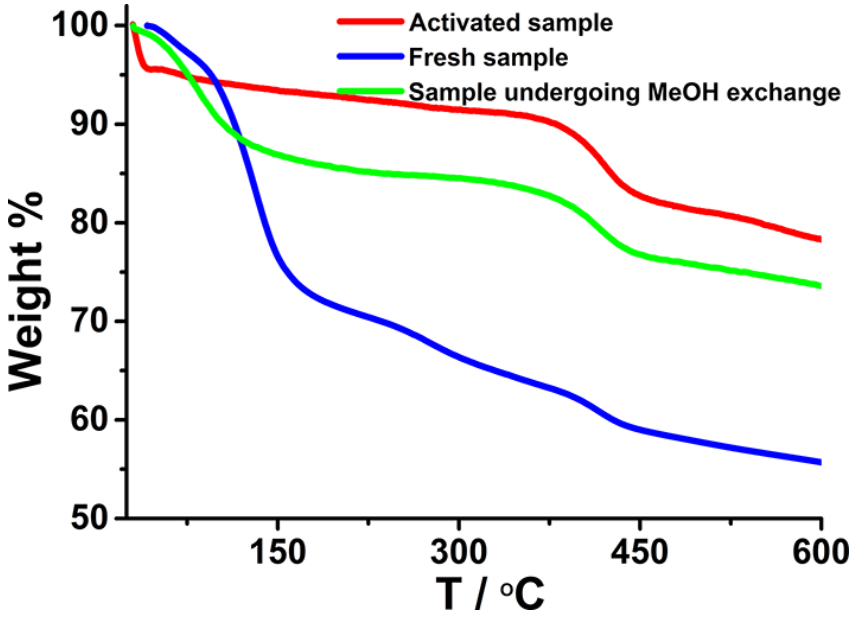

Figure S4. The TGA curves of fresh, activated and MeOH exchanged **Eu-SPFF**.

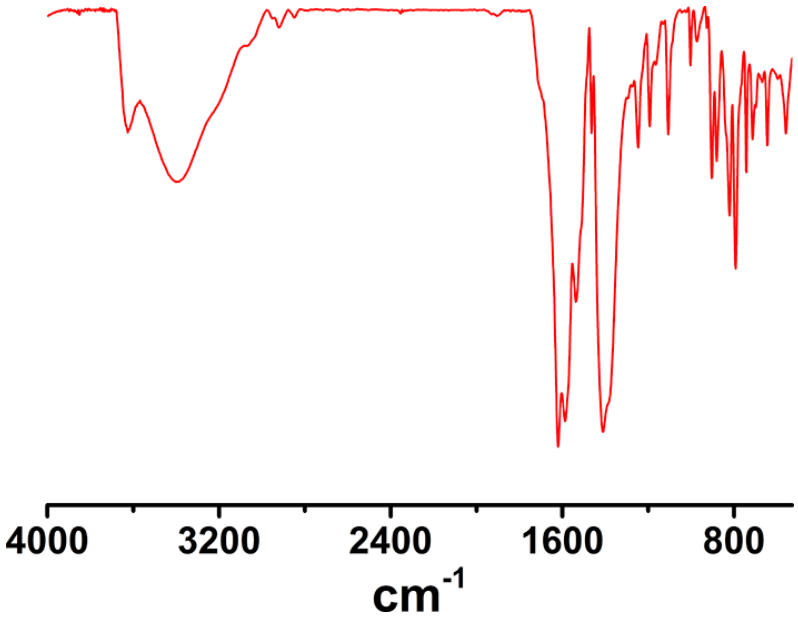

Figure S5. The FT-IR spectrum of **Eu-SPFF**.

The IAST Selectivity Calculations

Based on ideal adsorbed solution theory (IAST), the adsorption isotherm is fitted by the single-site Langmuir-Freundlich equation:

$$N=A_1b_1P^{c1}/ (1+ b_1P^{c1})$$

N: molar loading of species, mmol/g
A: saturation capacity of species, mmol/g
b: constant
c: constant

The adsorption selectivities, ***S***, for binary mixtures C_2H_6 / CH_4, C_2H_4 / CH_4, C_2H_2 / CH_4, C_3H_8 / CH_4, C_3H_6 / CH_4, C_3H_4 / CH_4, *n*-C_4H_{10} / CH_4, *i*-C_4H_{10} / CH_4, *1*-C_4H_8 / CH_4 and *t*-C_4H_8 / CH_4 (15:85).

$$S = (x_1/x_2)(y_2/y_1)$$

S: adsorption selectivity
x_i: the mole fractions of component in the adsorbed i (i = 1, 2)
y_i: the mole fractions of component in the bulk phases i (i = 1, 2)

The IAST calculations were carried out for equimolar binary gas-phase mixtures of C_2H_6 / CH_4, C_2H_4 / CH_4, C_2H_2 / CH_4, C_3H_8 / CH_4, C_3H_6 / CH_4, C_3H_4 / CH_4, *n*-C_4H_{10} / CH_4, *i*-C_4H_{10} / CH_4, *1*-C_4H_8 / CH_4 and *t*-C_4H_8 / CH_4 (15:85).

Table S1 Comparison of adsorption performance of MOFs adsorbents for CH_4, C_2H_6, C_3H_6, C_3H_8, *n*-C_4H_{10}, *1*-C_4H_8, *t*-C_4H_8 and *i*-C_4H_{10}

Compound	CH_4 (cm^3/g)	C_2H_6 (cm^3/g)	C_3H_8 (cm^3/g)	C_3H_6 (cm^3/g)	*n*-C_4H_{10} (cm^3/g)	*1*-C4H8 (cm^3/g)	*t*- C4H8 (cm^3/g)	*i*- C_4H_{10} (cm^3/g)
sPI−A−H[1]	8.736	35.616	44.8	60.08	70.56	79.30	-	-
sPI−M−H[1]	8.152	33.376	43.008	56	68.768	78.4	-	-
sPI−A−B[1]	7.84	29.792	40.992	51.3	56	59.808	-	-
sPI−M−B[1]	6.944	27.776	38.752	51.744	48.384	51.97	-	-
UPC-104[2]	18.1	133.8	232.8	253.9	165.1	164.8	-	-
UPC-100-In[3]	11.7	119.3	118.9	135				
UPC-101-Al[3]	24.4	111.7	137.5	154.5				
UPC-102-Zr[3]	9.4	74.0	137.8	141.9				
JLU-Liu18[4]	12	92	116					
UPC-99[5]	9.856	60.93	108.64	119.39	-	-	-	-
NCA 700[6]	29.792	170	258.94	263.6				
Zr-BPDC[7]	4.93	-	159.26	161.5	-	-	-	-
MFM-202a[8]	10.08	94.3	151.4	-	-	-	-	-
PAF-40[9]	12.096	43.68	53.5	-	-	-	-	-
JUC-100[10]	10.2	92.1	136	-	-	-	-	-
PCN-224[11]	10.75	65.63	184.8					
UiO-67[12]	11.2	65.63	183.68					
FIR-7a-ht[13]	10.36	90.9	162	-	-	-	-	-
LIFM-26[14]	11	103	117	-	-	-	-	-
UPC-32[15]	18.9	66.1	84.9	98.2	-	-	-	-
UTSA-30a[16]	∽14	∽45	∽50	-	-	-	-	-
ftw-MOF-ABTC[17]			55.104	51.52	60.48	-	-	-
ZJNU-61a[18]	6.2	55.3			-	-	-	-
In/Tb-CBDA[19]	8	50	61		-	-	-	-
ZJNU-63[20]	5.2	17.9	-	-	58.8	58.9	71.7	64.9
Eu-SPFF	**13.2**	**98.4**	**160.1**	**172.7**	**152.3**	**164.4**	**171.8**	**144.2**

Table S2 Comparison of gas separation of MOFs adsorbents for C_2H_6, C_3H_6, C_3H_8, *n*-C_4H_{10} and *i*-C_4H_{10} over CH_4

Compound	C_2H_6/CH_4	C_3H_6/CH_4	C_3H_8/CH_4	*n*-C_4H_{10}/CH_4	*i*-C_4H_{10}/CH_4
sPI−A−H[1]	13.3	-	66.4	154.8	-
sPI−M−H[1]	13.9	-	82.0	244.7	-
sPI−A−B[1]	19.6	-	204.7	356.7	-
sPI−M−B[1]	19.0	-	217.4	414.5	-
UPC-104[2]	12.3	97.9	79.0	28.5	163.7
JLU-Liu18[4]	13.1	-	108.2	-	-
UPC-99[5]		306.9	426.8	-	-
NCA-700[6]	65.7	419.8	501.9	-	-
Zr-BPDC[7]	-	50.2	65.8	-	-
PCN-224[11]	12	-	609	-	-
UiO-67[12]	8.1		73.3	-	-
UPC-32[15]	5.8	31.4	28.0	-	-
ZJNU-61a[18]	11.1	-	-	-	-
In/Tb-CBDA[19]	12	-	105		
ZJNU-63[20]	10.6	-	-	-	-
FIR-51[21]	39.6	-	326.8	-	-
Eu-SPFF	**9.8**	**90.2**	**92.6**	**652.0**	**420.0**

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