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Electronic Supplementary Information (ESI)

Detection of persistent organic pollutants of polychloriznated benzenes by a lanthanide metal-organic framework luminescent sensor

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Contents of ESI

Table S1. Crystal data and structural refinement parameters for Ln-MOF **1**.

	1
Formula	$C_{40}H_{40}N_{12}O_{16}Eu_2$
F.M	1248.74
T /K	122
Crystal system	Monoclinic
Space group	*I*2/*a*
a/ Å	17.4164(6)
b/ Å	14.2453(4)
c/ Å	20.4424(7)
α/°	90.00
β/°	114.512(4)
γ/°	90.00
V/ Å^3	4613.7(3)
Z	4
μ/mm^{-1}	2.765
Reflns collected	9331
Independ. reflns	4063
R_{int}	0.0389
R_1[a] ($I>2\sigma(I)$)	0.0282
wR_2[a] (all data)	0.0536
GOF	1.002

[a]$R_1 = \sum ||F_0| - |Fc|| / \sum |F_0|$. [b]$wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (º) for Ln-MOF **1**.

1					
Eu1-O6	2.387(5)	O6-Eu1-N7	73.49(16)	O12-Eu1-O9	107.33(16)
Eu1-N7	2.581(5)	O6-Eu1-O8	133.25(16)	O22-Eu1-O6	124.08(17)
Eu1-O8	2.474(4)	O6-Eu1-O9	82.70(16)	O22-Eu1-N7	148.39(18)
Eu1-O9	2.501(4)	O6-Eu1-O11	77.66(16)	O22-Eu1-O8	86.50(16)
Eu1-O11	2.401(4)	O6-Eu1-O12	141.47(18)	O22-Eu1-O9	133.29(16)
Eu1-O12	2.404(5)	O8-Eu1-N7	99.08(16)	O22-Eu1-O11	78.64(16)
Eu1-O22	2.297(5)	O8-Eu1-O9	52.62(15)	O22-Eu1-O12	76.24(19)
Eu1-O26	2.333(4)	O9-Eu1-N7	69.69(15)	O22-Eu1-O26	74.9(2)
		O11-Eu1-N7	80.61(15)	O26-Eu1-O6	78.75(19)
		O11-Eu1-O8	148.06(15)	O26-Eu1-N7	136.76(19)
		O11-Eu1-O9	148.04(15)	O26-Eu1-O8	76.76(16)
		O11-Eu1-O12	75.15(16)	O26-Eu1-O9	74.49(17)
		O12-Eu1-N7	75.55(17)	O26-Eu1-O11	124.88(17)
		O12-Eu1-O8	73.91(16)	O26-Eu1-O12	139.63(19)

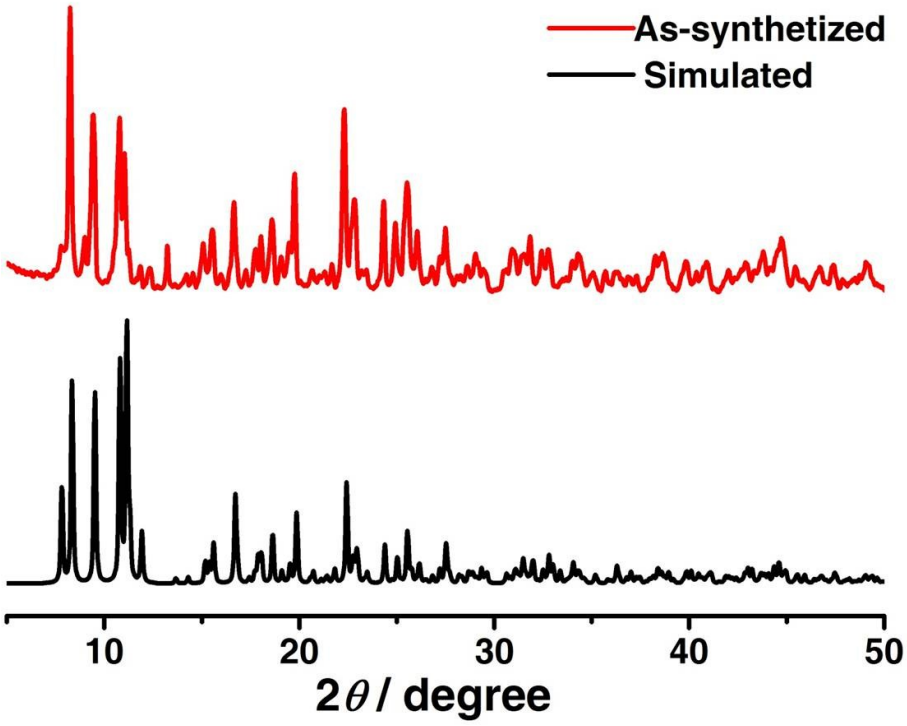

Fig. S1 Simulated and experimental powder X-ray diffraction patterns of Ln-MOF **1**.

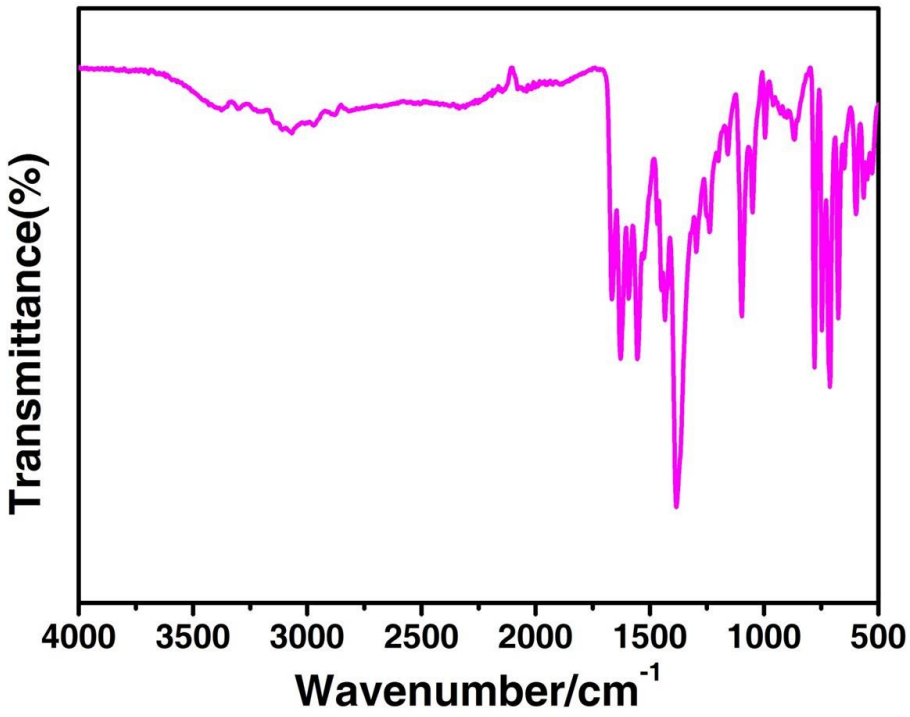

Fig. S2 Fourier transform infrared (FT-IR) spectrum of Ln-MOF **1**.

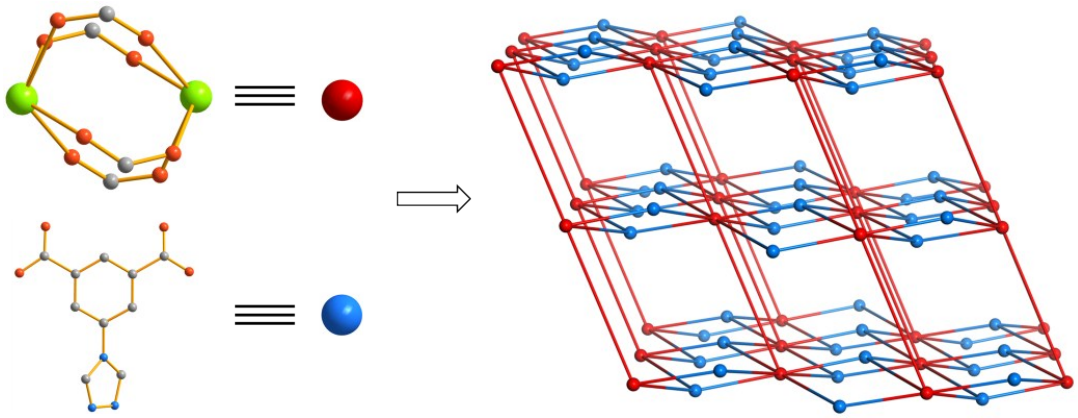

Fig. S3 Simplified topological structure of Ln-MOF **1**: (red) Ln_2 binuclear unit; (blue) L^{2-} ligand.

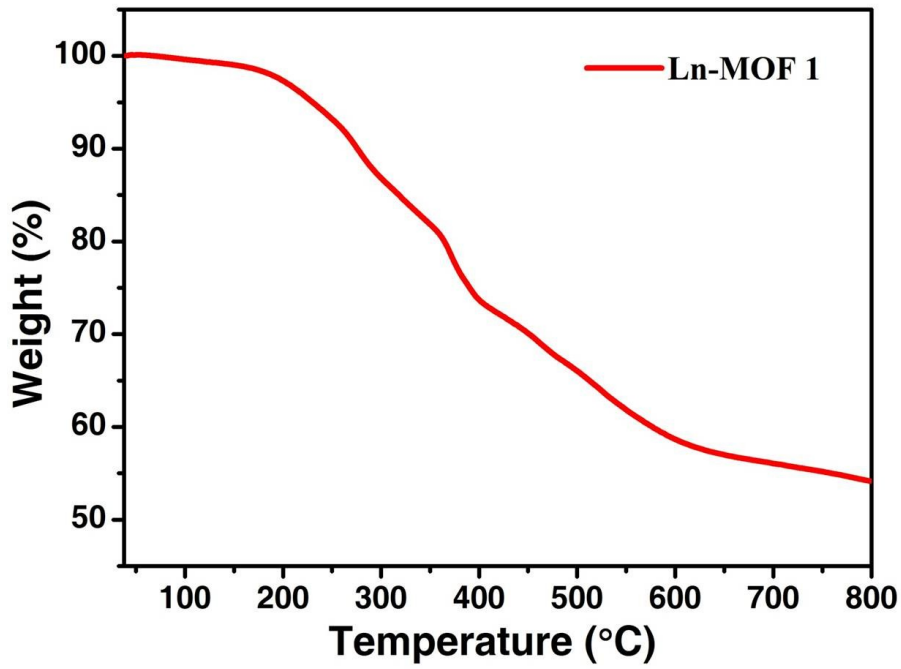

Fig. S4 Thermal gravimetric analyses (TGA) curve of Ln-MOF **1**.

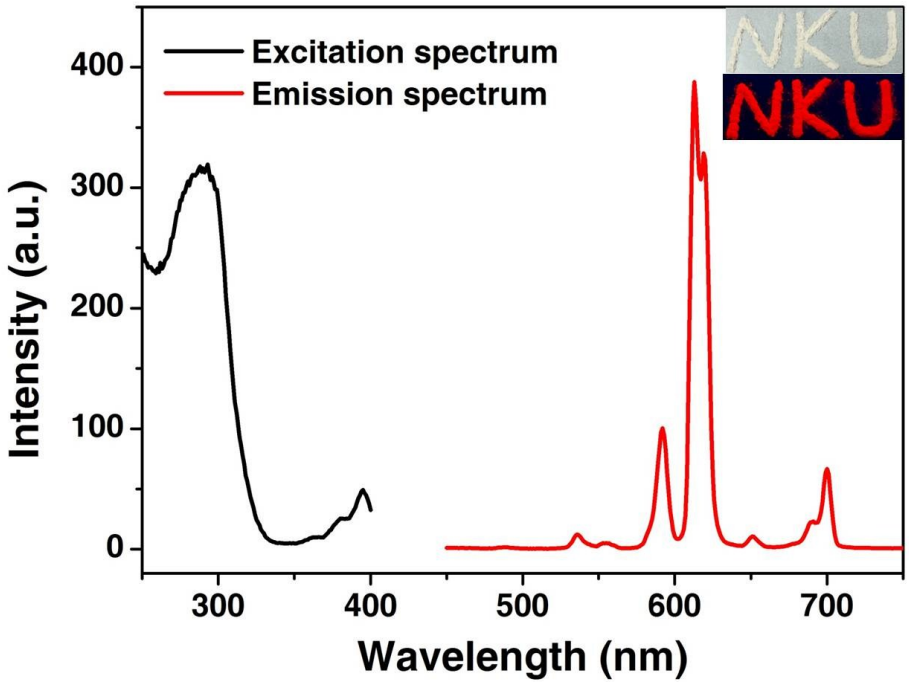

Fig. S5 The solid-state excitation and emission spectra with the excitation wavelength of 294 nm of Ln-MOF **1** at room temperature. Insert: the colors of Ln-MOF **1** before (above) and after (below) the irradiation of UV light of 254 nm.

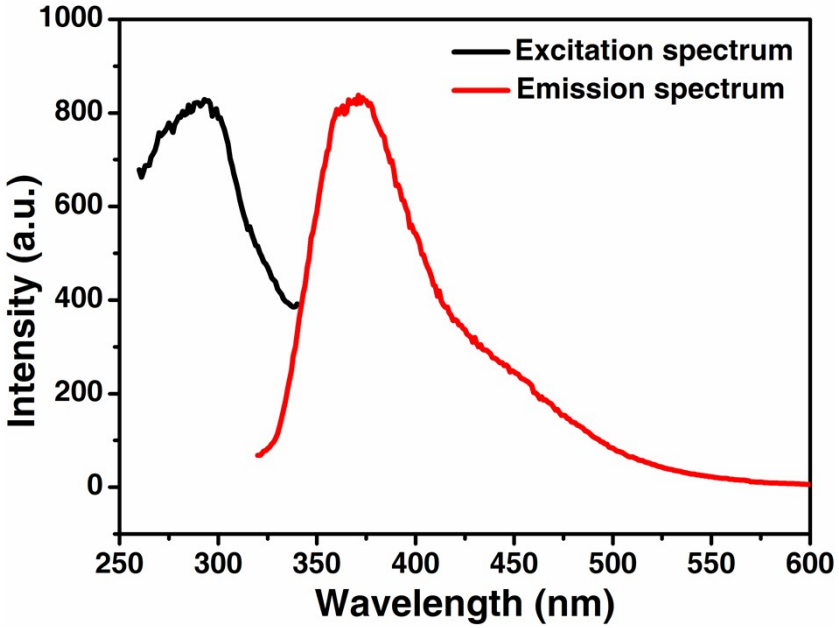

Fig. S6 The solid-state excitation and emission spectra of H_2L at room temperature.

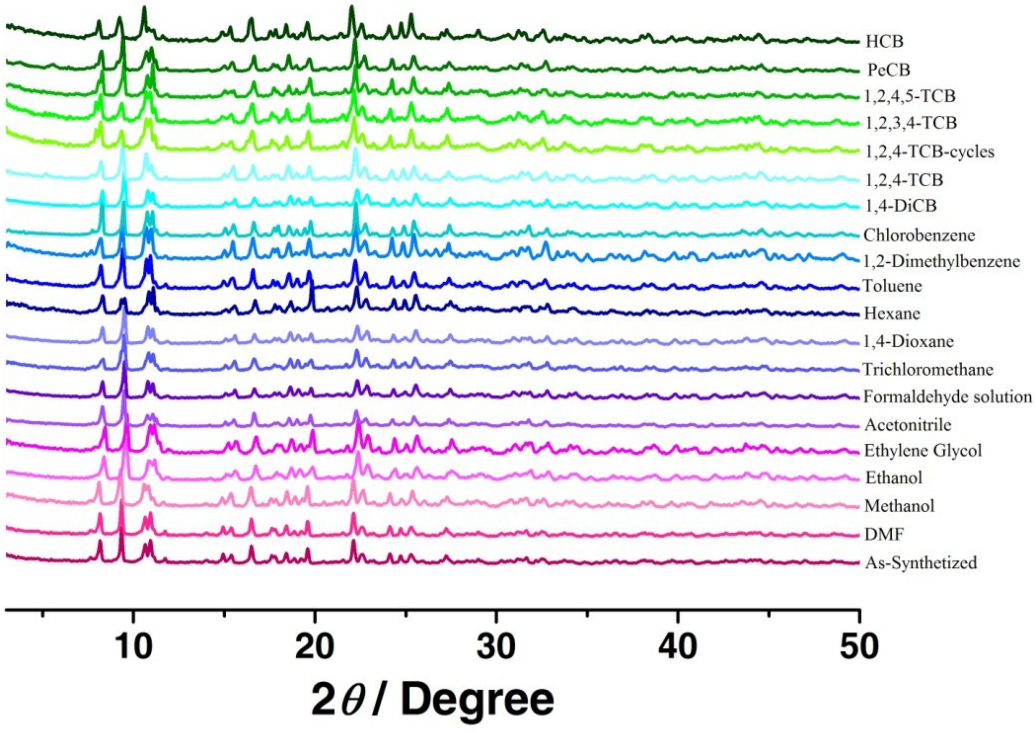

Fig. S7 Powder X-ray diffraction patterns of Ln-MOF **1** after immersing in different organic solvents.

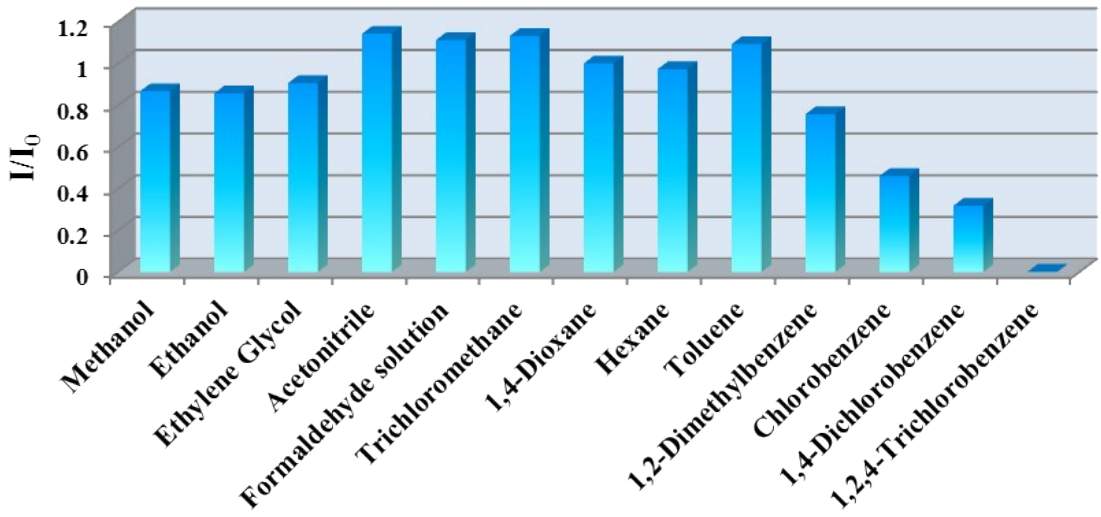

Fig. S8 Luminescence quenching (I/I_0) of Ln-MOF **1** (3 mg) dispersed in 3 mL DMF with different organic solvents added when excited at 294 nm.

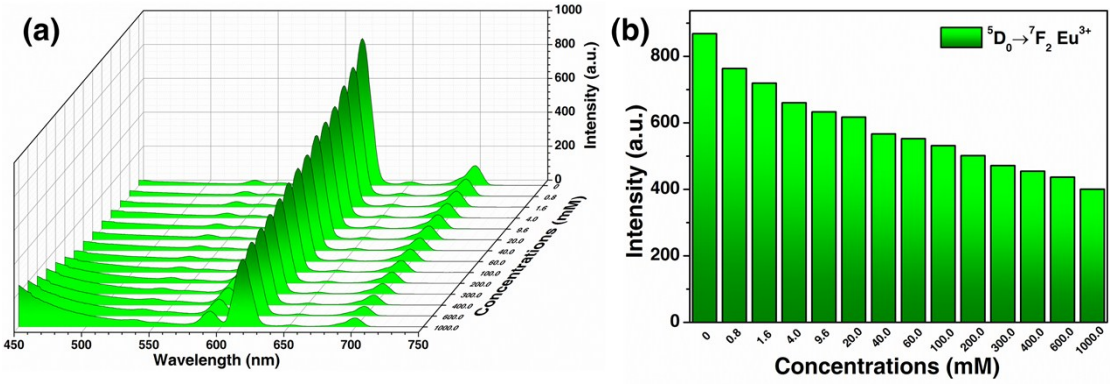

Fig. S9 (a) Suspension-state PL spectra and (b) the $^5D_0 \rightarrow {}^7F_2$ transition intensities of Ln-MOF **1** with different addition of chlorobenzene when excited at 294 nm.

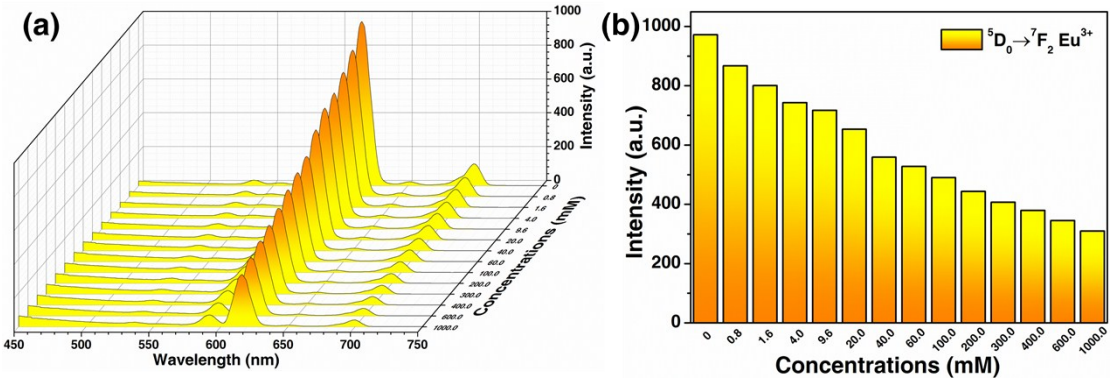

Fig. S10 (a) Suspension-state PL spectra and (b) the $^5D_0 \rightarrow {}^7F_2$ transition intensities of Ln-MOF **1** with different addition of 1,4-dichlorobenzene when excited at 294 nm.

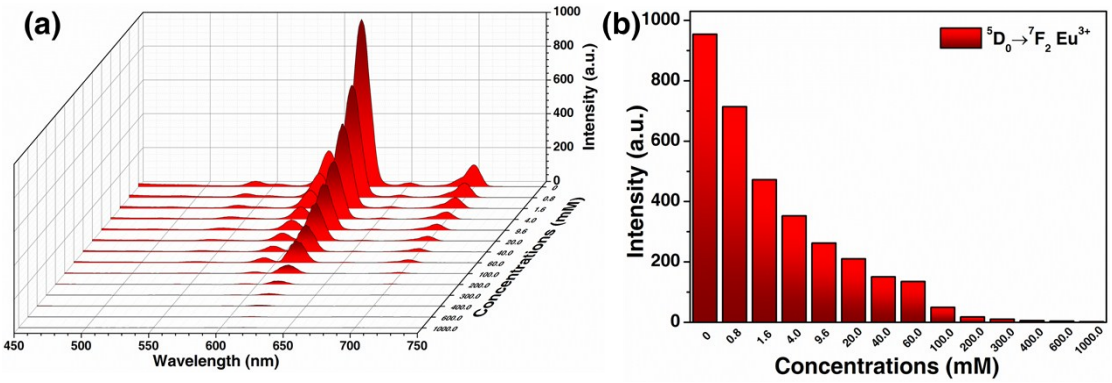

Fig. S11 (a) Suspension-state PL spectra and (b) the $^5D_0 \rightarrow {}^7F_2$ transition intensities of Ln-MOF **1** with different addition of 1,2,4-TCB when excited at 294 nm.

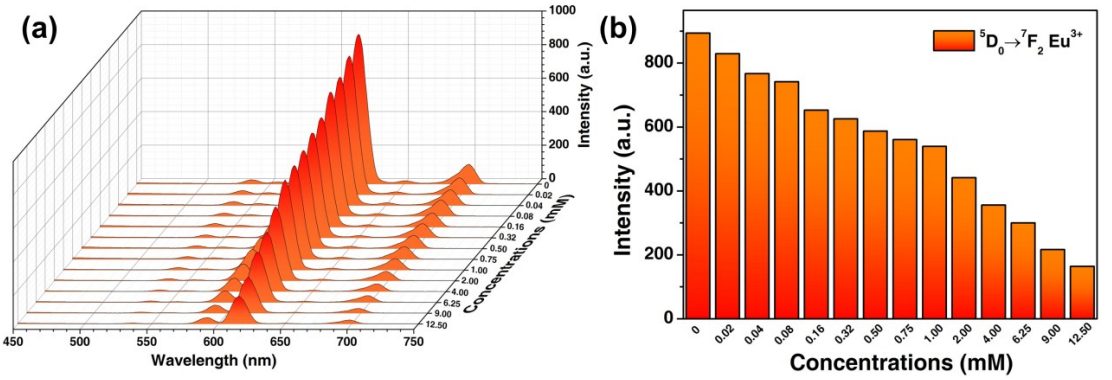

Fig. S12 (a) Suspension-state PL spectra and (b) the $^5D_0 \rightarrow {}^7F_2$ transition intensities of Ln-MOF **1** with different addition of 1,2,3,4-TCB when excited at 294 nm.

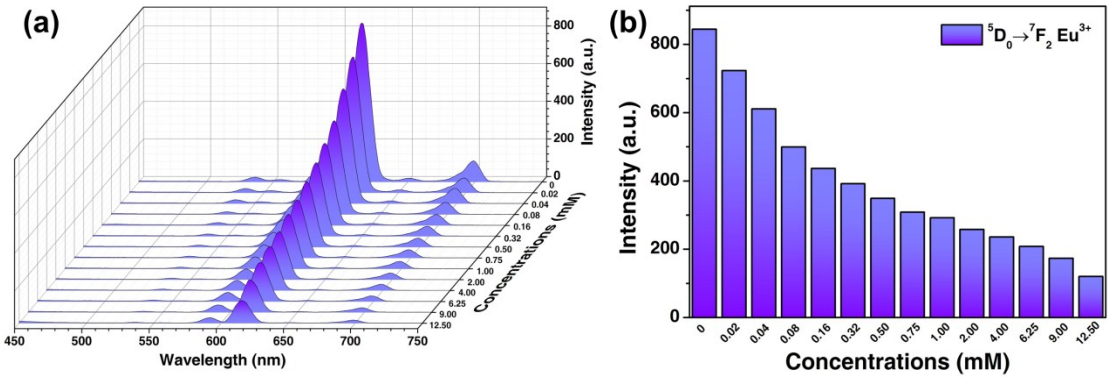

Fig. S13 (a) Suspension-state PL spectra and (b) the $^5D_0 \rightarrow {}^7F_2$ transition intensities of Ln-MOF **1** with different addition of 1,2,4,5-TCB when excited at 294 nm.

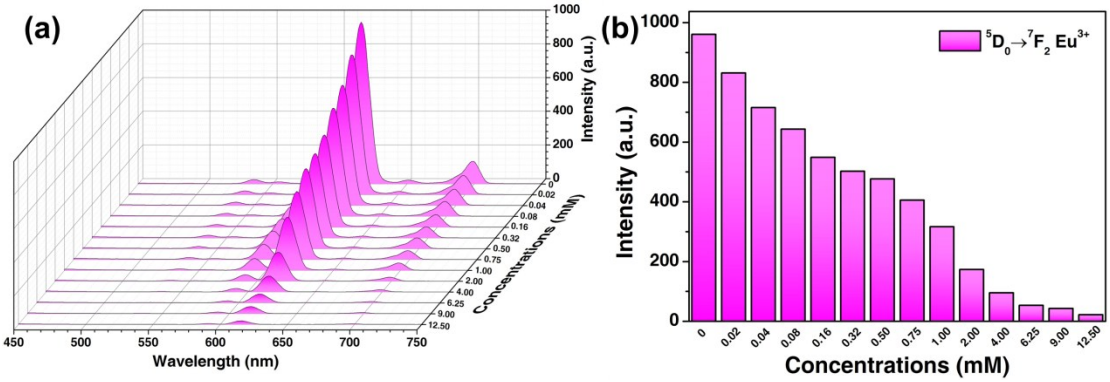

Fig. S14 (a) Suspension-state PL spectra and (b) the $^5D_0 \rightarrow {}^7F_2$ transition intensities of Ln-MOF **1** with different addition of PeCB when excited at 294 nm.

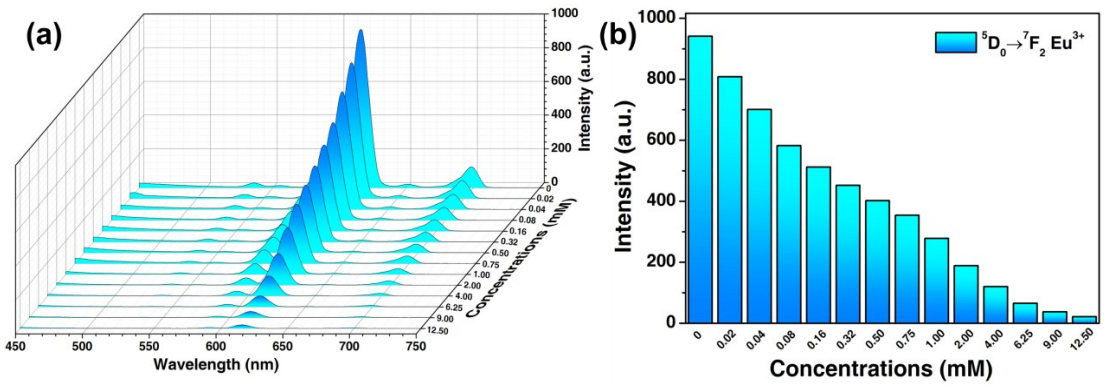

Fig. S15 (a) Suspension-state PL spectra and (b) the $^5D_0 \rightarrow {}^7F_2$ transition intensities of Ln-MOF **1** with different addition of HCB when excited at 294 nm.

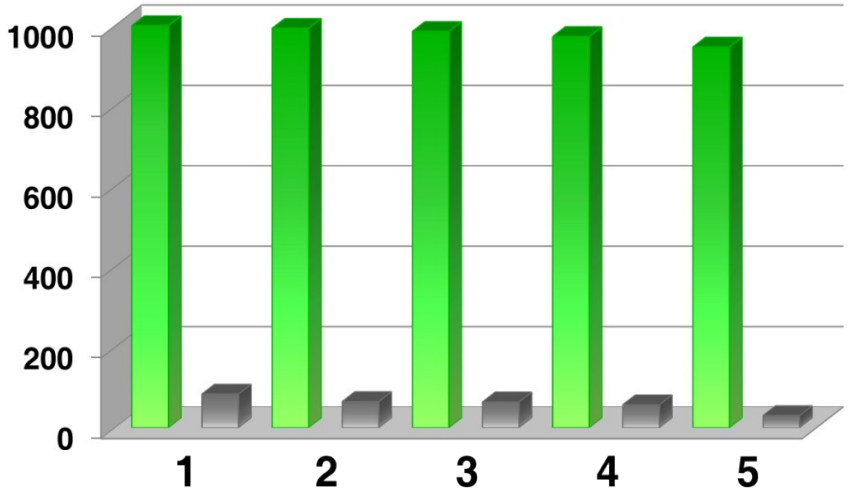

Fig. S16 Reproducibility of the quenching ability of Ln-MOF **1** for 1,2,4-TCB with five continuous quenching cycles.

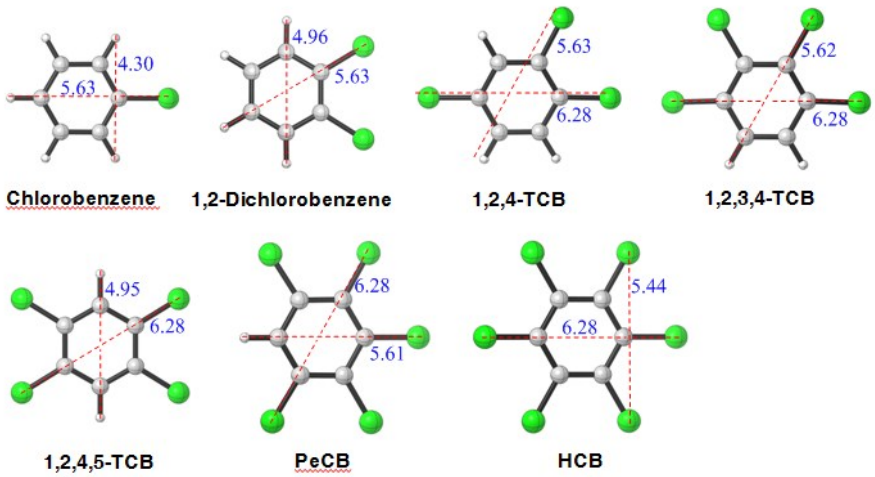

Fig. S17 Molecular structures and sizes of polychloriznated benzenes.

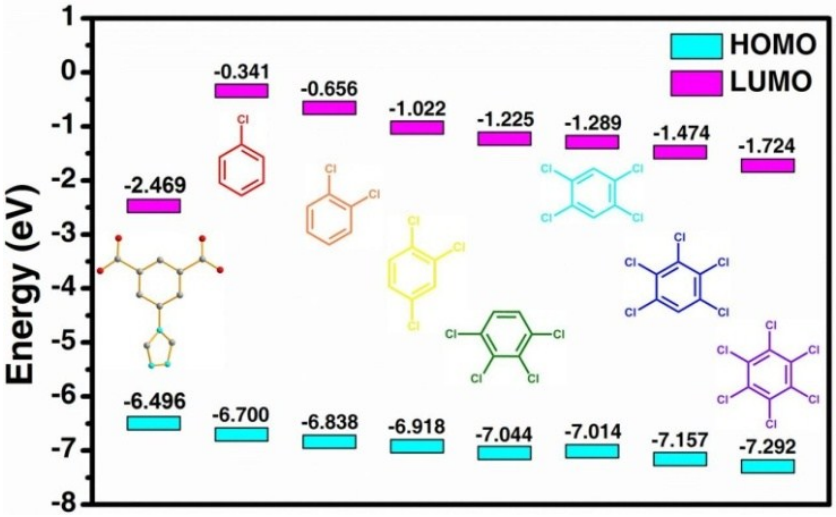

Fig. S18 HOMO and LUMO energies calculated for ligand H_2L and polychloriznated benzenes.

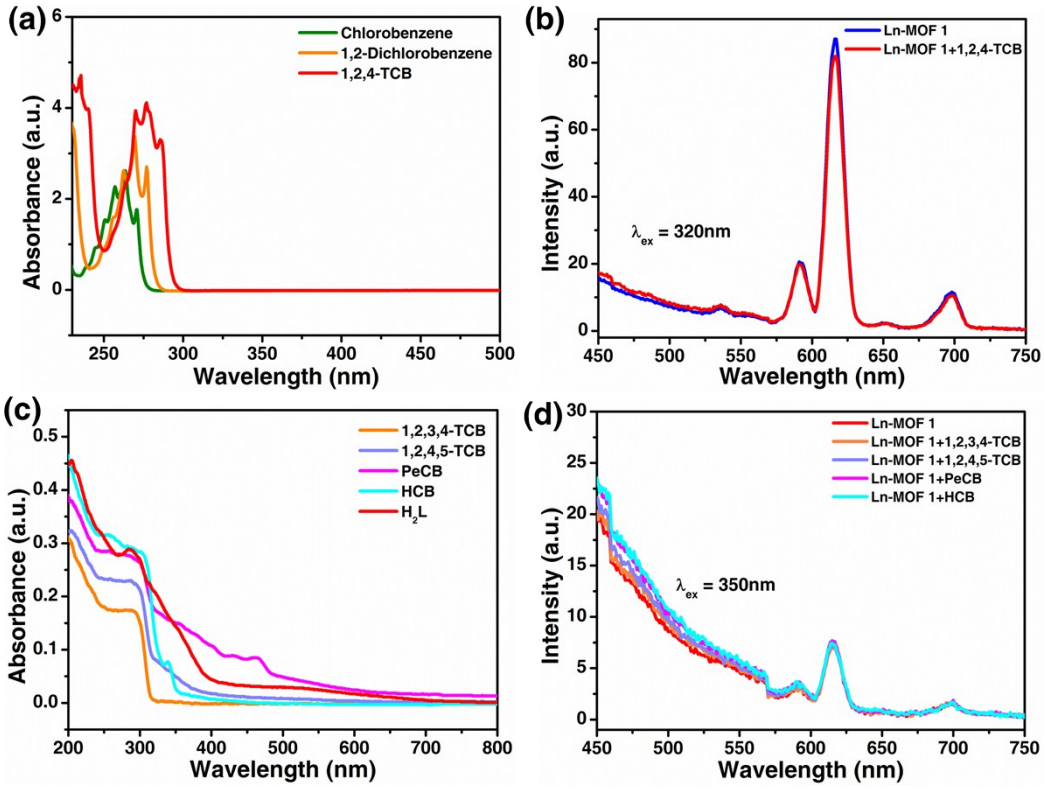

Fig. S19 The UV-vis absorption spectra for chlorobenzene, 1,2-dichlorobenzene, 1,2,4-TCB (a), 1,2,3,4-TCB, 1,2,4,5-TCB, PeCB, HCB and H_2L (c); comparison of

PL spectra of Ln-MOF **1** before and after adding 1,2,4-TCB (1.25%) (b), 1,2,3,4-TCB, 1,2,4,5-TCB, PeCB, HCB (4.00 mM) (d).

DFT Calculation.

The geometries of all minima were fully optimized in gas phase using the hybrid B3LYP[1] functional. The 6-31G(d) basis set was employed for all atoms except for Eu. The large core ECP52MWB[2] optimized by the Stuttgart/Cologne group was used for uranium centers. Frequency calculations were performed at 298.15 K to verify that the stationary points were the local minima. All of the calculations were performed with Gaussian 09.[3]

Tables S3−S9. The Cartesian Coordinates of the stationary points discussed in this paper.

For all minimum structures, no imaginary frequency was observed.

Table S3. Chlorobenzene

Atom	X	Y	Z
C	-1.574505	-1.207803	0.000000
C	-0.178309	-1.216394	0.000000
C	0.504285	0.000000	0.000000
C	-0.178309	1.216394	0.000000
C	-1.574505	1.207803	-0.000000
C	-2.275148	0.000000	0.000000
H	-2.112520	-2.151833	-0.000000
H	0.374772	-2.149683	-0.000000
H	0.374772	2.149683	0.000000
H	-2.112520	2.151833	-0.000000
H	-3.361301	0.000000	-0.000000
Cl	2.264455	0.000000	-0.000000

Table S4. 1,2-Dichlorobenzene

Atom	X	Y	Z
C	0.000000	2.392333	0.697816
C	-0.000000	1.185558	1.394869
C	0.000000	-0.027127	0.700823
C	0.000000	-0.027127	-0.700823
C	0.000000	1.185558	-1.394869
C	0.000000	2.392333	-0.697816
H	-0.000000	3.328481	1.248168
H	-0.000000	1.169473	2.479526
H	-0.000000	1.169473	-2.479526
H	-0.000000	3.328481	-1.248168
Cl	-0.000000	-1.517796	1.613147
Cl	-0.000000	-1.517796	-1.613147

Table S5. 1,2,4-TCB

Atom	X	Y	Z
C	-1.724824	-0.146562	-0.000000
C	-0.811558	0.904996	-0.000000
C	0.557015	0.625186	-0.000000
C	1.003376	-0.703799	-0.000000
C	0.069940	-1.743064	-0.000000
C	-1.296264	-1.473514	-0.000000
H	-1.151513	1.933561	0.000000
H	0.423255	-2.768520	0.000000
H	-2.017019	-2.283389	0.000000
Cl	1.676028	1.963104	0.000000
Cl	2.702985	-1.096880	0.000000
Cl	-3.440239	0.212534	0.000000

Table S6. 1,2,3,4-TCB

Atom	X	Y	Z
C	-1.395435	-0.817966	-0.000000
C	-0.704667	0.404342	-0.000000
C	0.704667	0.404342	-0.000000
C	1.395435	-0.817966	-0.000000
C	0.694632	-2.023501	-0.000000
C	-0.694632	-2.023501	-0.000000
H	1.243971	-2.958230	0.000000
Cl	1.577259	1.904245	0.000000
Cl	3.138080	-0.870070	0.000000
Cl	-3.138080	-0.870070	0.000000
H	-1.243971	-2.958230	0.000000
Cl	-1.577259	1.904245	0.000000

Table S7. 1,2,4,5-TCB

Atom	X	Y	Z
C	1.211775	-0.700870	-0.000000
C	0.000000	-1.391210	-0.000000
C	-1.211775	-0.700870	-0.000000
C	-1.211775	0.700870	-0.000000
C	-0.000000	1.391210	-0.000000
C	1.211775	0.700870	-0.000000
H	0.000000	-2.474552	0.000000
H	-0.000000	2.474552	0.000000
Cl	-2.693739	-1.616140	0.000000
Cl	-2.693739	1.616140	0.000000
Cl	2.693739	-1.616140	0.000000
Cl	2.693739	1.616140	0.000000

Table S8. PeCB

Atom	X	Y	Z
C	-1.206324	-1.100770	-0.000000
C	-1.222307	0.302216	-0.000000
C	0.000000	1.000312	-0.000000
C	1.222307	0.302216	-0.000000
C	1.206324	-1.100770	-0.000000
C	0.000000	-1.794747	-0.000000
Cl	0.000000	2.734474	0.000000
Cl	2.727550	1.162537	0.000000
Cl	-2.683187	-2.023102	0.000000
H	0.000000	-2.877608	-0.000000
Cl	-2.727550	1.162537	0.000000
Cl	2.683187	-2.023102	0.000000

Table S9. HCB

Atom	X	Y	Z
C	1.403655	-0.054786	0.000000
C	0.654528	-1.243185	0.000001
C	-0.749261	-1.188303	0.000001
C	-1.403655	0.054786	0.000001
C	-0.654528	1.243185	-0.000000
C	0.749261	1.188303	-0.000000
Cl	-1.674228	-2.654387	0.000001
Cl	-3.135747	0.121849	-0.000001
Cl	3.135747	-0.121849	0.000001
Cl	1.462601	-2.777156	-0.000001
Cl	-1.462601	2.777156	0.000001
Cl	1.674228	2.654387	-0.000001

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Phys. Rev. B., 1988, **37**, 785; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (d) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; (e) P. J. Stephens, F. J. Devlin, M. J. Frisch, C. F. Chabalowski, *J. Phys. Chem.*, 1994, **98**, 11623.

2. (a) M. Dolg, H. Stoll, A. Savin, H. Preuss, *Theor. Chim. Acta*, 1989, **75**, 173; (b) M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta*,1993, **85**, 441.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Revision E.01, Wallingford CT, 2013.