Electronic Supplementary Information

Efficient X-ray scintillating lead(II)-based MOFs derived from rigid luminescent naphthalene motif

Jian Lu,[a, b] Hue-Huan Xin,[a,b] Yang-Jie Lin,[a] Shuai-Hua Wang,[a] Jian-Gang Xu,[a] Fa-Kun Zheng,[a]* and Guo-Cong Guo [a]*

Jian Lu: lujian@fjirsm.ac.cn
Xue-Huan Xin: xhxin@fjirsm.ac.cn
Yang-Jie Lin: yjlin@fjirsm.ac.cn
Shuai-Hua Wang: shwang@fjirsm.ac.cn
Jian-Gang Xu: jgxu@fjirsm.ac.cn
Fa-Kun Zheng: zfk@fjirsm.ac.cn
Guo-Cong Guo: gcguo@fjirsm.ac.cn

[a]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China*
[b]*University of Chinese Academy of Sciences, Beijing 100039, P.R. China*

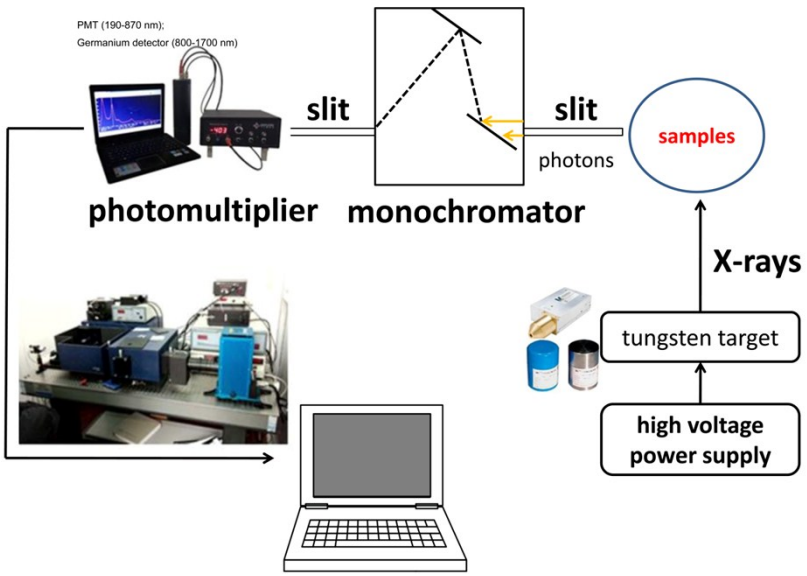


Fig. S1 The self-built scintillating measurement equipment. The whole backbone of the X-ray stimulated Fluorescence Spectrometer was from FLS920 Spectrometer, except that the excitation Xe lamp is replaced by a highly purified tungsten target (Moxtek® MAGPRO X-ray sources: http://moxtek.com/xray-product/60kv-70kv-12w-magpro-x-ray-source/).

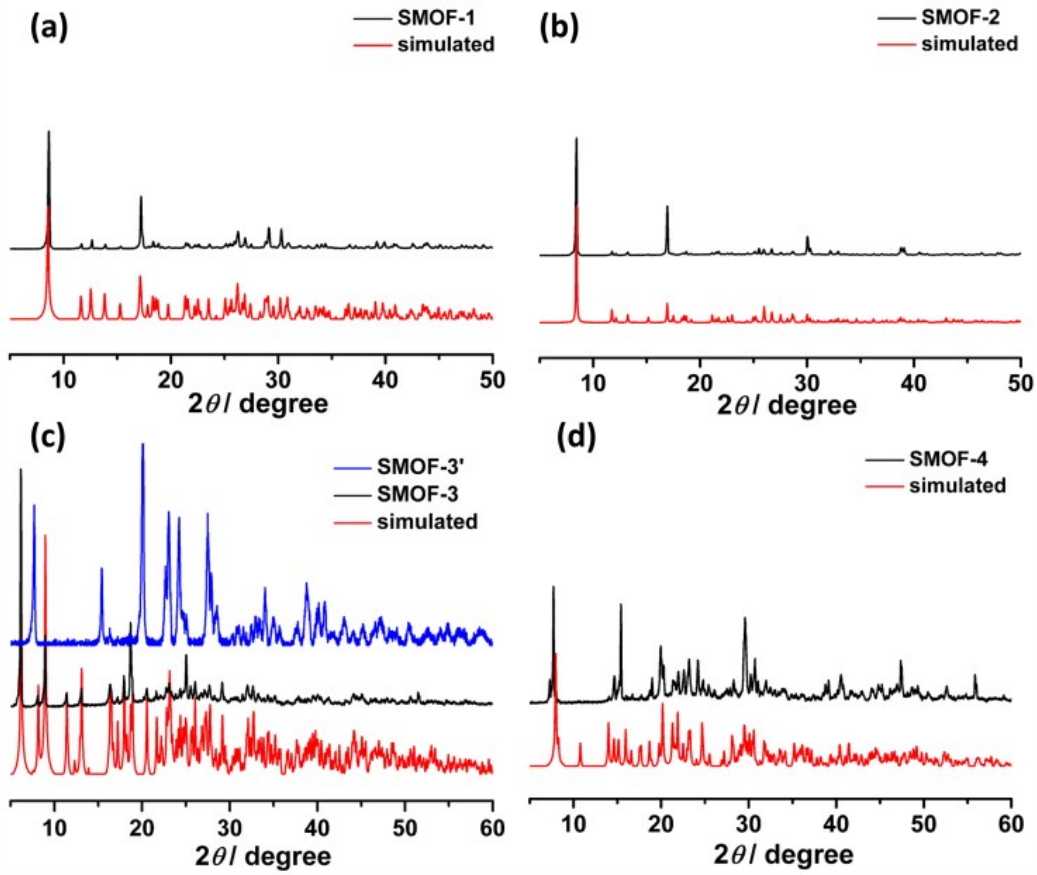


Fig. S2 The experimental and simulated powder X-ray diffraction patterns of **SMOF-1** (a), **SMOF-2** (b), **SMOF-3** & **SMOF-3'** (c) and **SMOF-4** (d).

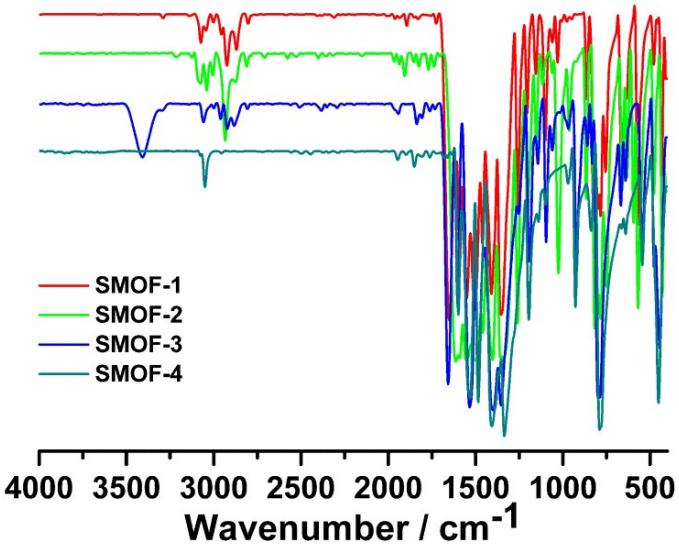


Fig. S3 The FT-IR spectra of **SMOFs 1-4**.

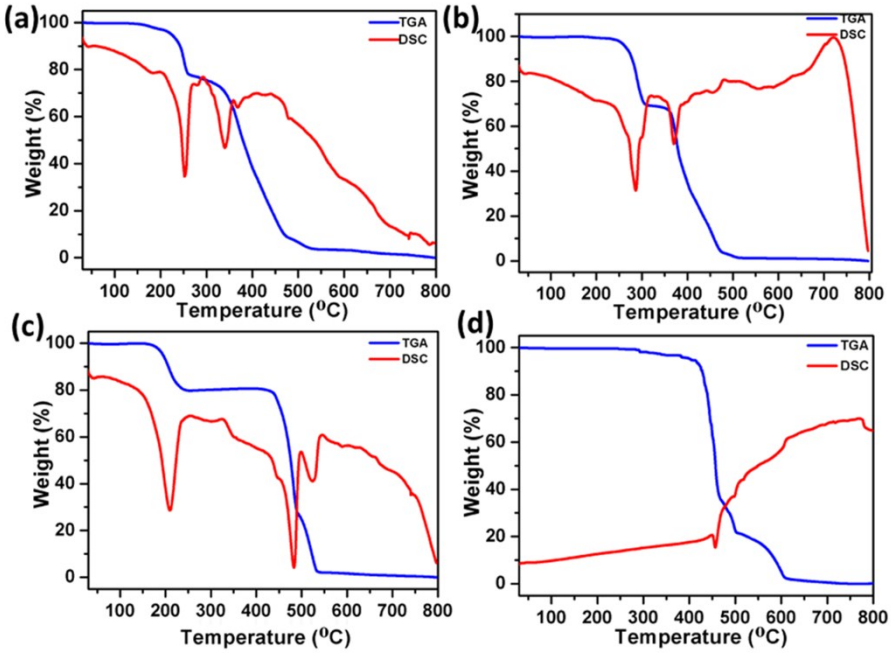


Fig. S4 The TGA and DSC curves of **SMOF-1** (a), **SMOF-2** (b), **SMOF-3** (c) and **SMOF-4** (d).

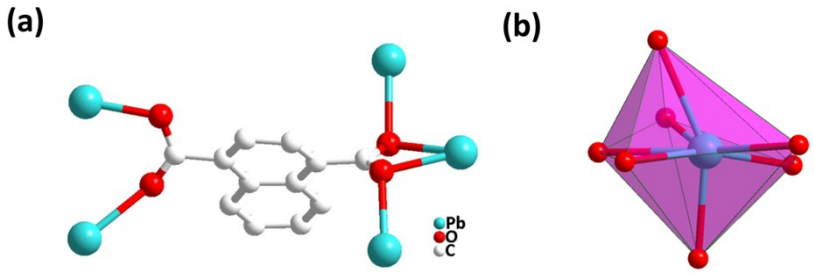


Fig. S5 For **SMOF-1**: (a) the coordination mode of 1,4-ndc^{2-}, (b) the holo-directed coordination structure of Pb(II) (seven coordinated).

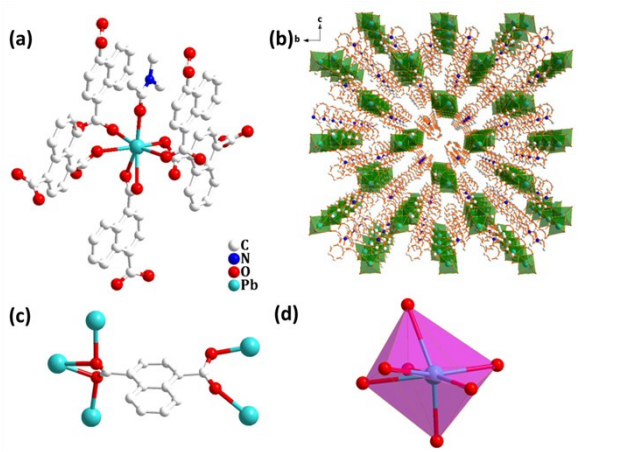


Fig. S6 For **SMOF-2**: (a) the coordination environment of Pb(II), (b) the 3D framework, (c) the μ_5- coordinated mode of 1,4-ndc^{2-}, (d) the holo-directed coordination structure of Pb(II) (seven coordinated).

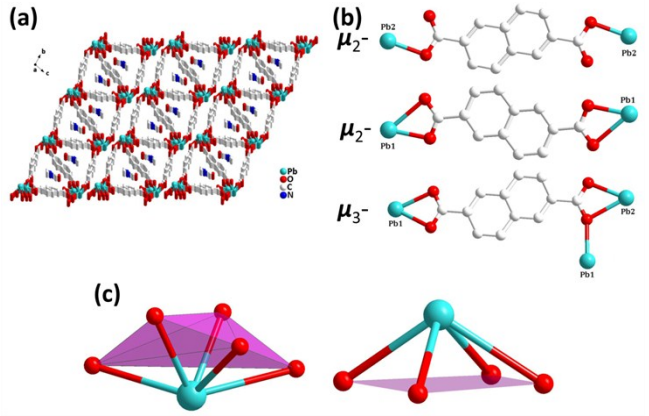


Fig. S7 For **SMOF-3**: (a) the 3D supramolecular network ("AAA" type), (b) the coordination mode of 2,6-ndc^{2-}, (c) geometrical configuration of Pb, hemi-directed coordination structure of Pb1(left) and Pb2 (right).

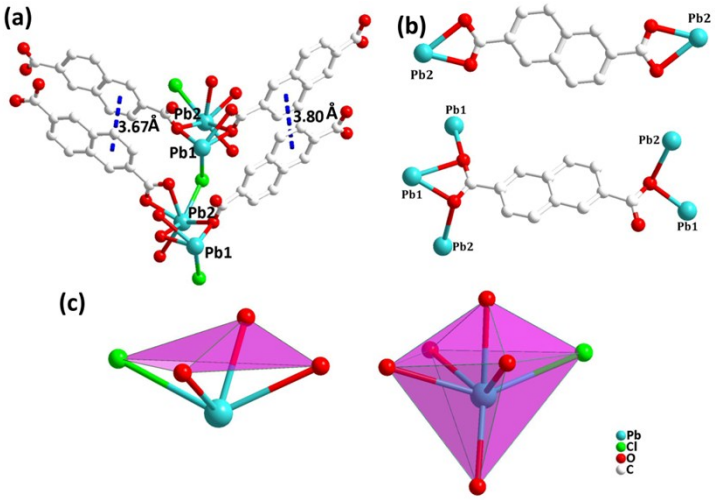


Fig. S8 For **SMOF-4**: (a) the aggregation model of π-π stacking, (b) the coordination mode of 2,6-ndc^{2-}, (c) geometrical configuration of Pb, hemi-directed coordination structure of Pb1 (left) and holo-directed coordination structure of Pb2 (right).

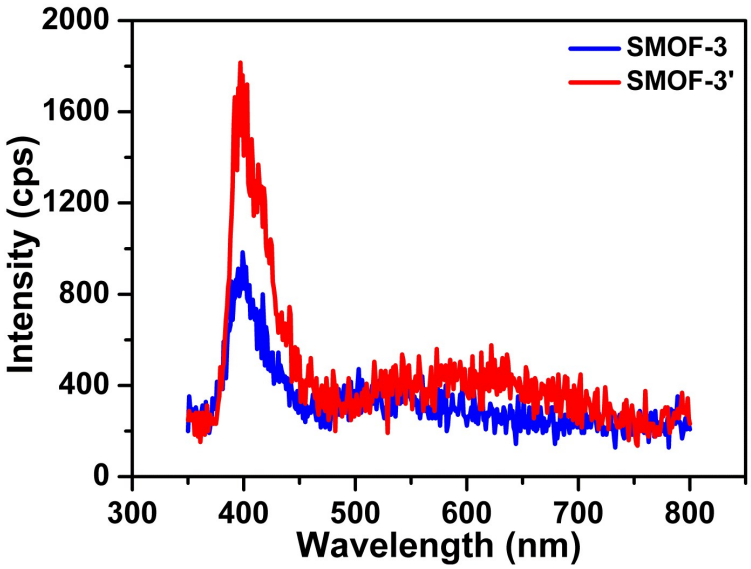


Fig. S9 The XSL spectra of **SMOF-3** (blue) and desolvated **SMOF-3'** (red) under the tube voltage 30 kV and tube current 100 μA.

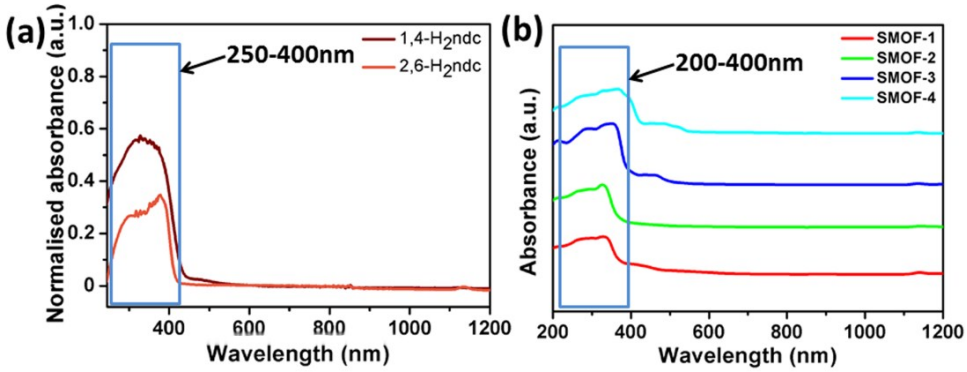


Fig. S10 The UV-Vis absorption spectra of free ligands 1,4-H_2ndc and 2,6-H_2ndc (a) and **SMOFs 1-4** (b).

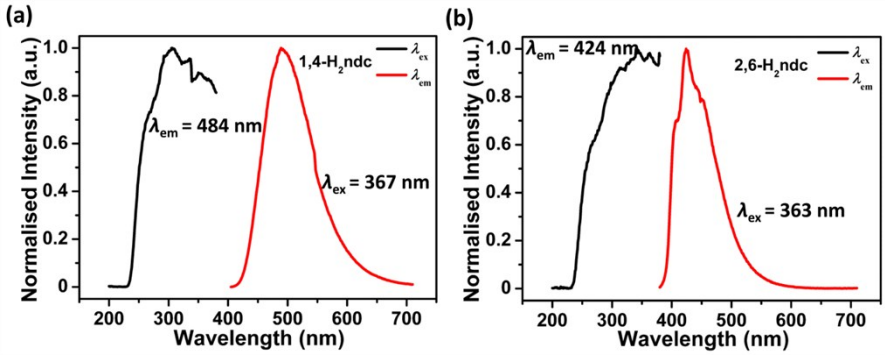


Fig. S11 The excitation and emission spectra of free ligands 1,4-H_2ndc and 2,6-H_2ndc.

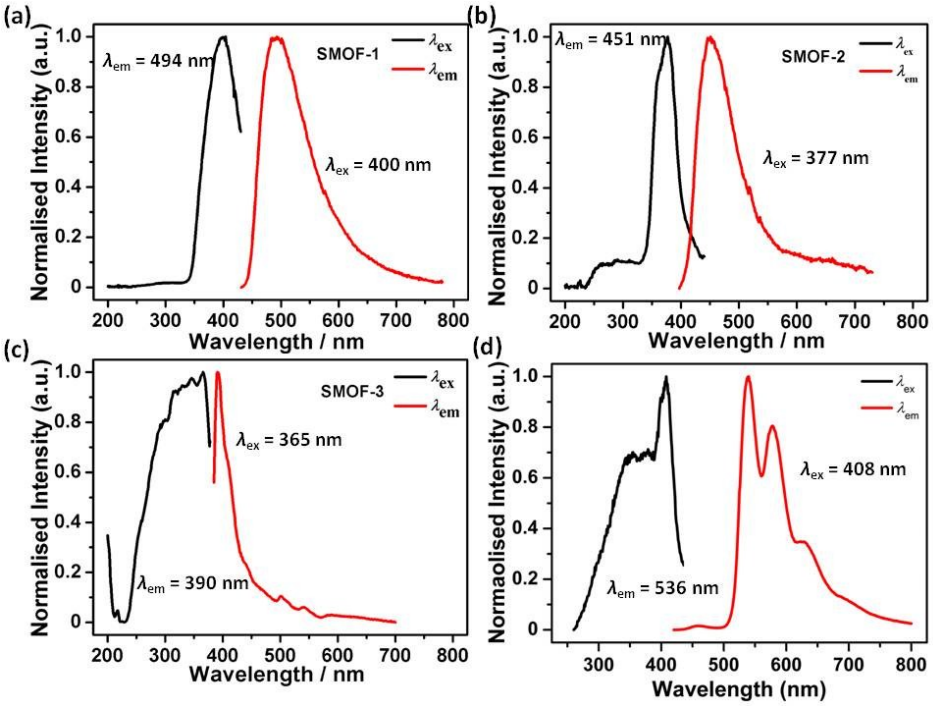


Fig. S12 Solid-state steady excitation and emission spectra of **SMOFs 1-4**.

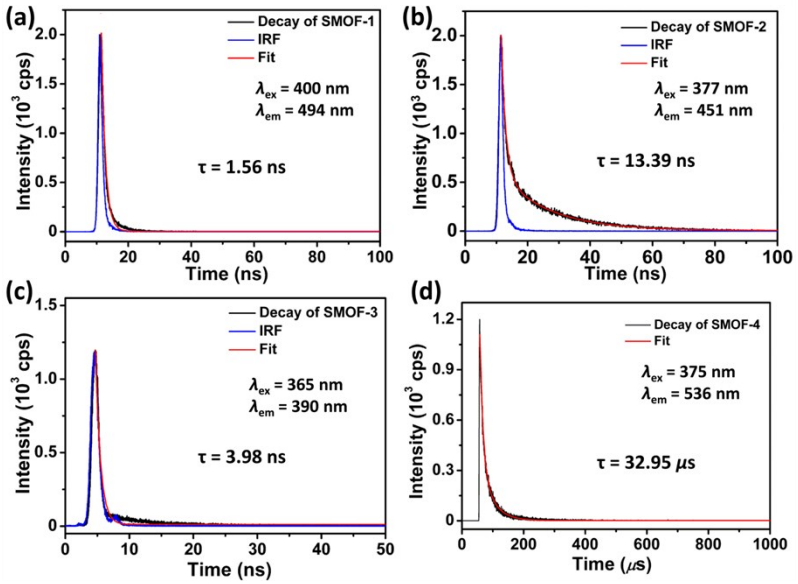


Fig S13. Luminescence lifetimes of **SMOF-1** (a), **SMOF-2** (b), **SMOF-3** (c) and **SMOF-4** (d) in the solid state measured at room temperature.

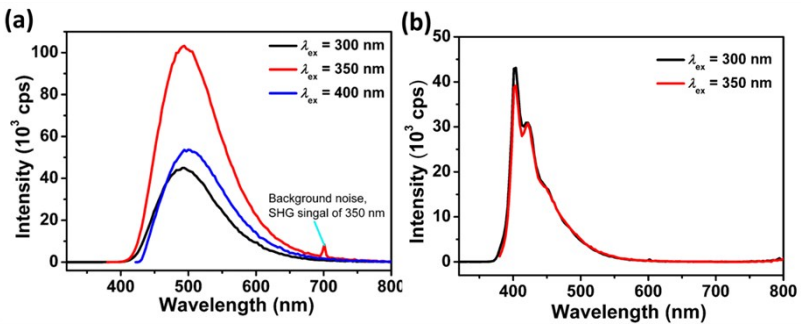


Fig. S14 Luminescent spectra of free ligands 1,4-H_2ndc (a) and 2,6-H_2ndc (b) towards varied excitation wavelengths, respectively.

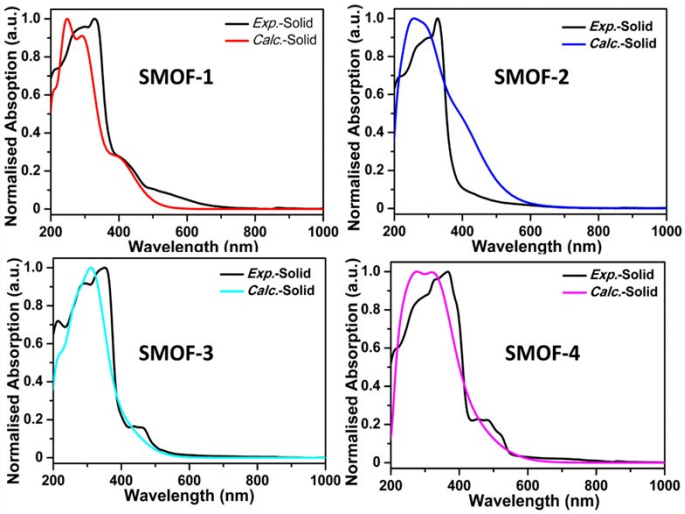


Fig. S15 Experimental UV-Vis normalized absorption spectra and calculated dielectric constants (imaginary part) of **SMOFs 1-4** transferred as in nm unit.

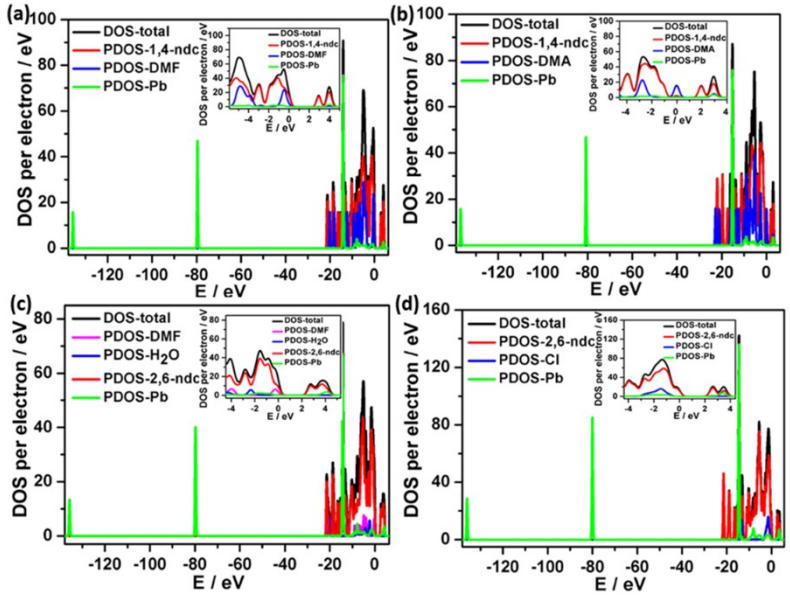


Fig. S16 Profiles of the total/partial electronic density of state of **SMOF-1** (a), **SMOF-2** (b), **SMOF-3** (c) and **SMOF-4** (d).

The bond lengths and angles information are listed in Tables S1-S4. Hydrogen bond information is listed in Table S5 with Olex2 1.2 program.[2-3]

Table S1 Selected bond lengths and bond angles for **SMOF 1**.

Pb(1)–O(3)#1	2.643(5)
Pb(1)–O(3)#2	2.683(5)
Pb(1)–O(4)#2	2.525(5)
Pb(1)–O(4)#3	2.706(4)
Pb(1)–O(1)	2.685(5)
Pb(1)–O(2)#4	2.344(6)
Pb(1)–O(5)	2.672(7)
O(3)#1–Pb(1)–O(3)#2	118.89(11)
O(3)#1–Pb(1)–O(4)#3	167.88(15)
O(3)#2–Pb(1)–O(4)#3	67.38(14)
O(3)#2–Pb(1)–O(1)	81.14(16)
O(3)#1–Pb(1)–O(1)	69.68(16)
O(3)#1–Pb(1)–O(5)	91.5(2)
O(4)#2–Pb(1)–O(3)#2	50.06(14)
O(4)#2–Pb(1)–O(3)#1	70.64(15)
O(4)#2–Pb(1)–O(4)#3	111.98(12)
O(4)#2–Pb(1)–O(1)	75.10(19)
O(4)#2–Pb(1)–O(5)	161.82(19)
O(1)–Pb(1)–O(4)#3	122.38(16)
O(2)#4–Pb(1)–O(3)#2	103.4(2)
O(2)#4–Pb(1)–O(3)#1	82.8(2)
O(2)#4–Pb(1)–O(4)#2	85.4(2)
O(2)#4–Pb(1)–O(4)#3	85.6(2)
O(2)#4–Pb(1)–O(1)	150.2(2)
O(2)#4–Pb(1)–O(5)	96.2(3)
O(5)–Pb(1)–O(3)#2	145.3(2)
O(5)–Pb(1)–O(4)#3	86.2(2)
O(5)–Pb(1)–O(1)	95.8(2)

Symmetric codes: #1 $1-x$, $-1/2+y$, $1/2-z$; #2 $1/2-x$, $1-y$, $1/2+z$; #3 $3/2-x$, $1-y$, $1/2+z$; #4 $1/2+x$, $1/2-y$, $1-z$.

Table S2 Selected bond lengths and bond angles for **SMOF-2**.

Pb(1)–O(1)#1	2.669(5)
Pb(1)–O(1)	2.552(5)
Pb(1)–O(2)#2	2.699(6)
Pb(1)–O(3)#3	2.372(6)
Pb(1)–O(4)#4	2.690(6)
Pb(1)–O(5)	2.525(7)

O(1)–Pb(1)–O(1)#1	115.24(14)
O(1)–Pb(1)–O(2)#2	73.31(17)
O(1)#1–Pb(1)–O(2)#2	168.21(17)
O(1)#1–Pb(1)–O(4)#3	119.41(19)
O(1)–Pb(1)–O(4)#3	76.9(2)
O(3)#4–Pb(1)–O(1)	86.4(2)
O(3)#4–Pb(1)–O(1)#1	85.4(2)
O(3)#4–Pb(1)–O(2)#2	87.2(2)
O(3)#4–Pb(1)–O(4)#3	154.3(2)
O(3)#4–Pb(1)–O(5)	92.1(3)
O(4)#3–Pb(1)–O(2)#2	69.41(18)
O(5)–Pb(1)–O(1)#1	86.6(3)
O(5)–Pb(1)–O(1)	157.9(3)
O(5)–Pb(1)–O(2)#2	84.6(3)
O(5)–Pb(1)–O(4)#3	96.0(3)

Symmetric codes: #1 1/2 + *x*, 1/2 – *y*, 2 – *z*; #2 1/2 + *x*, 1/2 – *y*, 1 – *z*; #3 3/2 – *x*, – *y*, – 1/2 + *z*; #4 1 – *x*, 1/2 + *y*, 3/2 – *z*.

Table S3 Selected bond lengths and bond angles for **SMOF-3**

Pb(1)–O(2)	2.664(4)
Pb(1)–O(1)	2.335(4)
Pb(1)–O(8)#1	2.500(4)
Pb(1)–O(9)#1	2.553(4)
Pb(1)–O(3)	2.580(4)
Pb(2)–O(5)	2.318(4)
Pb(2)–O(3)	2.646(4)
Pb(2)–O(1W)	2.376(5)
Pb(2)–O(4)	2.429(4)
O(1)–Pb(1)–O(2)	51.61(13)
O(1)–Pb(1)–O(8)#1	74.52(14)
O(1)–Pb(1)–O(9)#1	79.75(15)
O(1)–Pb(1)–O(3)	84.65(15)
O(8)#1–Pb(1)–O(2)	108.31(12)
O(8)#1–Pb(1)–O(9)#1	51.40(13)
O(8)#1–Pb(1)–O(3)	70.88(12)
O(9)#1–Pb(1)–O(2)	73.39(13)
O(9)#1–Pb(1)–O(3)	122.38(13)
O(3)–Pb(1)–O(2)	132.09(14)
O(5)–Pb(2)–O(3)	112.43(15)
O(5)–Pb(2)–O(1W)	75.98(16)

O(5)–Pb(2)–O(4)	81.79(16)
O(1W)–Pb(2)–O(3)	77.95(17)
O(1W)–Pb(2)–O(4)	108.6(2)
O(4)–Pb(2)–O(3)	50.68(13)

Symmetric code: #1 x, $1 + y$, z.

Table S4 Selected bond lengths and bond angles for **SMOF-4.**

Pb(1)–Cl(1)#1	2.8919(17)
Pb(1)–O(5)#1	2.414(4)
Pb(1)–O(6)#1	2.710(4)
Pb(1)–O(1)	2.355(4)
Pb(2)–Cl(1)#2	2.9173(17)
Pb(2)–O(3)	2.605(4)
Pb(2)–O(5)#1	2.731(5)
Pb(2)–O(6)#3	2.687(4)
Pb(2)–O(1)	2.677(4)
Pb(2)–O(4)	2.392(4)
O(5)#1–Pb(1)–Cl(1)#1	76.02(11)
O(5)#1–Pb(1)–O(6)#1	50.60(14)
O(6)#1–Pb(1)–Cl(1)	126.45(10)
O(1)–Pb(1)–Cl(1)	76.55(12)
O(1)–Pb(1)–O(5)#1	79.23(15)
O(1)–Pb(1)–O(6)#1	95.08(15)
O(3)–Pb(2)–Cl(1)#2	71.29(10)
O(3)–Pb(2)–O(5)#1	71.81(13)
O(3)–Pb(2)–O(6)#3	134.73(13)
O(3)–Pb(2)–O(1)	79.26(14)
O(5)#1–Pb(2)–Cl(1)#2	142.11(10)
O(6)#3–Pb(2)–Cl(1)#2	120.16(11)
O(6)#3–Pb(2)–O(5)#1	92.24(14)
O(1)–Pb(2)–O(5)#1	68.43(13)
O(1)–Pb(2)–O(6)#3	134.73(14)
O(1)–Pb(2)–Cl(1)# 1	96.39(10)
O(4)–Pb(2)–Cl(1)# 2	81.96(12)
O(4)–Pb(2)–O(3)	52.58(14)
O(4)–Pb(2)–O(5)#1	82.55(14)
O(4)–Pb(2)–O(6)#3	84.13(14)
O(4)–Pb(2)–O(1)	129.88(15)

Symmetric codes: #1 $1 - x$, $1/2 + y$, $1/2 - z$; #2 $2 + x$, $3/2 - y$, $-1/2 + z$; #3 $2 - x$, $1/2 + y$, $1/2 - z$.

Table S5 Hydrogen bonding distance/Å and angle/° in the crystal structure of **SMOF-3.**

D–H…A	d(D–H)	d(H..A)	d(D..A)	∠DHA
O1W–H1WA…O10#4	0.941	1.855	2.640	139.25
O1W–H1WB…O(1)	0.947	1.883	2.790	159.59

Table S6 The geometrical parameters of π–π interactions between aromatic rings in **SMOF-4** calculated by the PLATON software.[4]

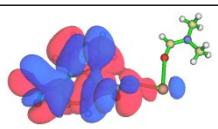
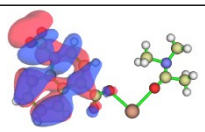
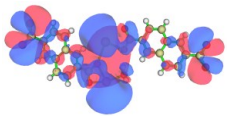
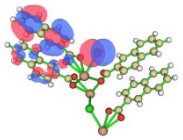
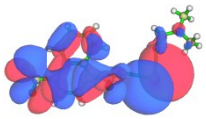
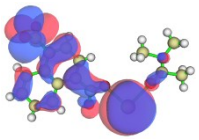
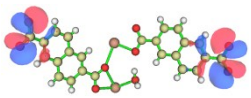
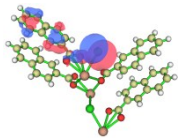
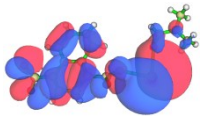
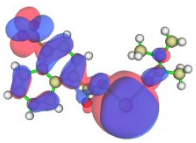
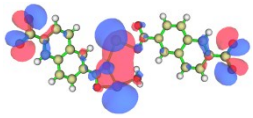
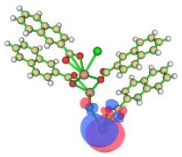
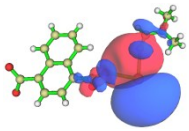
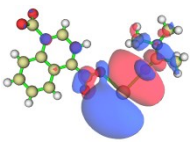
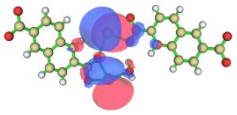
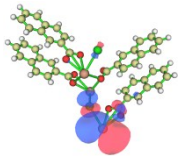
Cg(I)-Cg(J)	Cg-Cg(Å)	Alpha(°)	Beta(°)	Gamma(°)	CgI_Perp(Å)	CgJ_Perp(Å)	Slippage(Å)
Cg1-Cg3	3.718(4)	1.3(3)	22.8	22.4	3.437(3)	3.429(3)	1.439
Cg1-Cg3	3.664(4)	1.3(3)	19.2	20.3	-3.437(3)	3.461(3)	1.202
Cg1-Cg4	3.664(4)	1.3(3)	19.2	20.3	3.437(3)	3.461(3)	1.202
Cg1-Cg4	3.718(4)	1.3(3)	22.8	22.4	-3.437(3)	3.429(3)	1.439
Cg2-Cg2	3.800(4)	0.0(3)	26.8	26.8	-3.391(3)	-3.391(3)	1.715
Cg2-Cg3	3.756(4)	5.1(3)	25.5	27.8	3.322(3)	3.390(3)	1.618
Cg2-Cg4	3.756(4)	5.1(3)	25.5	27.8	-3.322(3)	3.390(3)	1.618
Cg3-Cg1	3.718(4)	1.3(3)	22.4	22.8	3.428(3)	3.436(3)	1.419
Cg3-Cg1	3.664(4)	1.3(3)	20.3	19.2	3.461(3)	-3.436(3)	1.270
Cg3-Cg2	3.755(4)	5.1(3)	27.8	25.5	3.389(3)	3.322(3)	1.751
Cg4-Cg1	3.664(4)	1.3(3)	20.3	19.2	3.461(3)	3.436(3)	1.270
Cg4-Cg1	3.718(4)	1.3(3)	22.4	22.8	3.428(3)	-3.436(3)	1.419
Cg4-Cg2	3.755(4)	5.1(3)	27.8	25.5	3.390(3)	-3.322(3)	1.751

Notes: Cg(I) / Cg(J) = the plane of the ring in the structure, Alpha = dihedral angle between planes of ring I and J (°), Beta = Angle Cg(I)- Cg(J) or Cg(I)-->Me vector and normal to plane I (°), Gamma = Angle Cg(I)-Cg(J) vector and normal to plane J (°), Cg-Cg = distance between ring centroids (Å), CgI_Perp = perpendicular distance of Cg(I) on ring J (Å), CgJ_Perp = Perpendicular distance of Cg(J) on ring I (°), Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (°).

Table S7 Fluorescence decay parameters of **SMOFs 1-4**.

λ_{em} / nm	τ_1	A_1 (%)	τ_2	A_2 (%)	τ_3	A_3 (%)	τ
SMOF-1							
494	1.01 ns	77.68	3.68 ns	22.32			1.56 ns
SMOF-2							
451	1.53 ns	21.07	16.64 ns	78.93			13.39 ns
SMOF-3							
390	0.52 ns	55.04	8.23 ns	44.96			3.98 ns
SMOF-4							
424	0.78 ns	31.43	5.08 ns	20.80	28.98 ns	47.77	14.37 ns
536	7.78 μs	19.77	24.61 μs	59.93	82.80 μs	20.30	32.95 μs
578	7.94 μs	18.65	23.75 μs	58.84	80.36 μs	22.51	33.55 μs
633	7.49 μs	17.25	23.17 μs	53.72	91.56 μs	29.04	47.15 μs

Table S8 Schematic representation of the optimized geometrical structure and HOMO–1, HOMO, LUMO and LUMO+1 orbits of **SMOFs 1-4** drawn with Multiwfn software.[5]

SMOF	1	2	3	4
HOMO–1				
HOMO				
LUMO				
LUMO+1				

References

1 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys Rev Lett*, 1996, **77**, 3865–3868.

2 O. V. Dolomanov, L.J. Bourhis, R.J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl.Cryst*., 2009, **42**, 339–341.

3 G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–8.

4 A. L. Spek, *J. Appl. Cryst.,* 2003. **36**, 7–13.

5 T. Lu and F. Chen, *J. Comput. Chem*., 2012, **33**, 580–592.