Lead-MOFs derived from an aggregation-induced emission ligand: heat-induced fluorescence "turn-on" thermometer and the role of Na^+ cation†

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Experimental Section

Materials and methods

All the chemicals and solvent are purchased commercially and directly used without further purification. Organic ligand H_4ETTC was synthesized according to the previously reported procedure.[S1] FT-IR spectra were recorded in the range of 400-4000 cm^{-1} on a Bruker Vector 22 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 449F3 thermal analyzer under nitrogen with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were collected at room temperature on bulk samples with Cu Kα radiation (1.54059 Å) on a Bruker D8 Advance X-ray diffractometer. The photoluminescence spectra were on an Edinburgh Instruments FLS1000 spectrometer. The temperature-dependent emission spectra were recorded with the same spectrometer by encapsulating the samples of MOFs into the sample tank of ARS Optical Crystat (4K-300K) fluorescent controller.

X-ray crystallography

Single crystal X-ray diffraction (SC-XRD) data of complex **1-2** was collected on a Bruker D8 Advance diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the φ–ω scan technique. The integration of diffraction data and intensity corrections for the Lorentz and polarization effects were performed by using SAINT program.[S2] Semi-empirical absorption corrections were applied using SADABS program.[S3] The structures were solved by direct methods with SHELXT-2018, expanded by subsequent Fourier-difference synthesis, and all the non-hydrogen atoms were refined anisotropically on F^2 using the full-matrix least-squares technique using the SHELXL-2018 crystallographic software package.[S4,S5] The free solvent molecules in the unit cell have been taken into account to SQUEEZE option of the PLATON program.[S6] Hydrogen atoms except those of coordinated water molecules were introduced at the calculated positions. The final chemical formulas were obtained based on volume/count electron analysis and TG analysis. The coordinated DMA molecules in complex 1 are disordered into two positions with a site occupancy of 0.5:0.5. The atoms C1, C48-C54, O2, O7 and O8 in compound **2** are all disordered into two positions with a site occupancy of ~0.58 (C48-C54, O7 and O8) for and ~0.33 (C1

and O2). The reported refinements were of the guest-free structures obtained by the SQUEEZE routine and the results were attached to the CIF files. The details of crystal parameters, data collection and refinements are listed in Table S1, and the selected bond lengths and angles are given in Table S2.

Table S1. Crystal Data and Structure Refinements for **1, 1a** and **2**.

	1	**2**	**1a**
Formula	$C_{70}H_{68}N_4O_{12}Pb_2$	$C_{132}H_{123.5}N_{6.5}O_{21.5}Pb_2Na$	$C_{70}H_{70}N_4O_{13}Pb_2$
Formula weight	1571.66	2582.24	1589.68
T (K)	193	297	140
Crystal system	Triclinic	monoclinic	Triclinic
Space group	*P*-1	*C*2/*c*	*P*-1
a (Å)	11.9516(10)	33.065(4)	12.117(2)
b (Å)	13.8011(12)	9.8681(12)	13.616(2)
c (Å)	19.8121(18)	41.786(5)	19.781(4)
α (°)	94.707(3)	90	94.633(6)
β (°)	100.551(3)	101.575(4)	99.997(6)
γ (°)	93.367(3)	90	93.336(5)
V (Å^3)	3192.7(5)	13357(3)	3194.8(9)
Z	2	4	2
D_{calc} (g cm^{-3})	1.635	1.284	1.653
μ (mm^{-1})	5.332	2.586	5.331
F(000)	1552	5232	1572
R_{int}	0.0455	0.0780	0.0524
Reflections collected	22596	211547	22251
Unique reflections	11444	15400	11477
Goodness-of-fit on F^2	1.049	1.005	1.044
R_1,	0.0519	0.0570	0.0635
wR_2 [I > 2σ(*I*)][a, b]	0.1183	0.1556	0.1885
R_1,	0.0717	0.1061	0.0720
wR_2 [all data]	0.1303	0.1860	0.2005

[a]R_1 =$\Sigma||F_o|$ - $|F_c||/\Sigma|F_o|$. [b]wR_2 = $|\Sigma w(|F_o|^2$ - $|F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where w = m= $1/[\sigma^2(F_o^2)$ $+(aP)^2+bP]$. P = $(F_o^2 + 2F_c^2)/3$.

Table S2. Selected bond lengths (Å) and angles (°) for **1, 1a** and **2**.

1			
Pb(1)-O(2)	2.353(6)	Pb(1)-O(5)#1	2.357(7)
Pb(1)-O(4)#2	2.631(6)	Pb(1)-O(6)#3	2.676(7)
Pb(1)-O(6)#1	2.715(6)	Pb(1)-O(1F)	2.630(2)
Pb(1)-O(1)	3.058(2)	Pb(1)-O(1E)	3.060(16)
Pb(1)-O(7)#4	3.076(2)	Pb(2)-O(1)	2.411(7)
Pb(2)-O(7)#4	2.418(6)	Pb(2)-O(4)#2	2.486(5)
Pb(2)-O(1D)	2.507(2)	Pb(2)-O(3)#2	2.576(6)
Pb(2)-O(1C)	2.650(2)	Pb(2)-O(8)#4	2.790(2)
Pb(2)-O(8)#5	2.817(2)		
O(1)-Pb(1)-O(2)	46.4(5)	O(1)-Pb(1)-O(7)#4	62.8(4)
O(1)-Pb(1)-O(4)#2	64.6(5)	O(1)-Pb(1)-O(6)#3	78.1(5)
O(1)-Pb(1)-O(5)#1	121.8(6)	O(1)-Pb(1)-O(6)#1	122.8(5)
O(1)-Pb(1)-O(1E)	132.3(6)	O(1)-Pb(1)-O(1F)	143.1(7)
O(2)-Pb(1)-O(4)#2	73.5(2)	O(2)-Pb(1)-O(5)#1	79.8(3)
O(2)-Pb(1)-O(6)#3	77.0(2)	O(2)-Pb(1)-O(6)#1	82.0(2)
O(2)-Pb(1)-O(7)#4	107.2(6)	O(2)-Pb(1)-O(1F)	148.0(8)
O(2)-Pb(1)-O(1E)	153.5(4)	O(4)#2-Pb(1)-O(7)#4	62.3(4)
O(4)#2-Pb(1)-O(5)#1	82.6(2)	O(4)#2-Pb(1)-O(1E)	83.2(4)
O(4)#2-Pb(1)-O(1F)	86.5(6)	O(4)#2-Pb(1)-O(6)#1	130.8(18)
O(4)#2-Pb(1)-O(6)#3	142.3(19)	O(5)#1-Pb(1)-O(6)#1	50.9(2)
O(5)#1-Pb(1)-O(1F)	72.8(6)	O(5)#1-Pb(1)-O(1E)	84.8(4)
O(5)#1-Pb(1)-O(6)#3	114.8(2)	O(5)#1-Pb(1)-O(7)#4	139.1(6)
O(6)#1-Pb(1)-O(6)#3	66.0(2)	O(6)#1-Pb(1)-O(1F)	93.2(6)
O(6)#1-Pb(1)-O(1E)	104.8(4)	O(6)#1-Pb(1)-O(7)#4	166.6(6)
O(6)#3-Pb(1)-O(7)#4	106.0(5)	O(6)#3-Pb(1)-O(1E)	129.3(4)
O(6)#3-Pb(1)-O(1F)	129.7(8)	O(7)#4-Pb(1)-O(1E)	71.5(5)
O(7)#4-Pb(1)-O(1F)	84.0(5)	O(1E)-Pb(1)-O(1F)	12.9(4)
O(1)-Pb(2)-O(4)#2	77.4(2)	O(1)-Pb(2)-O(3)#2	79.6(2)
O(1)-Pb(2)-O(7)#4	82.9(2)	O(1)-Pb(2)-O(8)#4	88.2(6)
O(1)-Pb(2)-O(8)#5	88.8(5)	O(1)-Pb(2)-O(1C)	157.21(8)
O(1)-Pb(2)-O(1D)	159.0(6)	O(3)#2-Pb(2)-O(4)#2	51.8(19)
O(3)#2-Pb(2)-O(1C)	85.1(6)	O(3)#2-Pb(2)-O(8)#5	98.0(5)
O(3)#2-Pb(2)-O(1D)	103.6(6)	O(3)#2-Pb(2)-O(7)#4	126.1(2)
O(3)#2-Pb(2)-O(8)#4	167.7(7)	O(4)#2-Pb(2)-O(7)#4	74.7(2)
O(4)#2-Pb(2)-O(1C)	79.9(6)	O(4)#2-Pb(2)-O(1D)	88.3(6)
O(4)#2-Pb(2)-O(8)#4	124.0(6)	O(4)#2-Pb(2)-O(8)#5	148.3(6)
O(7)#4-Pb(2)-O(8)#4	49.8(5)	O(7)#4-Pb(2)-O(1D)	78.5(5)
O(7)#4-Pb(2)-O(1C)	92.8(6)	O(7)#4-Pb(2)-O(8)#5	132.3(6)

O(8)#4-Pb(2)-O(8)#5	83.1(5)	O(8)#4-Pb(2)-O(1D)	87.3(6)
O(8)#4-Pb(2)-O(1C)	106.2(6)	O(8)#5-Pb(2)-O(1C)	110.1(7)
O(8)#5-Pb(2)-O(1D)	111.0(7)	O(1C)-Pb(2)-O(1D)	19.1(5)

2

Pb(1)-O(7)#2	2.35(4)	Pb(1)-O(7A)#2	2.57(5)
Pb(1)-O(5)#1	2.512(5)	Pb(1)-O(1)	2.515(5)
Pb(1)-O(1A)	2.515(5)	Pb(1)-O(2A)	2.474(10)
Pb(1)-O(2B)	2.697(15)	Pb(1)-O(6)#1	2.719(5)
Pb(1)-O(8)#2	2.730(9)	Pb(1)-O(8)#6	2.885(3)
Na(1)-O(1)	2.3596(5)	Na(1)-O(1)#3	2.359(5)
Na(1)-O(5)#1	2.511(5)	Na(1)-O(5)#4	2.511(5)
Na(1)-O(7)#2	2.35(3)	Na(1)-O(7)#5	2.35(3)
Na(1)-O(7A)#5	2.18(4)	Na(1)-O(7A)#2	2.18(4)
Na(1)-O(1A)	2.359(5)		
O(1)-Pb(1)-Na(1)	43.35(11)	O(1)-Pb(1)-O(5)#1	75.20(17)
O(1)-Pb(1)-O(6)#1	82.06(18)	O(1)-Pb(1)-O(7A)#2	68.8(11)
O(1)-Pb(1)-O(8)#2	99.0(3)	O(2A)-Pb(1)-Na(1)	89.7(2)
O(2A)-Pb(1)-O(1)	54.4(3)	O(2A)-Pb(1)-O(5)#1	129.6(3)
O(2A)-Pb(1)-O(6)#1	116.4(4)	O(2A)-Pb(1)-O(7A)#2	86.6(13)
O(2A)-Pb(1)-O(8)#2	70.5(4)	O(5)#1-Pb(1)-O(6)#1	48.95(15)
O(5)#1-Pb(1)-O(7A)#2	74.1(11)	O(5)#1-Pb(1)-O(8)#2	122.8(3)
O(5)#1-Pb(1)-O(2B)	117.1(4)	O(6)#1-Pb(1)-O(8)#2	171.3(3)
O(7)#2-Pb(1)-O(1)	75.6(8)	O(7)#2-Pb(1)-O(2A)	93.1(9)
O(7)#2-Pb(1)-O(5)#1	72.4(8)	O(7)#2-Pb(1)-O(6)#1	120.9(8)
O(7)#2-Pb(1)-O(8)#2	51.7(8)	O(7A)#2-Pb(1)-O(8)#2	52.2(10)
O(7A)#2-Pb(1)-O(2B)	102.7(13)	O(1A)-Pb(1)-O(8)#2	99.0(3)
O(1A)-Pb(1)-O(2B)	48.2(3)	O(2B)-Pb(1)-O(8)#2	94.6(5)
O(8)#6-Pb(1)-O(7)#2	104.6(4)	O(8)#6-Pb(1)-O(5)#1	112.9(3)
O(8)#6-Pb(1)-O(1)	171.2(4)	O(8)#6-Pb(1)-O(2A)	125.0(5)
O(8)#6-Pb(1)-O(8)#2	74.0(4)	O(8)#6-Pb(1)-O(6)#1	106.0(4)
O(1)-Na(1)-O(1)#3	180.0	O(1)-Na(1)-O(5)#1	78.03(15)
O(1)-Na(1)-O(5)#4	101.97(15)	O(1)#3-Na(1)-O(5)#1	101.97(15)
O(1)#3-Na(1)-O(5)#4	78.03(15)	O(1)#3-Na(1)-O(7)#2	101.3(12)
O(1)#3-Na(1)-O(7)#5	78.7(12)	O(1)-Na(1)-O(7)#2	78.7(12)
O(1)-Na(1)-O(7)#5	101.3(12)	O(5)#4-Na(1)-O(5)#1	180.00(10)
O(7)#2-Na(1)-O(5)#4	107.5(5)	O(7)#5-Na(1)-O(5)#1	107.5(5)
O(7)#2-Na(1)-O(5)#1	72.5(5)	O(7)#5-Na(1)-O(5)#4	72.5(5)

O(7)#5-Na(1)-O(7)#2	180(2)	O(7A)#2-Na(1)-O(1A)	78.5(19)
O(7A)#5-Na(1)-O(1A)	101.5(19)		

1a

Pb(1)-O(6)#1	2.736(6)	Pb(1)-O(4)	2.501(5)
Pb(1)-O(1)#2	2.410(6)	Pb(1)-O(5)#1	2.389(6)
Pb(1)-O(3)	2.588(6)	Pb(1)-O(9)	2.575(8)
Pb(2)-O(4)	2.629(5)	Pb(2)-O(7)#3	2.670(5)
Pb(2)-O(7)#4	2.678(5)	Pb(2)-O(2)#2	2.339(6)
Pb(2)-O(8)#3	2.357(6)		
O(4)-Pb(1)-O(6)#1	124.92(19)	O(4)-Pb(1)-O(3)	51.65(18)
O(4)-Pb(1)-O(9)	84.3(2)	O(1)#2-Pb(1)-O(6)#1	88.7(2)
O(1)#2-Pb(1)-O(4)	77.93(19)	O(1)#2-Pb(1)-O(3)	79.0(2)
O(1)#2-Pb(1)-O(9)	153.6(2)	O(5)#1-Pb(1)-O(6)#1	50.69(19)
O(5)#1-Pb(1)-O(4)	74.39(19)	O(5)#1-Pb(1)-O(1)#2	81.1(2)
O(5)#1-Pb(1)-O(3)	125.14(18)	O(5)#1-Pb(1)-O(9)	75.3(2)
O(3)-Pb(1)-O(6)#1	167.6(2)	O(9)-Pb(1)-O(6)#1	85.5(2)
O(9)-Pb(1)-O(3)	105.1(2)	O(4)-Pb(2)-O(7)#3	129.26(17)
O(4)-Pb(2)-O(7)#4	143.53(17)	O(7)#3-Pb(2)-O(7)#4	65.69(19)
O(2)#2-Pb(2)-O(4)	73.51(19)	O(2)#2-Pb(2)-O(7)#3	78.94(19)
O(2)#2-Pb(2)-O(7)#4	78.8(2)	O(2)#2-Pb(2)-O(8)#3	80.1(2)
O(8)#3-Pb(2)-O(4)	81.69(18)	O(8)#3-Pb(2)-O(7)#4	116.58(18)
O(8)#3-Pb(2)-O(7)#3	51.79(18)		

Symmetry codes:#1 x+1, y+1, z; #2 -x+2, -y+2, -z+1; #3 -x+1, -y+1, -z; #4 x+1, y, z-1; #5 -x+1, -y+1, -z+1 for **1**. #1 x-1/2, y-1/2, z; #2 x-1/2, -y+3/2, z-1/2; #3 -x, -y+1, -z; #4 -x+1/2, -y+3/2, -z; #5 -x+1/2, y-1/2, -z+1/2; #6 -x+1/2, -y+1/2, z for **2**. #1 -x+1,-y+1,-z+1; #2 -x,-y+1,-z+2; #3 -x+1,-y+2,-z+2; #4 x-1,y-1,z-1 for **1a**.

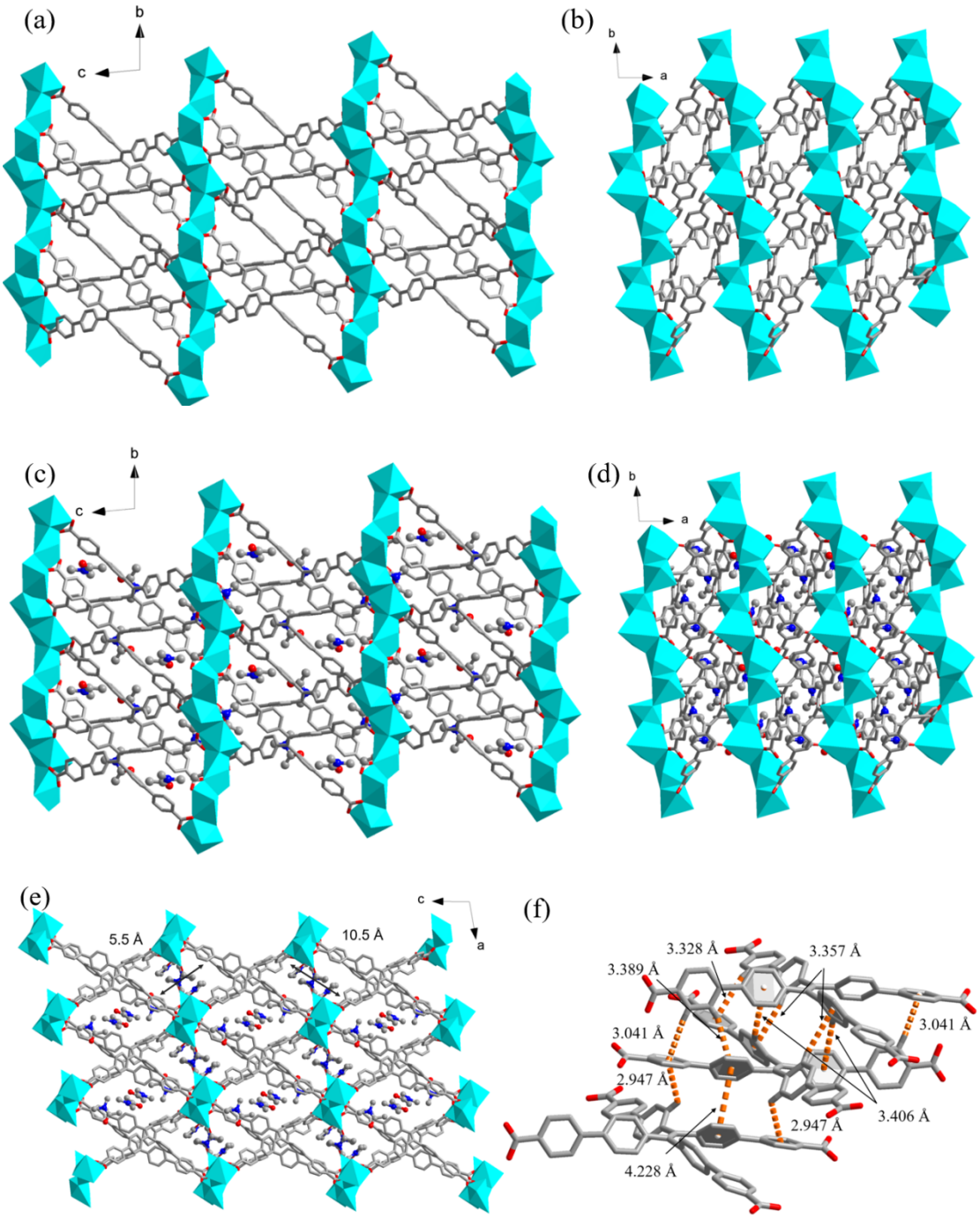


Fig. S1. 3D coordination framework of complex **1** along *a*-axis (a, c), *b*-axis (e), and *c*-axis (b, d) without and with DMA molecules filled in the channels. (f) The π…π interactions between the $ETTC^{4-}$ ligands in **1**.

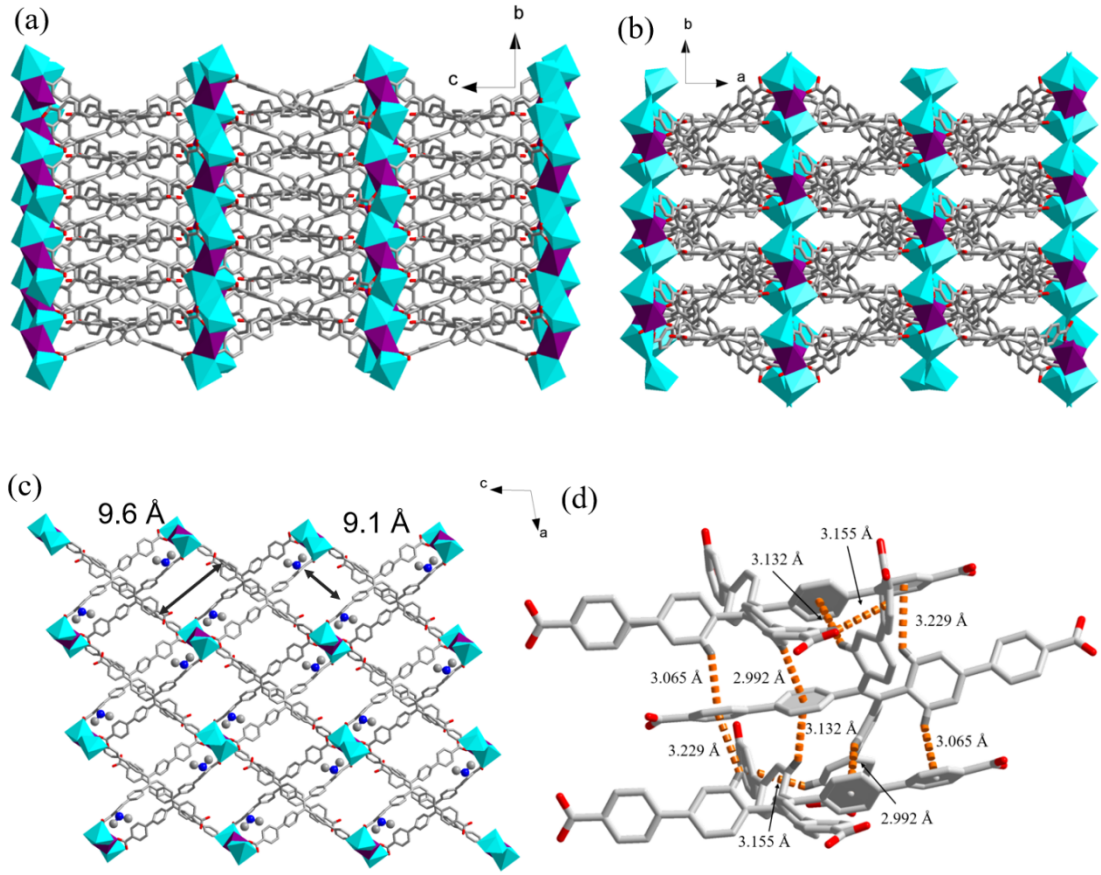


Figure S2. 3D coordination framework of complex **2** along *a*-axis (a) and *c*-axis (b). (c) The final strcuture of complex 2 with $[(CH_3)_2NH_2]^+$ cations filled in the pores along *b*-axis. (d) The π…π interactions between the $ETTC^{4-}$ ligands in **2**.

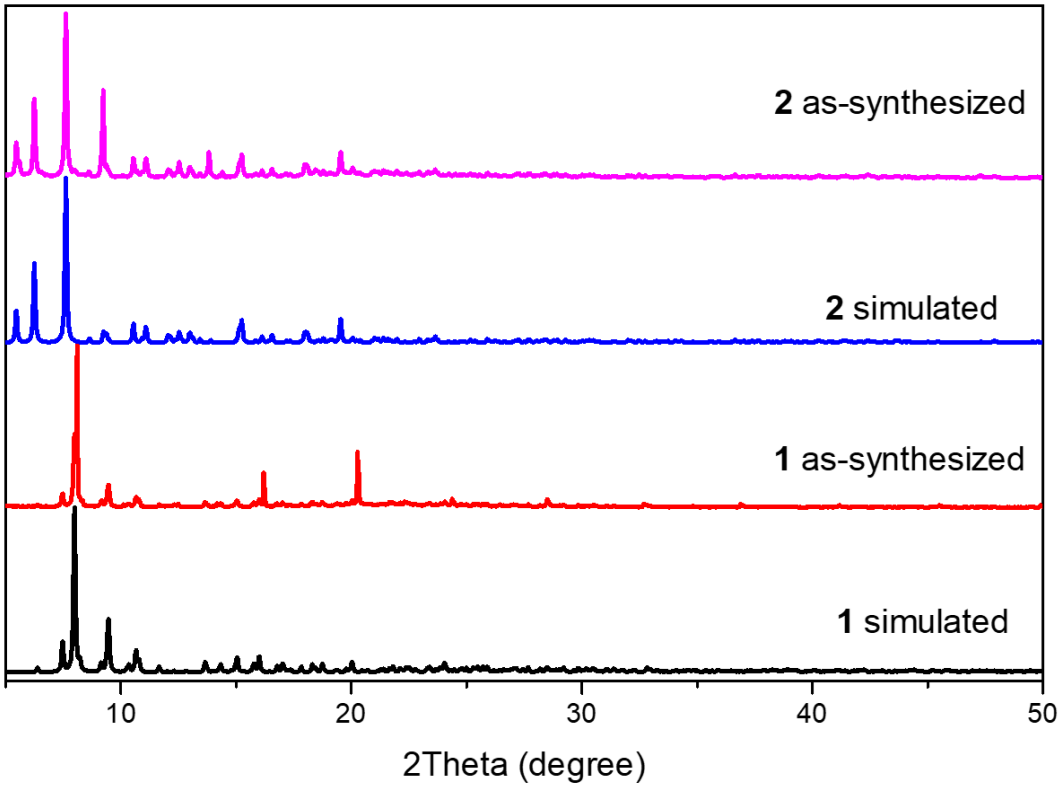


Fig. S3. PXRD patterns of MOFs **1** and **2**.

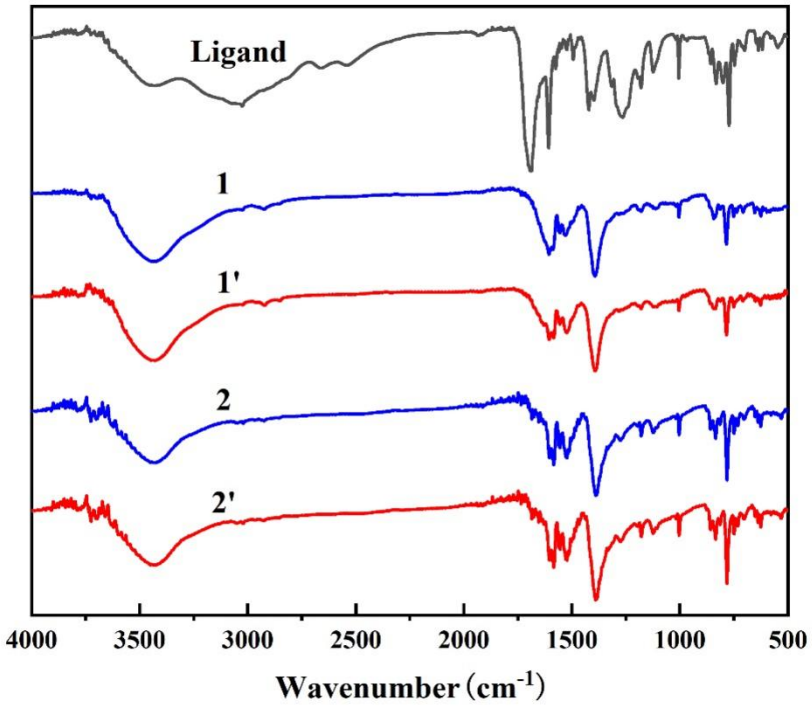


Figure S4. FT-IR spectra of organic ligand H_4ETTC, MOFs **1** and **2**, MOFs **1'** and **2'** after recyclability tests.

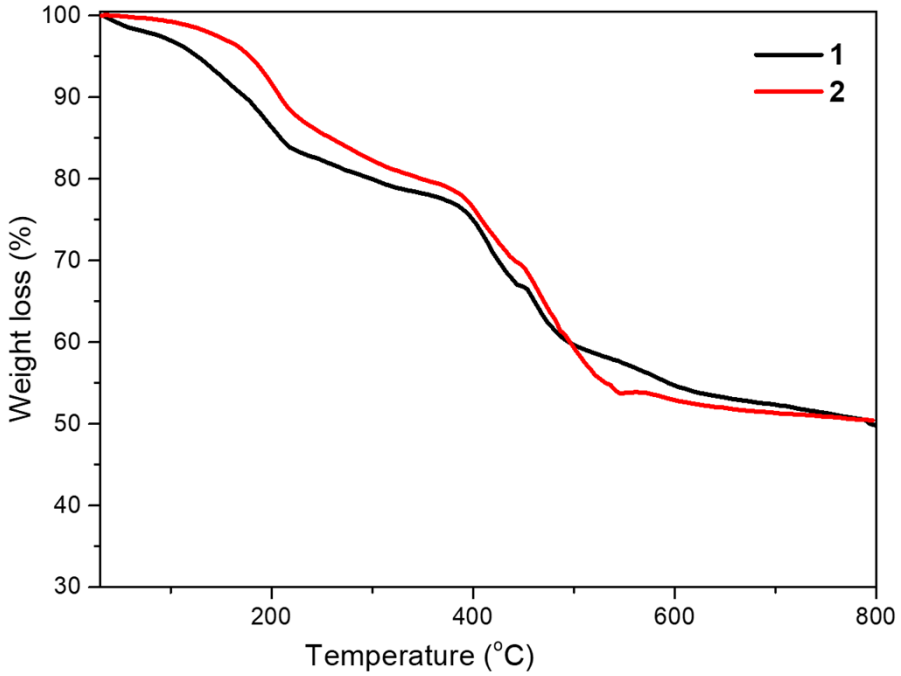
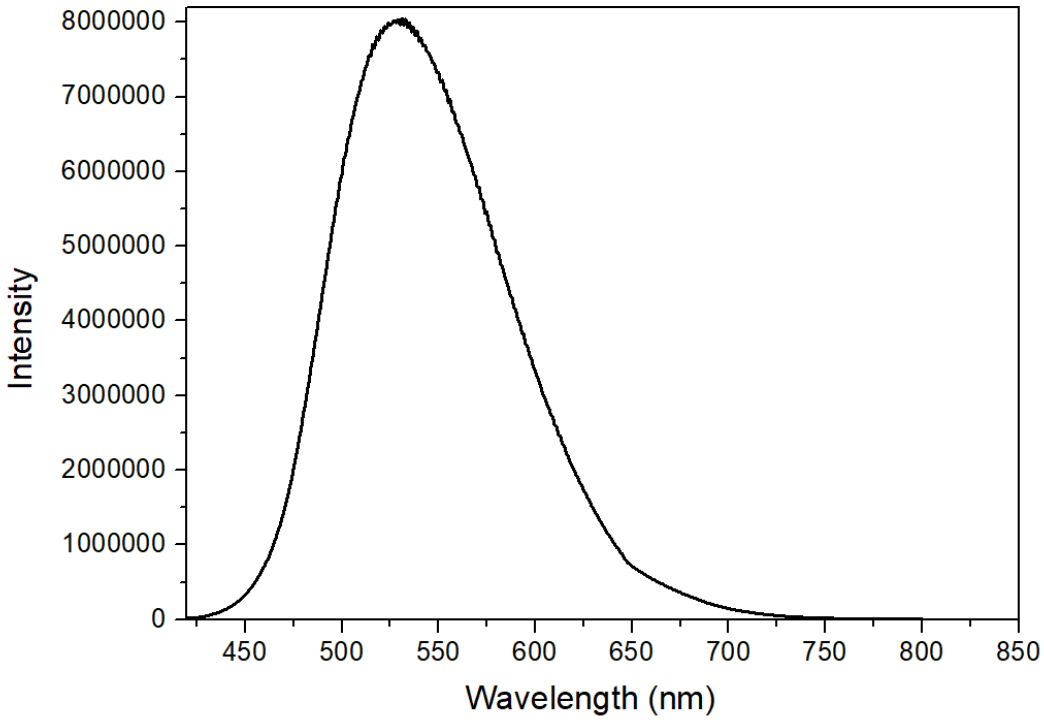
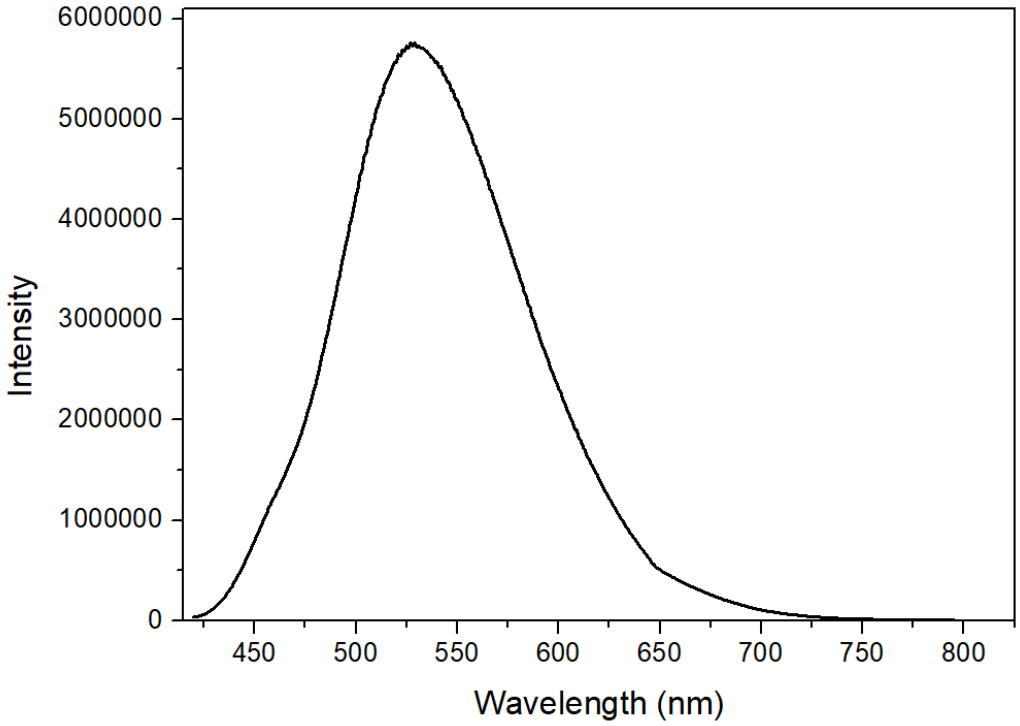


Fig. S5. TG curves of MOFs **1** and **2**.

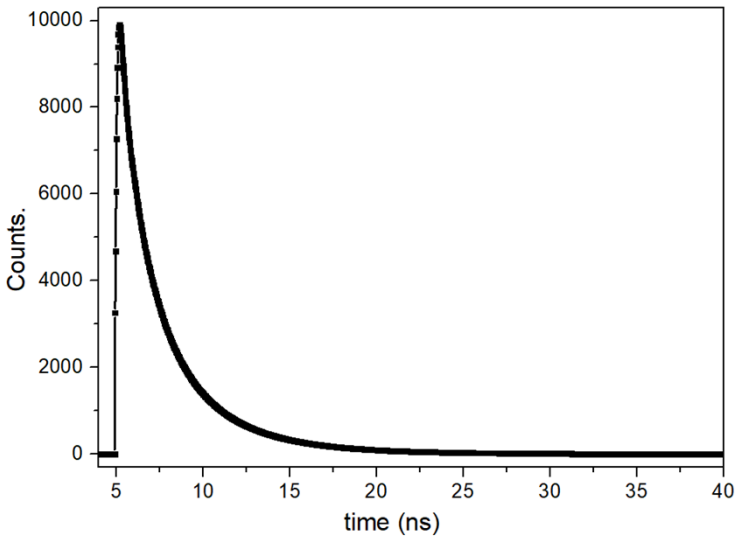


(a)

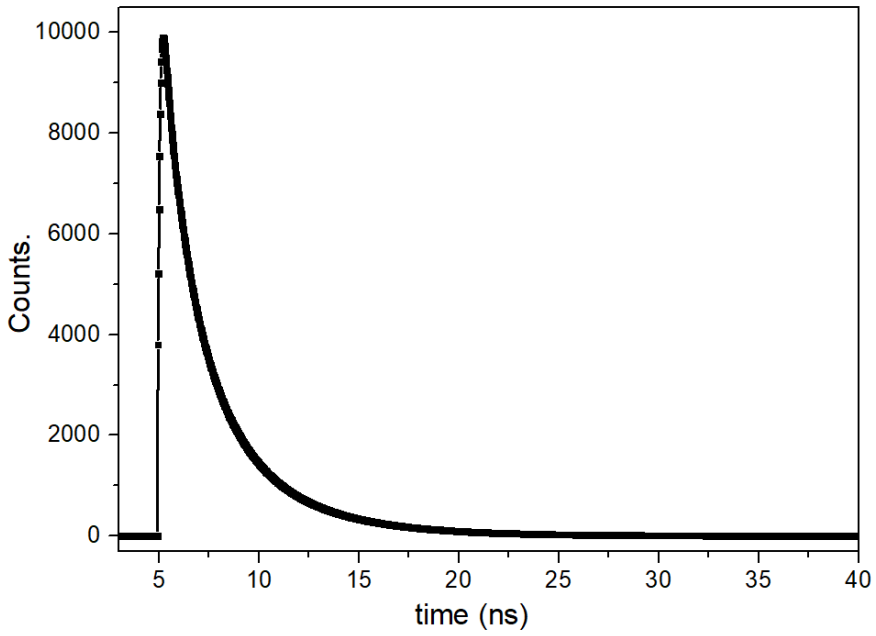


(b)

Fig. S6. The solid-state fluorescnece emission of complex **1** (a) and **2** (b).

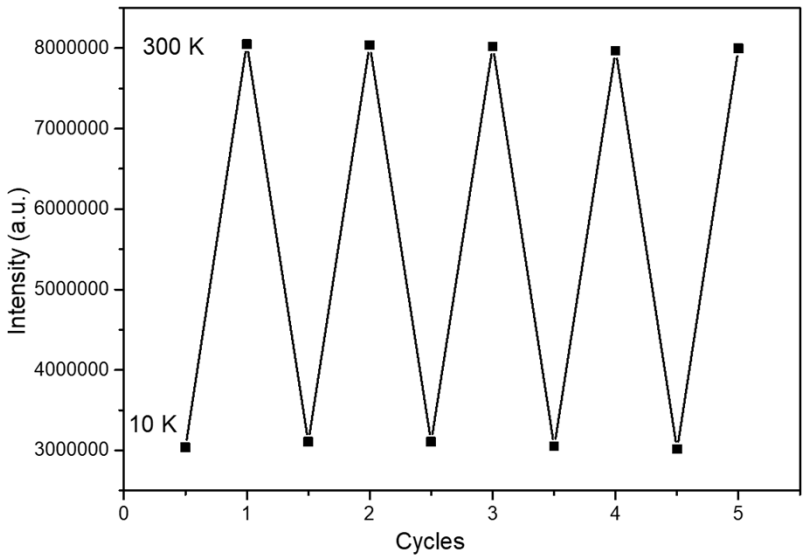


(a)

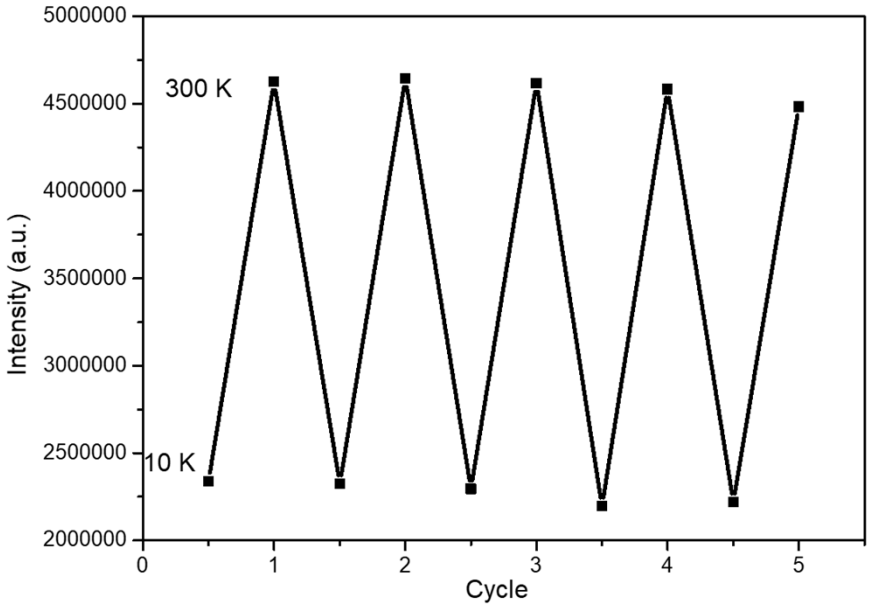


(b)

Figure S7. Fluorescence lifetime measurements for a powder sample of MOFs **1** (a) and **2** (b) at room temperature.



(a)



(b)

Fig. S8. Recyclability tests for MOF **1** and **2** as thermometers.

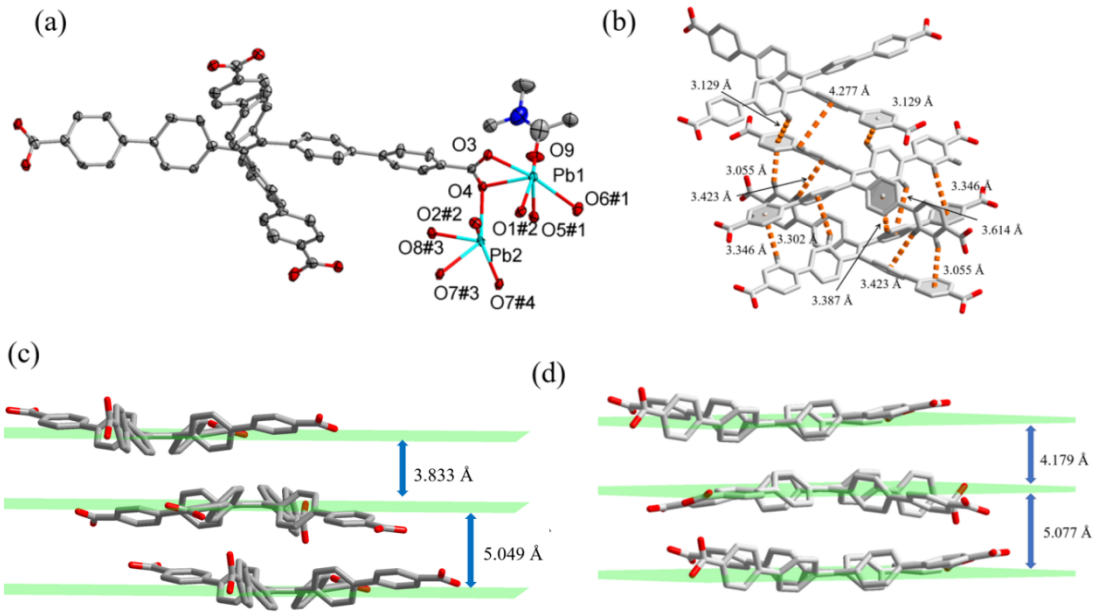


Fig. S8. (a) The coordination environments of Pb^{2+} cations in **1a** with the ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Symmetric code: #1 -x+1,-y+1,-z+1; #2 -x,-y+1,-z+2; #3 -x+1,-y+2,-z+2; #4 x-1,y-1,z-1. (b) The π…π interactions between the $ETTC^{4-}$ ligands in **1a**. The distances distance between adjacent $ETTC^{4-}$ ligands in **1a** (c) and **1** (d).

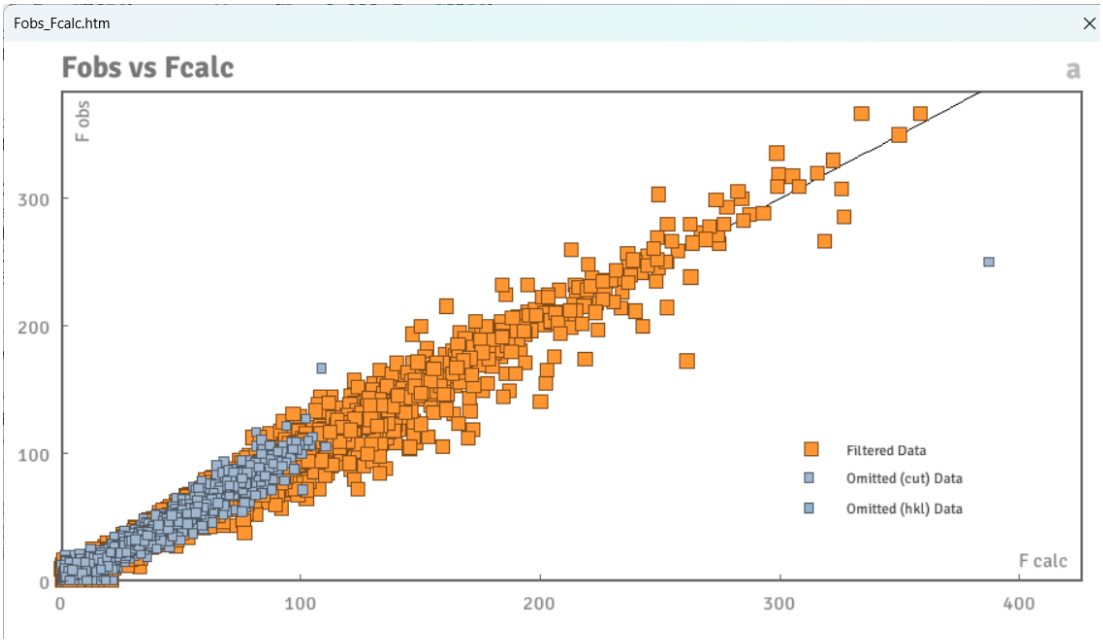


Fig. S9. the plot of Fobs versus Fcalc for complex **1'**

(The data obtained for complex **1'** were unsatisfactory due to weathering caused by temperature increase during the testing process)

Reference:

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