Calcium-based efficient cathode-ray scintillating metal-organic frameworks constructed from π-conjugated luminescent motifs†‡

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Experimental section

All of the chemicals were purchased from commercial sources and were used without further purification. Metal ion salt $Ca(NO_3)_2{\cdot}4H_2O$ was purchased from Adamas-beta® chemical industrial company. Synthetic precursors include 9-anthraldehyde, 1-pyrenecarboxaldehyde and 5-aminoisophthalic acid were acquired from TCI (Shanghai) chemical industry development Co., LTD. *N,N*-Dimethylformamide (DMF, 99.9%) and ethanol were from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water was self-prepared and used throughout all experiments.

Synthesis of Ca-SMOFs

The synthesis of H_2L^1 (5-[(anthracen-9-ylmethyl)-amino]-isophthalic acid) and H_2L^2 (5-[(pyren-1-ylmethyl)-amino]-isophthalic acid) were based on our previously reported study.[1-2]

$[Ca_2(L^1)_2(DMF)_2(H_2O)]_n$ Ca-SMOF-1 The containing ligand H_2L^1 (39.0 mg, 0.10

mmol) and $Ca(NO_3)_2 \cdot 4H_2O$ (28.3 mg, 0.12 mmol) were added in a mixed solvent (6 mL, DMF/EtOH/H_2O = 3/2/1), and stirred vigorously for 20 mins to from a clear yellow solution. The reactants then were transferred and sealed into a 10 mL vial, and heated under autogenous pressure to 100 °C for 3 days, and then allowed to cool to room temperature naturally. Deep yellow sheet crystals of **Ca-SMOF-1** were collected in 78% yield (basd on H_2L^1). FT-IR (KBr pellet, cm^{-1}): 3626 (m), 3411 (m), 3310 (m), 3060 (w), 2922 (w), 2880 (w), 2833 (w), 1804 (w), 1662 (s), 1562 (s), 1431 (s), 1389 (s), 1273 (m), 1143 (w), 1095 (m), 1045 (m), 989 (w), 893 (m), 783 (m), 723 (m), 667 (m), 602 (w), 523 (m).

$[Ca_2(L^2)_2(DMF)_2]_n \cdot 0.5nH_2O$ Ca-SMOF-2 The reaction is very similar with that of **Ca-SMOF-1**, except that the ligand H_2L^2 (41.0 mg, 0.10 mmol) were used instead of H_2L^1. Deep yellow sheet crystals of **Ca-SMOF-2** were obtained in 84% yield (basd on H_2L^2). FT-IR (KBr pellet, cm^{-1}): 3641 (m), 3388 (m), 3219 (w), 3126 (w), 3040 (w), 2929 (w), 2852 (w), 1796 (w), 1664 (s), 1555 (s), 1429 (s), 1377 (s), 1242 (m), 1186 (w), 1099 (m), 983 (w), 925 (w), 842 (m), 781 (m), 727 (m), 675 (w), 622 (m), 515 (w).

X-ray Crystallography

Single-crystal X-ray diffraction measurements of **Ca-SMOF-1** and **Ca-SMOF-2** were carried out on a Rigaku Mercury CCD diffractometer at 293 K and 100 K, respectively. The diffractometer was equipped with Mo-Kα radiation (λ = 0.71073 Å), using the ω-scan technique for collections of the intensity data sets. The primitive structures were solved by the direct methods and reduced by *CrysAlisPro* software. The subsequent successive difference Fourier syntheses yielded the other non-hydrogen atoms. The hydrogen atoms of ligands were added geometrically and refined using the riding model. The final structures were refined using a full-matrix least-squares refinement on F^2. All of the calculations were performed by the Olex2 1.2 crystallographic software.[3]

Physical characterization

Powdered X-ray diffraction patterns (PXRD) were recorded with a Miniflex 600 at 40 kV, 40 mA for Cu-K_α with a scan speed of 0.10 s per step and a step size of 0.02° within 2θ range of 5–60 °. The Mercury Version 4.1.0 software (https://www.ccdc.cam.ac.uk/support-and-resources/Downloads/#8a6058f8-d386-e511-91c5-005056868fc8_ce657cfc-4cbd-e611-807a-005056868fc8_collapse) was utilized to achieve simulated PXRD patterns dependent on the X-ray crystallographic structure. Fourier transform infrared spectra (FT-IR) were measured with KBr slices from 4000 to 400 cm^{-1} using a VERTEX70 infrared spectrum radiometer. The absorption spectra were conducted under dilute solution state by Shimadzu UV2600 spectrophotometer. Thermogravimetric analysis (TGA) was measured using a METTLER TOLEDO system at a heating rate of 10 K min^{-1} under nitrogen atmosphere.

Luminescent measurements

The photoluminescence spectra were recorded on an Edinburgh FL920 using a 450W Xenon lamp as excitation source. Luminescence lifetimes measurements were carried out on an Edinburgh FLS980 phosphorimeter using a nanosecond pulse lamp as excitation source. The quantitative value of lifetime is calculated by exponential decay fitting.

Scintillating measurements

The cathode-ray stimulated luminescence (CL) spectra were recorded on a FEI Quanta 400F scanning electron microscope (SEM) equipped with a Gatan MonoCL3+ cathodoluminescence spectrometer and collected data were processed with the Gatan Digital Micrograph CL software. The spectra were collected using a beam of 0.9 nA and an accelerating voltage of 20 kV. The samples were aligned to image the sample at a magnification of 100X–500X for a moderate view, and were arranged at a working distance of 12.354 nm. Spectra were obtained using 0.3 nm slit widths with collecting

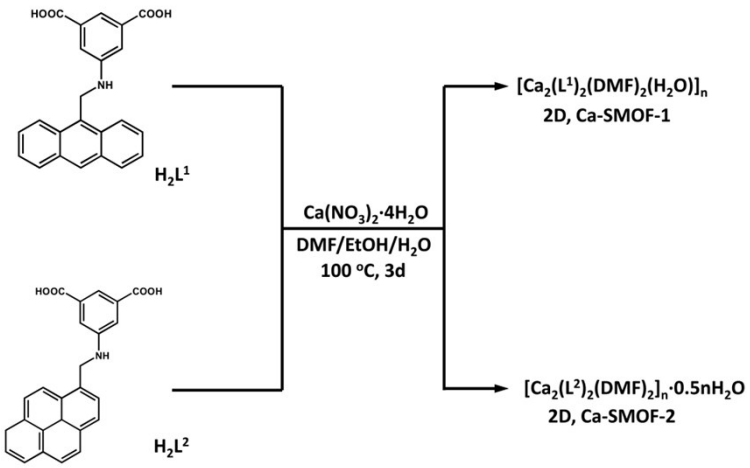
range from 200 ~ 800 nm.

In situ fluorescence measurements

The *in situ* vacuum ultraviolet (VUV) fluorescence measurements were carried out at 4B8 working station at Beijing Synchrotron Radiation Facility (BRSF, http://www.ihep.cas.cn/dkxzz/bsrf/facility/shiyanzhan/vuv/).

Calculations of HOMO and LUMO of Ca-SMOFs

DFT calculations were performed using the B3LYP hybrid function implemented in the Gaussian-09 suite of programe.[4] 6-31G(d) were set for C, H, N, O and SDD for Ca.



Scheme S1. The synthetic routine of **Ca-SMOF-1** and **Ca-SMOF-2**.

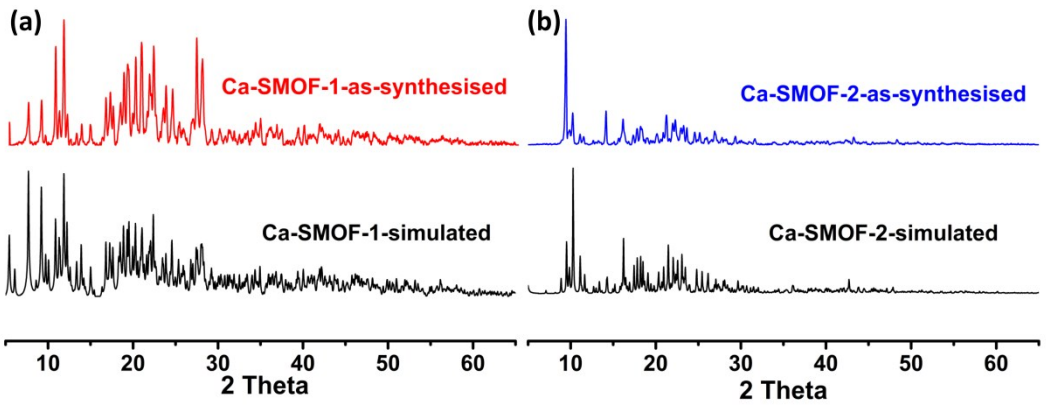


Fig. S1 The powdered X-ray diffraction (PXRD) patterns of **Ca-SMOF-1** (a) and **Ca-SMOF-2** (b).

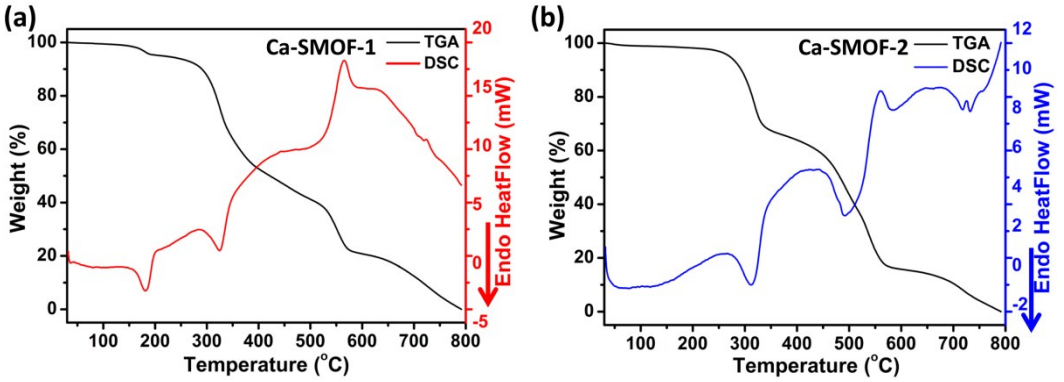


Fig. S2 The TG&DSC curves of **Ca-SMOF-1** and **Ca-SMOF-2**.

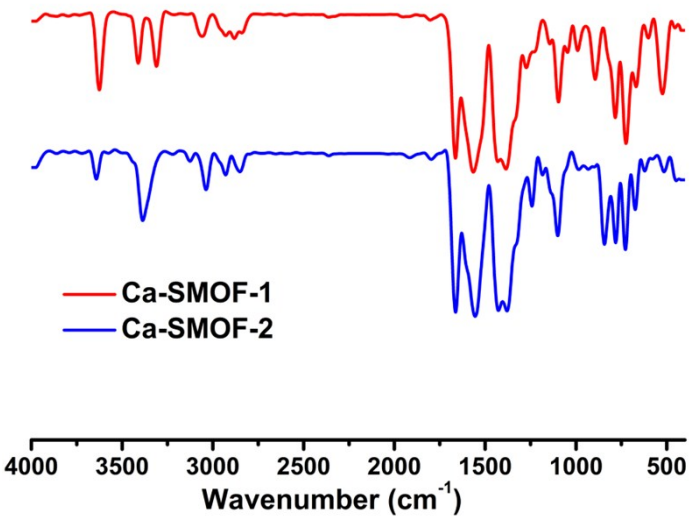


Fig. S3 The FT-IR profiles of **Ca-SMOF-1** and **Ca-SMOF-2**.

Analysis:

For **Ca-SMOF-1**: The vibration modes of the $\nu_{as(COO)}$, $\nu_{s(COO)}$ and $\nu_{(COC)}$ are 1662, 1431 and 1143 cm^{-1}, respectively, providing strong information of COO^- groups coordinated to Ca(II) ions.

For **Ca-SMOF-2**: The vibration modes of the $\nu_{as(COO)}$, $\nu_{s(COO)}$ and $\nu_{(COC)}$ are 1664, 1429 and 1186 cm^{-1}, respectively, also providing strong information of COO^- groups coordinated to Ca(II) ions.

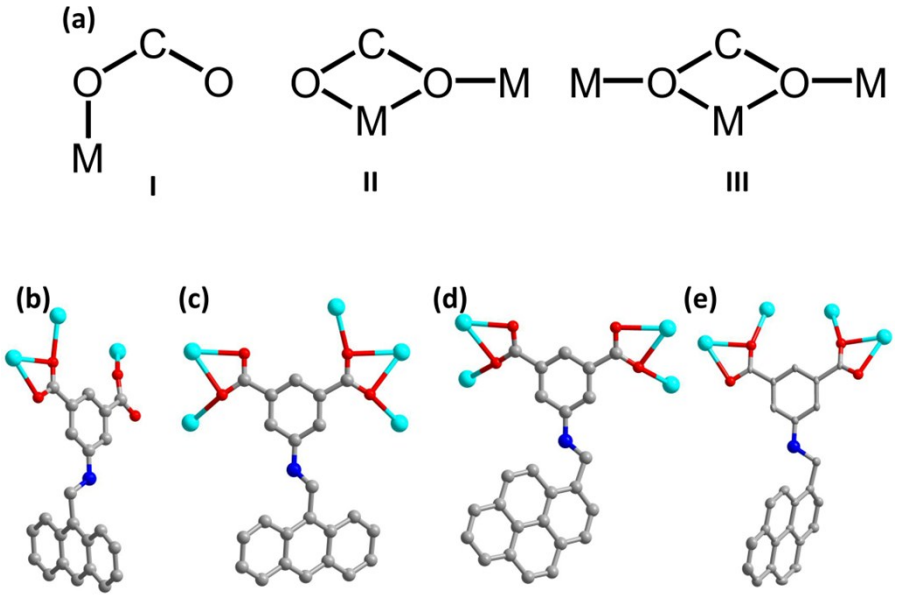


Fig. S4 The coordination mode of carboxylate group with Ca^{2+} (a), and the bridging μ_3 mode of L_1^{2-} (b), μ_5 mode of L_1^{2-} (c) (c) and μ_4 mode of L_2^{2-} (d,e).

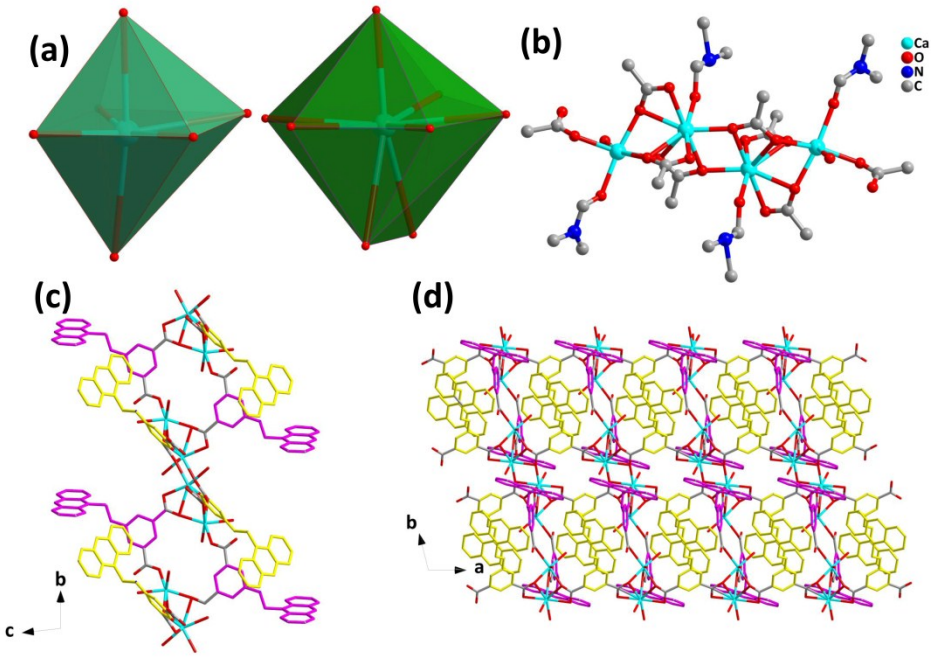


Fig. S5 For **Ca-SMOF-1**: the coordination configuration of Ca1 and Ca2 (a), the quadri- nuclear cluster secondary building unit (SBU) (b), the line-shaped 2D plane viewing from [1 0 0] direction (c) and the 2D plane viewing from [0 0 1] direction (d).

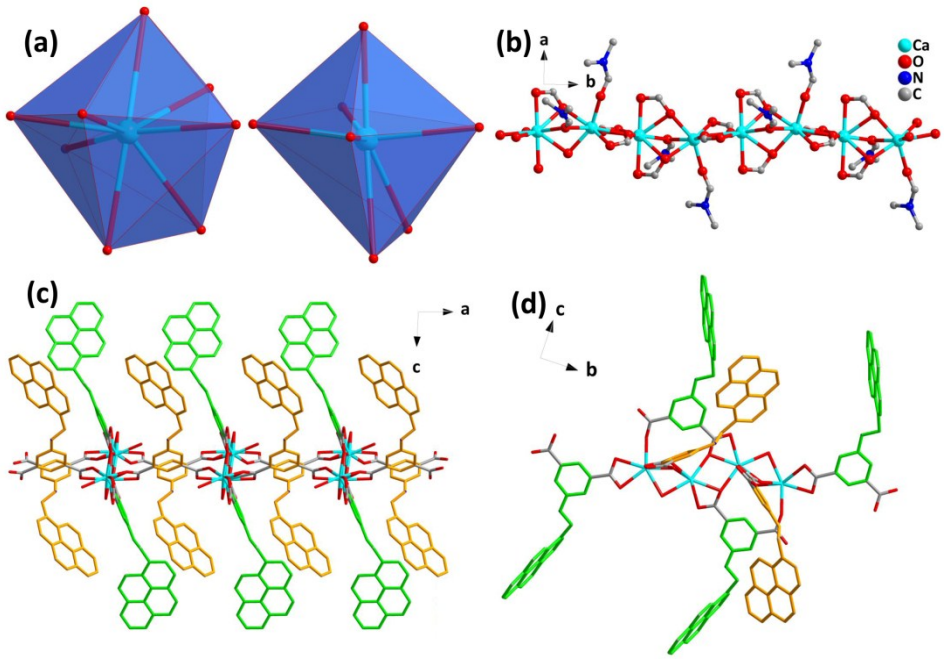


Fig. S6 For **Ca-SMOF-**2: the coordination configurations of Ca1 and Ca2 (a), 1D-rod cluster secondary building unit (SBU) (b), the line-shaped 2D plane viewing from [0 1 0] direction (c) and the line-shaped 2D plane viewing from [1 0 0] direction (d).

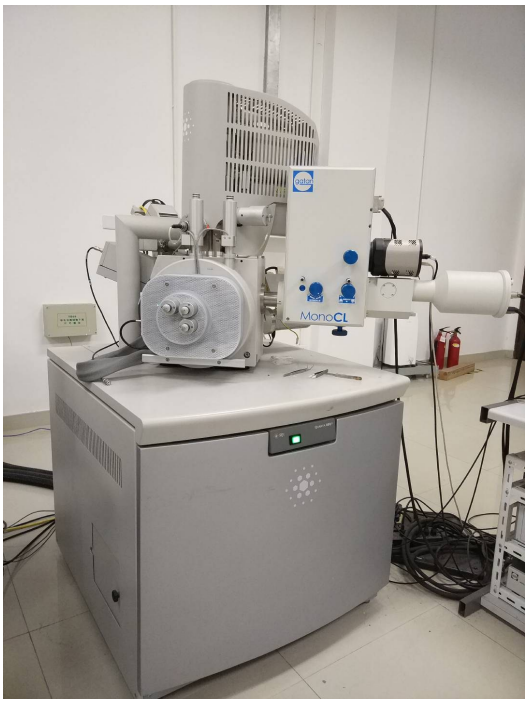


Fig. S7 FEI Quanta 400F scanning electron microscope (SEM) equipped with a Gatan MonoCL3+ cathodoluminescence spectrometer.

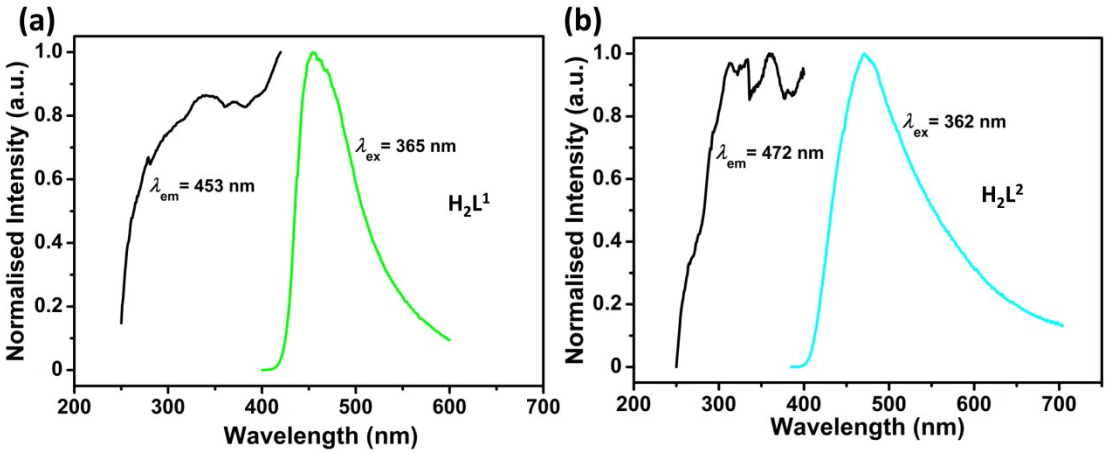


Fig. S8 The excitation and emission spectra of solid-state free ligands H_2L^1 (a) and H_2L^2 (b).

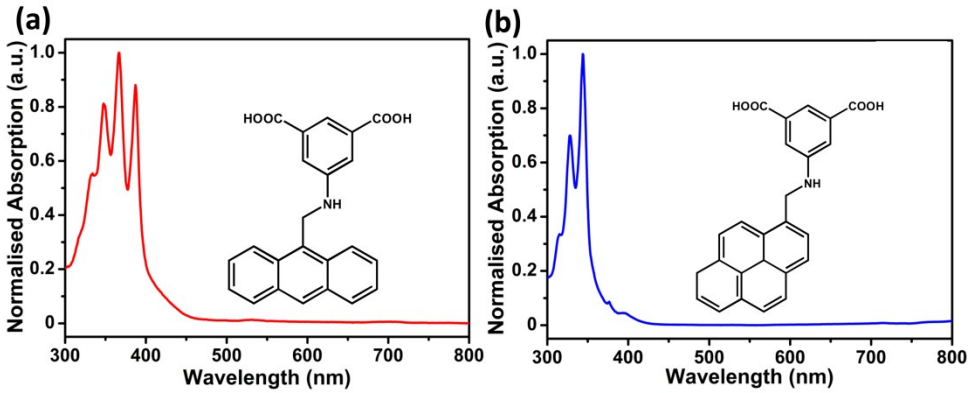


Fig. S9 The liquid-state UV-Vis absorption spectra of H_2L^1 and H_2L^2 measured in dilute DMF solution (~10^{-5} mol/L) at room temperature.

Analysis:

a) The successive main peaks of H_2L^1 is around 387, 366 and 347 nm, which should be ascribed to the refined structured *B* absorption band of derivatives of anthracene, owing to the π→π* charge transfer, while the shoulder at 334 nm should be attributed to the n→π* charge transfer.

b) The main peaks of H_2L^2 is around 344 and 328 nm, which should be ascribed to the refined structured *B* absorption band of derivatives of, owing to the π→π* charge transfer, while the shoulder at 315 nm should be attributed to the n→π* charge transfer.

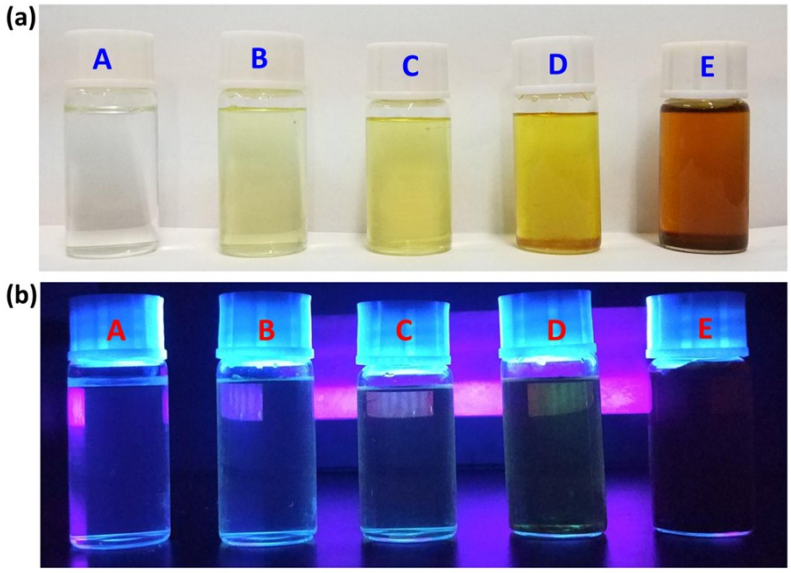


Fig. S10 The aggregation-caused quenching (ACQ) phenomenon of ligand H_2L^1, and photographs taken by Minote 2 cellphone of H_2L^1 in DMF with different concentrations at daylight (a) and 365 nm ultraviolet lamp (b): A: ~1.0×10^{-5} M; B: ~1.0×10^{-4} M; C: ~1.0×10^{-3} M; D: ~1.0×10^{-2} M; E: ~1.0×10^{-1} M.

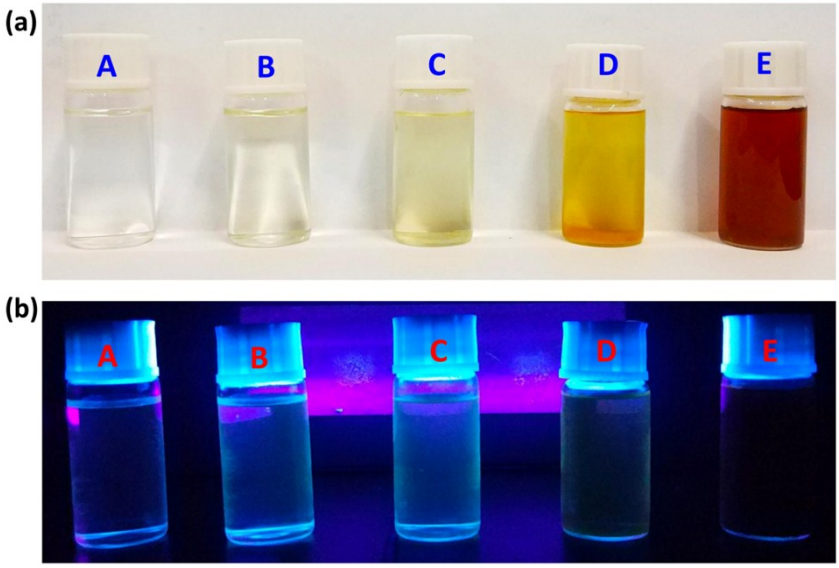


Fig. S11 The aggregation-caused quenching (ACQ) phenomenon of ligand H_2L^2, and photographs taken by Minote 2 cellphone of H_2L^2 in DMF with different concentrations at daylight (a) and 365 nm ultraviolet lamp (b): A: ~1.0×10^{-5} M; B:

~1.0×10^{-4} M; C: ~1.0×10^{-3} M; D: ~1.0×10^{-2} M; E: ~1.0×10^{-1} M.

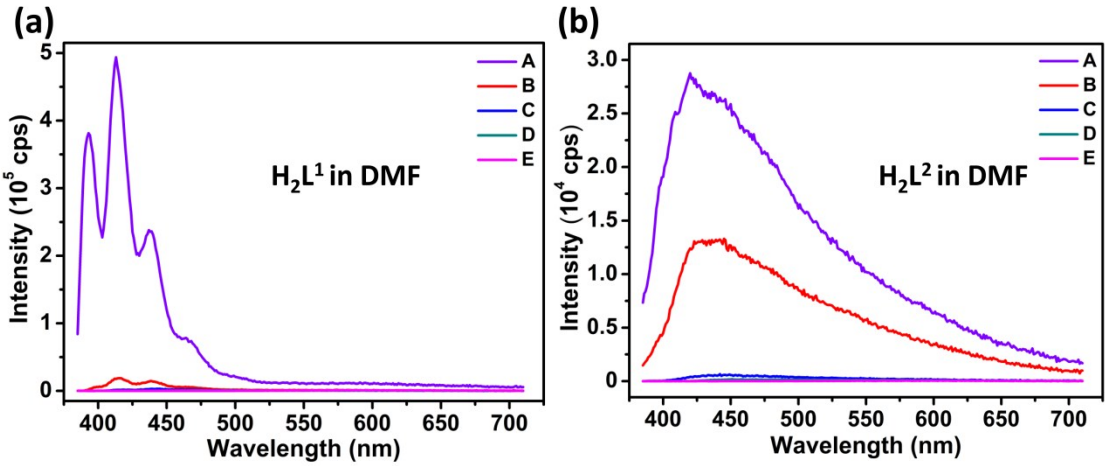


Fig. S12 The aggregation-caused quenching (ACQ) luminescent intensities of ligand H_2L^1 (a) and H_2L^2 (b) in DMF, respectively. Concentrations: A, ~1.0×10^{-5} M; B, ~1.0×10^{-4} M; C, ~1.0×10^{-3} M; D, ~1.0×10^{-2} M; E, ~1.0×10^{-1} M.

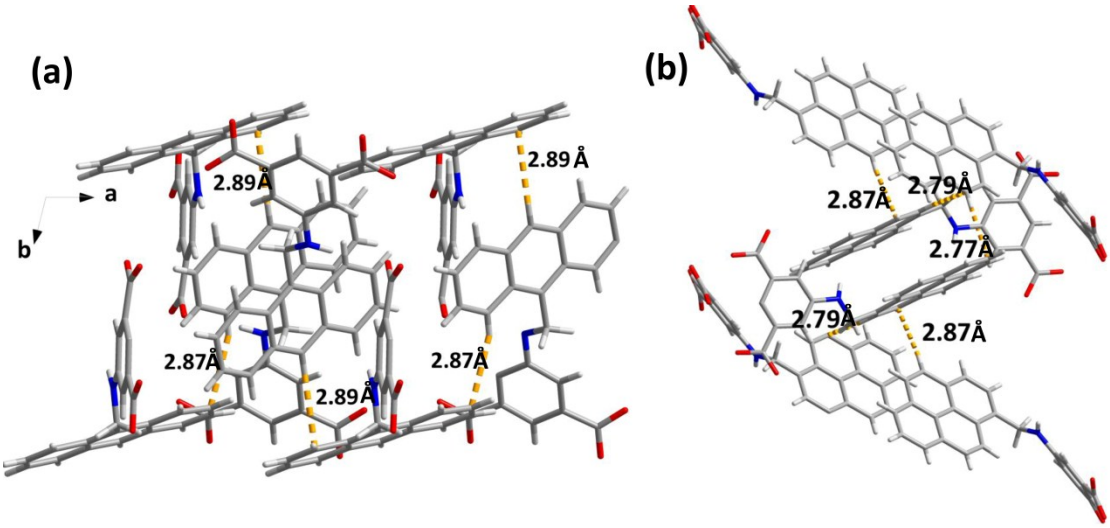


Fig. S13 Images of the C–H···π interactions between adjacent anthracene rings of **Ca-SMOF-1** (a) and pyrene rings of **Ca-SMOF-2** (b). For clarity, all the moieties except the anthracene rings and pyrene rings are removed.

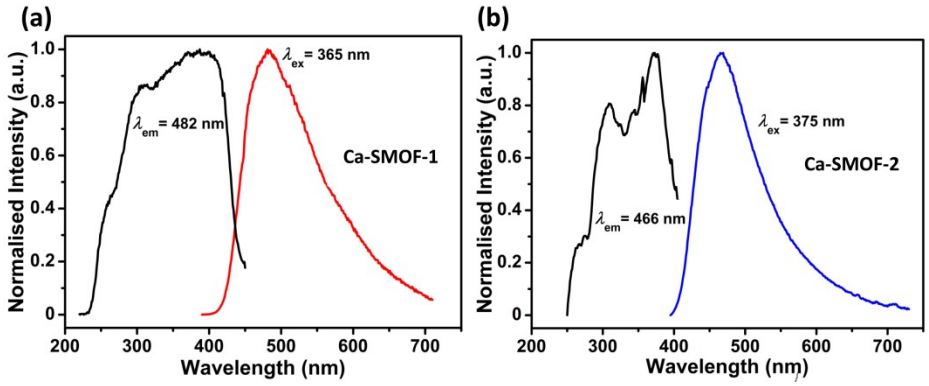


Fig. S14 The excitation and emission spectra of solid-state **Ca-SMOF-1** (a) and **Ca-SMOF-2** (b), respectively.

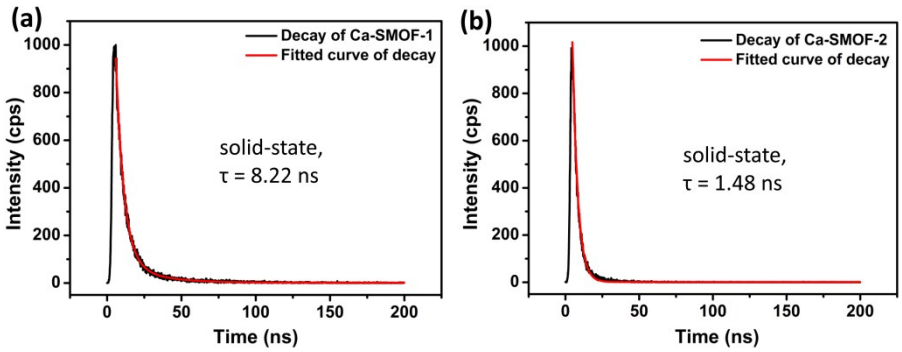


Fig. S15 Photoluminescence lifetime profiles of **Ca-SMOF-1** and **Ca-SMOF-2** measured at 298 K.

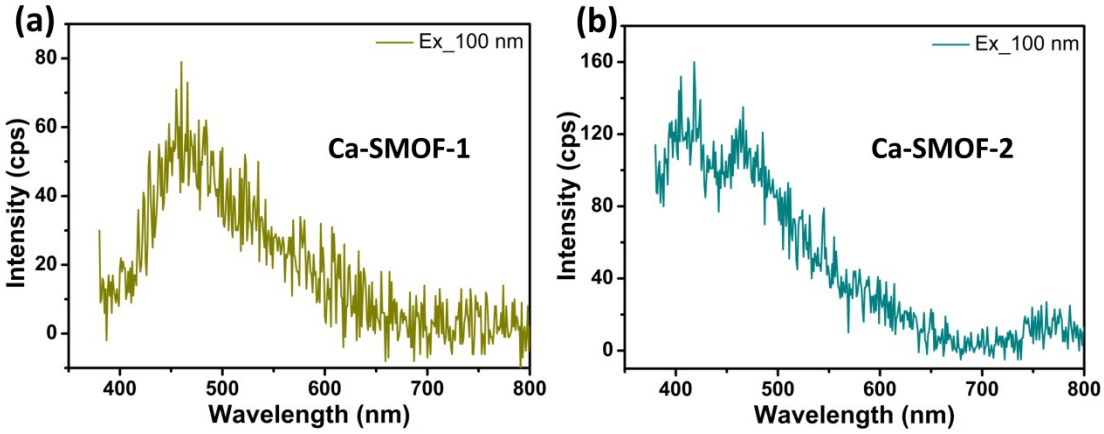


Fig. S16 The vacuum ultraviolet stimulated fluorescence spectra of **Ca-SMOF-1** (a) and **Ca-SMOF-2** (b) upon excitation at 100 nm.

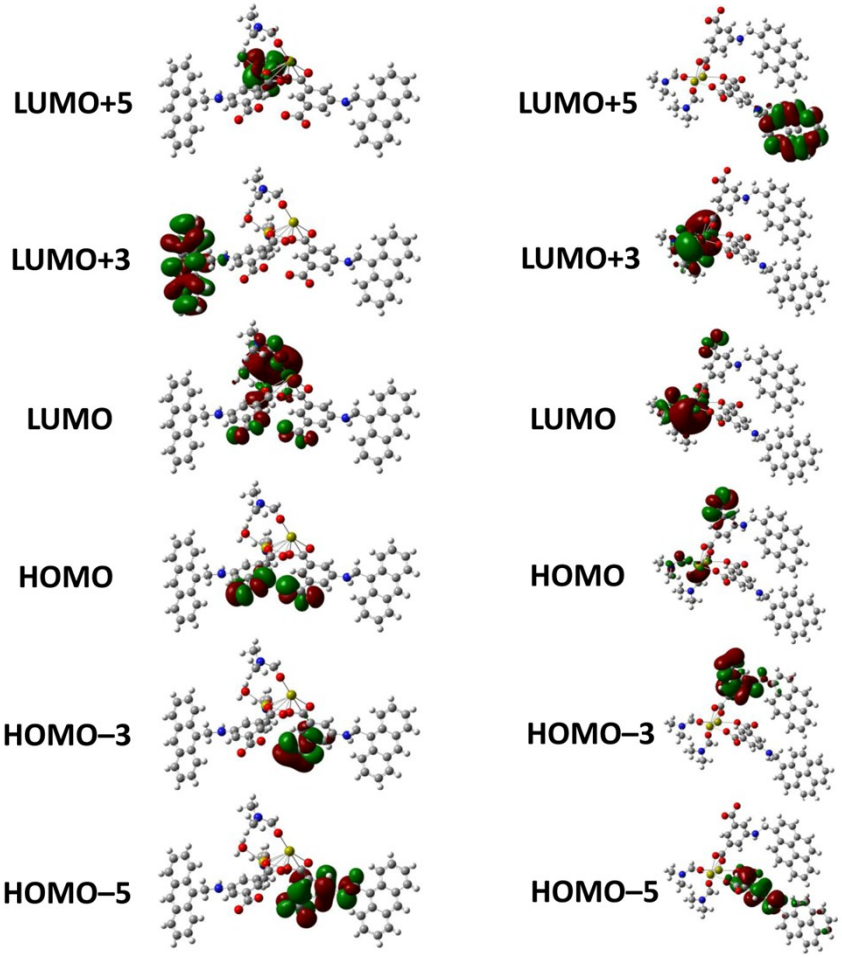


Fig. S17 Representative calculated LUMO and HOMO of **Ca-SMOF-1** (left) and **Ca-SMOF-2** (right).

Table S1. Crystallographic data for **Ca-SMOF-1**and **Ca-SMOF-2**

Crystal data	**Ca-SMOF-1**	**Ca-SMOF-2**
CCDC number	1949394	1949395
Empirical formula	$C_{52}H_{46}Ca_2N_4O_{11}$	$C_{56}H_{45}Ca_2N_4O_{10.5}$
Formula weight	983.09	1022.12
Temperature (K)	293(2)	100(3)
Wavelength (Å) /MoK_α	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	*P*–1	$P2_1/c$
a (Å)	9.9541(2)	9.9576(3)
b (Å)	15.0085(3)	13.2038(3)
c (Å)	16.4447(3)	37.1629(13)
α (°)	94.7350(10)	90
β (°)	96.2260(10)	92.879(3)
γ (°)	103.502(2)	90
V (Å^3)	2359.95(8)	4879.9(3)
Z	2	4
Caled. density (g cm^{-3})	1.383	1.391
Absorption coefficient (mm^{-1})	0.309	0.301
F(000)	1028	2132
2θ range	7.526 to 62.908	3.786 to 62.172
Reflections collected	191912	43941
Completeness	0.931	0.998
Data/restraints/parameters	14571/ 399/ 707	12493/ 0/ 679
Goodness-of-fit on F^2	1.061	1.045
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0484	R_1 = 0.0589
	wR_2 = 0.1197	wR_2 = 0.1278

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

Table S2. Selected bond lengths (Å) and bond angles (°) in **Ca-SMOF-1** and **Ca-SMOF-2.**

Ca-SMOF-1

Ca(1)–O(1W)	2.3791(13)	Ca(2)–O(5)#1	2.4776(10)
Ca(1)–O(1)	2.3032(13)	Ca(2)–O(6)#1	2.4461(11)
Ca(1)–O(3)#2	2.3048(12)	Ca(2)–O(7)#4	2.5706(10)
Ca(1)–O(5)	2.3324(11)	Ca(2)–O(7)	2.3191(10)
Ca(1)–O(8)#3	2.3557(11)	Ca(2)–O(8)#4	2.4932(10)
Ca(1)–O(9)	2.3252(15)	Ca(2)–O(10)#1	2.386(4)
Ca(2)–O(1)#1	2.6988(15)	Ca(2)–O(10B)	2.360(4)
Ca(2)–O(2)#1	2.4023(14)		

O(1)–Ca(1)–O(2)#1	49.52(4)	O(5)#1–Ca(2)–O(7)#4	121.88(3)
O(1)–Ca(1)–O(1W)	156.31(5)	O(5)#1–Ca(2)–O(8)#4	71.11(3)
O(1)–Ca(1)–O(3)#2	119.67(6)	O(6)#1–Ca(2)–O(1)#1	90.53(6)
O(1)–Ca(1)–O(5)	76.75(5)	O(6)#1–Ca(2)–O(5)#1	53.21(3)
O(1)–Ca(1)–O(8)#3	78.38(5)	O(6)#1–Ca(2)–O(7)#4	170.14(5)
O(1)–Ca(1)–O(9)	93.39(7)	O(6)#1–Ca(2)–O(8)#4	124.23(3)
O(3)#2–Ca(1)–O(1W)	80.70(4)	O(7)–Ca(2)–O(1)	131.51(4)
O(3)#2–Ca(1)–O(5)	97.24(5)	O(7)–Ca(2)–O(1)#4	94.98(5)
O(3)#2–Ca(1)–O(8)#3	159.31(4)	O(7)–Ca(2)–O(2)#1	81.43(5)
O(3)#2–Ca(1)–O(9)	88.60(6)	O(7)–Ca(2)–O(5)#1	154.98(4)
O(3)#2–Ca(1)–O(1W)	89.44(5)	O(7)–Ca(2)–O(6)#1	105.32(4)
O(5)–Ca(1)–O(8)#3	76.13(4)	O(7)–Ca(2)–O(7)#4	77.00(3)
O(8)#3–Ca(1)–O(1W)	79.67(4)	O(7)–Ca(2)–O(8)#4	127.48(3)
O(9)–Ca(1)–O(1W)	99.46(6)	O(7)–Ca(2)–O(10)	82.29(11)

O(9)–Ca(1)–O(5)	170.06(6)	O(8)#4–Ca(2)–O(1)#1	68.97(4)
O(9)–Ca(1)–O(8)#3	101.00(5)	O(8)#4–Ca(2)–O(7)#4	51.21(3)
O(2)#1–Ca(2)–O(1)#1	50.25(4)	O(10)–Ca(2)–O(1)#1	146.14(11)
O(2)#1–Ca(2)–O(5)#1	113.31(5)	O(10)–Ca(2)–O(2)#1	162.32(11)
O(2)#1–Ca(2)–O(6)#1	102.11(6)	O(10)–Ca(2)–O(5)#1	79.80(11)
O(2)#1–Ca(2)–O(7)#4	87.69(6)	O(10)–Ca(2)–O(6)#1	75.70(14)
O(2)#1–Ca(2)–O(8)#4	102.15(6)	O(10)–Ca(2)–O(7)#4	95.31(14)
O(5)#1–Ca(2)–O(1)#1	67.39(4)	O(10)–Ca(2)–O(8)#4	93.20(12)

Ca-SMOF-2

Ca(1)–O(1)#1	2.5326(17)	Ca(2)–O(1)	2.3006(17)
Ca(1)–O(2)	2.4090(18)	Ca(2)–O(4)#1	2.3306(17)
Ca(1)–O(3)#1	2.4965(18)	Ca(2)–O(5)#3	2.4351(17)
Ca (1)–O(4)#1	2.4257(17)	Ca(2)–O(6)#3	2.4366(19)
Ca(1)–O(5)	2.3513(18)	Ca(2)–O(7)	2.3524(18)
Ca(1)–O(7)#2	2.4158(17)	Ca(2)–O(9)	2.3326(19)
Ca(1)–O(8)#2	2.4613(19)	Ca(2)–O(10)	2.5128(19)
Ca(1)–O(10)	2.4363(18)		

O(2)–Ca(1)–O(1)	53.14(6)	O(1)–Ca(2)–O(4)#1	78.66(6)
O(2)–Ca(1)–O(3)#1	174.93(7)	O(1)–Ca(2)–O(5)#3	121.46(6)
O(2)–Ca(1)–O(4) #1	124.53(6)	O(1)–Ca(2)–O(6)#3	98.32(6)
O(2)–Ca(1)–O(7) #2	86.20(6)	O(1)–Ca(2)–O(7)	85.36(6)
O(2)–Ca(1)–O(8) #2	86.20(7)	O(1)–Ca(2)–O(9)	151.85(7)
O(2)–Ca(1)–O(10)	97.59(7)	O(1)–Ca(2)–O(10)	73.26(6)
O(3)#1–Ca(1)–O(1)	125.67(6)	O(4)#1–Ca(2)–O(5)#3	151.94(6)

O(4)#1–Ca(1)–O(1)	72.56(6)	O(4)#1–Ca(2)–O(6)#3	149.28(6)
O(4)#1–Ca(1)–O(3)#1	53.40(5)	O(4)#1–Ca(2)–O(7)	90.67(6)
O(4)#1–Ca(1)–O(8)#1	141.97(6)	O(4)#1–Ca(2)–O(9)	81.41(7)
O(4)#1–Ca(1)–O(10)	71.64(6)	O(4)#1–Ca(2)–O(10)	71.84(6)
O(5)–Ca(1)–O(1)	87.22(6)	O(5)#3–Ca(2)–O(6)#3	53.66(6)
O(5)–Ca(1)–O(2)	85.09(7)	O(5)#3–Ca(2)–O(10)	129.89(6)
O(5)–Ca(1)–O(3)#1	125.72(7)	O(6)#3–Ca(2)–O(10)	77.99(6)
O(5)–Ca(1)–O(4)#1	81.57(6)	O(7)–Ca(2)–O(5)#3	73.31(6)
O(5)–Ca(1)–O(7)#2	73.68(6)	O(7)–Ca(2)–O(6)#3	119.75(6)
O(5)–Ca(1)–O(10)	149.21(6)	O(7)–Ca(2)–O(10)	154.46(6)
O(7)#2–Ca(1)–O(1)	136.73(6)	O(9)–Ca(2)–O(5)#3	84.59(7)
O(7)#2–Ca(1)–O(3)#1	93.43(6)	O(9)–Ca(2)–O(6)#3	88.80(7)
O(7)#2–Ca(1)–O(4)#1	138.65(6)	O(9)–Ca(2)–O(7)	114.66(7)
O(7)#2–Ca(2)–O(8)#2	53.85(6)	O(9)–Ca(2)–O(10)	81.77(7)
O(7)#2–Ca(1)–O(10)	137.00(6)		
O(8)#2–Ca(1)–O(3)#1	97.66(6)		
O(10)–Ca(1)–O(1)	70.73(6)		
O(10)–Ca(1)–O(3)#1	86.14(6)		
O(10)–Ca(1)–O(8)#2	83.54(6)		

Symmetry codes for **Ca-SMOF-1**: #1 1 – ***x***, –*y*, 1 – *z*; #2 2 – *x*, 1 – *y*, 1 – *z*; #3 1 + *x*, *y*, *z*; #4 –*x*, –*y*, 1 – *z*.

Symmetry codes for **Ca-SMOF-2**: #1 1 + *x*, *y*, *z*; #2 1 – *x*, –1/2 + *y*, 1/2 – *z*; #3 1 – *x*, 1/2 + *y*, 1/2 – *z*.

Table S3. Concentrations of π-conjugated linkers in **Ca-SMOF-1** and **Ca-SMOF-2**.

	supercell considered	Supercell Volume (L)	Nos. of π-conjugated linkers	Concentration (M)
Ca-SMOF-1	2 * 2 * 2	$1.89 * 10^{-23}$	32	0.282
Ca-SMOF-2	2 * 2 * 2	$3.90 * 10^{-23}$	65	0.572

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