Electronic Supplementary Information (ESI)

Synthesis of $[Zn_3(H_2O)_4(tbip)_3\cdot 2(H_2O)]_n$ (**ZnZn-tbip**)

A mixture of zinc acetylacetonate hydrate (1.0 mmol), $NH_3\cdot H_2O$ (5.0 mmol), and 5-tert-butylisophthalic acid (2.0 mmol) in 20 mL H_2O are stirred for 10 min at room temperature. The mixture is then transferred into a 40 mL, Teflon-lined stainless-steel vessel. The mixture is heated at 210℃ for five days under autogenously pressure. After the reaction mixture has slowly cooled down to room temperature, fawn-colored prism crystals of **ZnZn-tbip** are filtered off, washed with distilled water, and dried in air. Yield: ~60%. Elemental analysis (%) for $C_{36}H_{48}O_{18}Zn_3$：calcd. C 44.81, H 5.01, Zn 20.33; found C 44.76, H 4.97, Zn 20.27. IR (KBr pellet, cm^{-1}): 3438 s, 3001 w, 2974 m, 2922 w, 2870 w, 1626 vs, 1608 w, 1582 w, 1553 s,1437 m, 1413 w, 1381 vs, 1390 m, 1247 w, 1208 w, 1185 w, 1121 w, 1049 w, 938 w, 912 w, 817 w, 770 m, 715 m, 695 w, 504 w, 457 w.

Synthesis of $[Zn_2Ca(H_2O)_4(tbip)_3\cdot 3(H_2O)]_n$ (**ZnCa-tbip**)

A mixture of zinc acetylacetonate hydrate (1.0 mmol), $NH_3\cdot H_2O$ (5.0 mmol), calcium nitrate (2.0 mmol) and 5-tert-butylisophthalic acid (2.0 mmol) in 20 mL H_2O are stirred for 10 min at room temperature. The mixture is then transferred into a 40 mL, Teflon-lined stainless-steel vessel. The mixture is heated at 210℃ for five days under autogenously pressure. After the reaction mixture has slowly cooled down to room temperature, fawn-colored prism crystals of **ZnCa-tbip** are filtered off, washed with distilled water, and dried in air. Yield: ~50%. Elemental analysis (%) for $C_{36}H_{50}O_{19}Zn_2Ca$ ：calcd. C 45.15, H 5.26, Zn 13.66, Ca 4.19; found C 45.20, H 5.22 , Zn 13.59, Ca 4.16. IR (KBr pellet, cm^{-1}): 3666 w, 3392 s, 3268 w, 2962 m, 2903 w, 2870 w, 1846 w, 1617 s, 1579 s, 1463 w, 1440 m, 1391 s, 1367 w, 1344 m, 1312 w, 1272 m, 1243 w, 1202 w, 1118 w, 1046 w, 1002 w, 912 w, 828 w, 808 w, 779 s, 756 m,727 s, 695 m, 591w, 538 w, 483 w, 460 w.

Synthesis of $[Zn_2Ca(H_2O)_2(mip)_3\cdot 2(H_2O)]_n$ (**ZnCa-mip**)

A mixture of zinc acetylacetonate hydrate (1.0 mmol), $NH_3\cdot H_2O$ (5.0 mmol), calcium acetate (1.0 mmol) and 5-methylisophthalic acid (2.0 mmol) in 12 mL H_2O are stirred for 10 min at room temperature. The mixture is then transferred into a 20 mL, Teflon-lined stainless-steel vessel. The mixture is heated at 200℃ for five days under autogenously pressure. After the reaction mixture has slowly cooled down to room temperature, fawn-colored block crystals of **ZnCa-mip** are filtered off, washed with distilled water, and dried in air. Yield: ~55%. Elemental analysis (%) for $C_{27}H_{26}O_{16}Zn_2Ca$：calcd. C 41.72, H 3.37, Zn 16.82 ,Ca 5.16; found C 41.65, H 3.33, Zn 16.73 ,Ca 5.09. IR (KBr pellet, cm^{-1}): 3438 s,3379s, 2972w, 2952w, 2913w, 2860w, 1831w, 1624 s, 1606s, 1576 vs, 1427 s, 1408s, 1376 vs, 1350s, 1318w, 1306w, 1264w, 1239m, 1140w, 1117w , 1042w, 1007w, 943w, 928w, 895w, 804w, 773m, 732m, 723m, 672w, 604w, 580w, 560w, 525w, 499w, 472w, 446w.

Synthesis of $[Zn_2Cd(H_2O)_2(mip)_3\cdot 2(H_2O)]_n$ (**ZnCd-mip**)

A mixture of zinc acetylacetonate hydrate (1.0 mmol), $NH_3\cdot H_2O$ (5.0 mmol), cadmium acetate (1.0 mmol) and 5-methylisophthalic acid (2.0 mmol) in 12 mL H_2O are stirred for 10 min at room temperature. The mixture is then transferred into a 20 mL, Teflon-lined stainless-steel vessel. The mixture is heated at 200℃ for five days under autogenously pressure. After the reaction mixture has slowly cooled down to room temperature, fawn-colored prism crystals of **ZnCd-mip** are filtered off, washed with distilled water, and dried in air. Yield: ~50%. Elemental analysis (%) for $C_{27}H_{26}O_{16}Zn_2Cd$: calcd. C 38.17, H 3.08, Zn 15.39, Cd 13.23; found C 38.21, H 3.12 Zn 15.34, Cd 13.12. IR (KBr pellet, cm^{-1}): 3444 m, 3066 w, 2975 w, 2955 w, 2909 w, 1840 w, 1625 s, 1572 s, 1422 m, 1376 s, 1350 s, 1239 m, 1142 m, 1115 m , 1037 w, 1005 w, 939 w, 900 w, 802 m, 776 s, 724 s, 601 w, 496 w, 443 w.

Notice 1: $[Zn_2Ca(H_2O)_4(tbip)_3\cdot 3(H_2O)]_n$ (**ZnCa-tbip**) can also be obtained through the following synthetic method.

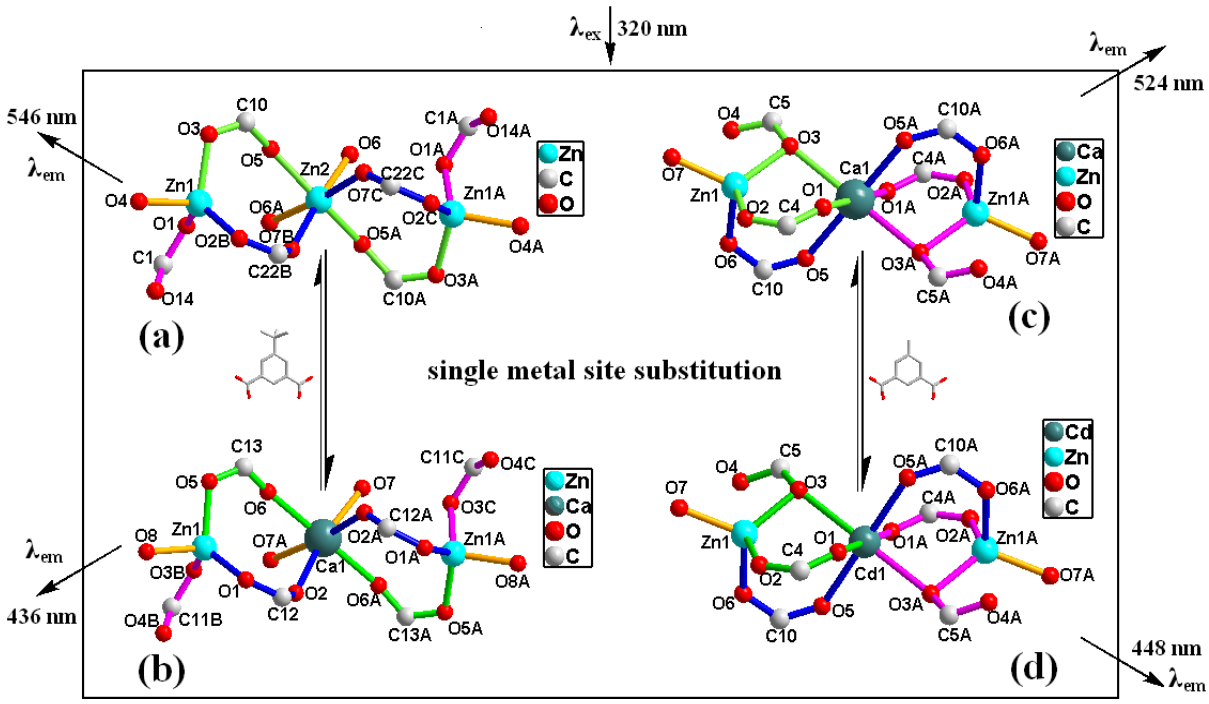
A mixture of zinc acetylacetonate hydrate (1.0 mmol), $NH_3\cdot H_2O$ (5.0 mmol) and 5-tert-butylisophthalic acid (2.0 mmol) in 20 mL H_2O are stirred for 10 min at room temperature. The mixture is then transferred into a 40 mL, Teflon-lined stainless-steel vessel. The mixture is heated at 210℃ for five days under autogenously pressure. After the reaction mixture has slowly cooled down to room temperature, calcium nitrate (2.0 mmol) is added to it. Then the reaction mixture is further heated at 210℃ for five days under autogenously pressure. After the new reaction mixture has slowly cooled down to room temperature, fawn-colored prism crystals are obtained. The results of the structural characterization (including single-crystal X-ray diffraction data and the XRPD patterns) confirm that the final products are the same as the **ZnCa-tbip**.

Notice 2: Typical hydrothermal reactions of the single crystal of **ZnZn-tbip**, calcium nitrate and water only afford to the colorless solutions, and no single crystal of **ZnCa-tbip** is found.

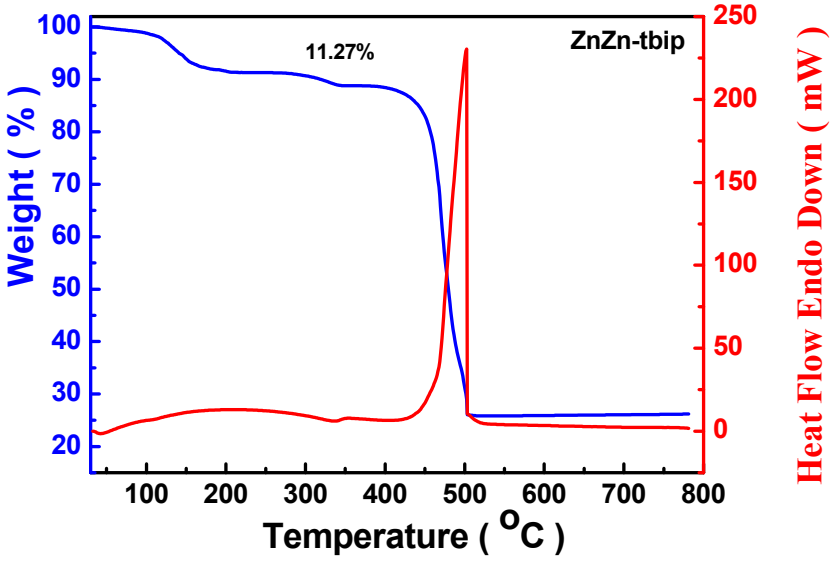
Crystal structure determination and refinement

Crystal data of the compounds **ZnZn-tbip**, **ZnCa-tbip**, **ZnCa-mip** and **ZnCd-mip** are collected on an Xcalibur, Eos, Gemini diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å). Data reduction is accomplished by the CrysAlisPro (Oxford Diffraction Ltd., Version 1.171.33.55) program. The structures are solved by direct method and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program. All of the non-hydrogen atoms are refined anisotropically. The organic hydrogen atoms are generated geometrically; the aqua hydrogen atoms are located from difference maps and refined with isotropic temperature factors. Drawings of the molecule were performed with the program Diamond [K. Brandenburg, *DIAMOND-Crystal and Molecular Structure Visualization*, Bonn, Germany, 2010.]. The crystallographic data and structure refinement for the Zn-based MOFs containing ligands tbip and mip are summarized in the following table:

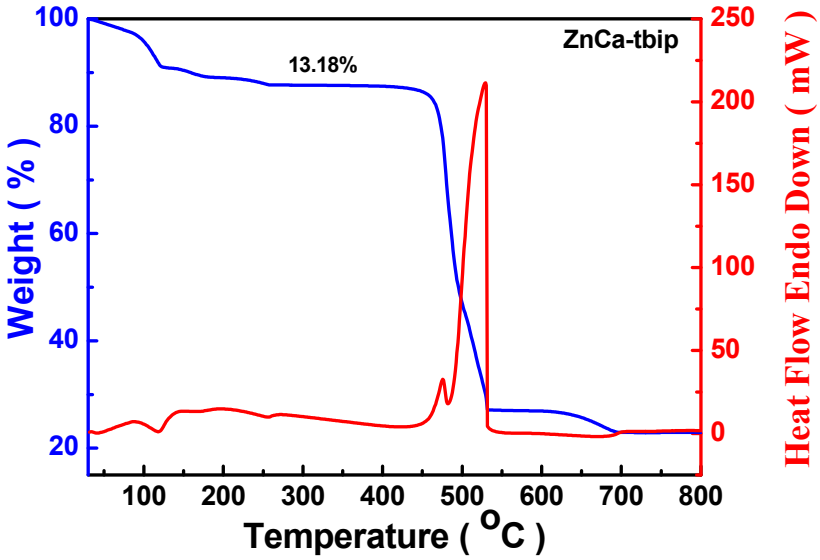
Compound	**ZnZn-tbip**	**ZnCa-tbip**	**ZnCa-mip**	**ZnCd-mip**
Empirical formula	$C_{36}H_{48}O_{18}Zn_3$	$C_{36}H_{50}O_{19}Zn_2Ca$	$C_{27}H_{26}O_{16}Zn_2Ca$	$C_{27}H_{26}O_{16}Zn_2Cd$
Formula weight	964.85	957.58	777.30	849.62
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnna*	*Pnna*	*Pnma*	*Pnma*
a / Å	16.0781(5)	15.7091(7)	7.35853(19)	7.30775(10)
b / Å	21.0471(6)	21.6243(9)	23.5965(5)	23.3444(3)
c / Å	12.8084(4)	13.2974(5)	18.7029(4)	18.8151(3)
α / deg	90	90	90	90
β /deg	90	90	90	90
γ / deg	90	90	90	90
Volume/ Å^3	4334.3(2)	4517.1(3)	3247.49(13)	3209.75(7)
Z	4	4	4	4
ρ_{cal} /g·cm^{-3}	1.479	1.408	1.590	1.758
μ /mm^{-1}	1.717	1.246	1.707	2.212
F (000)	1992	1992	1584	1696
Refl. collected	14179	14733	9617	11167
Unique refl.	4418	4615	2929	2900
R_{int}	0.0327	0.0396	0.0226	0.0174
GOF	1.088	1.034	1.092	1.098
R_1 (I>2σ(I))	0.0577	0.0539	0.0393	0.0270
wR_2 (I>2σ(I))	0.1454	0.1415	0.1233	0.0790
R_1 (all data)	0.0696	0.0778	0.0433	0.0311
wR_2 (all data)	0.1547	0.1595	0.1263	0.0802



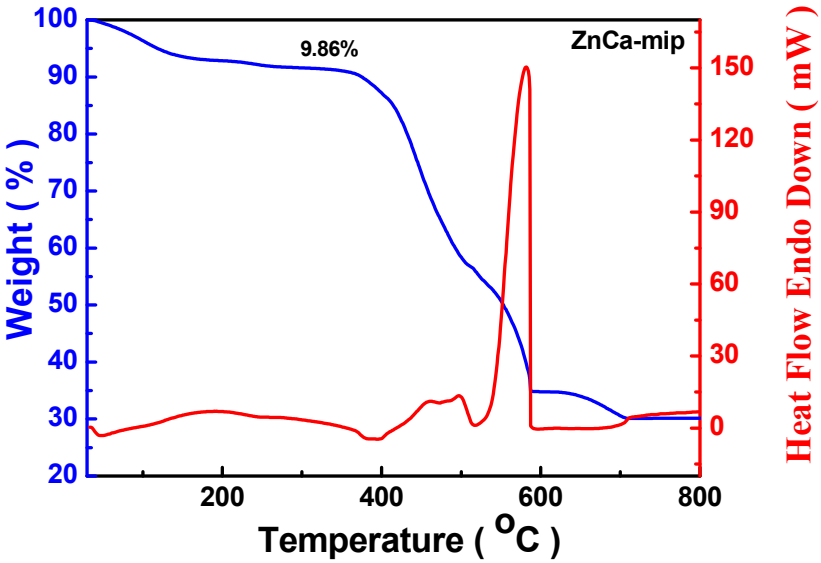
ESI. 1 Schematic representation of 6-connected SBUs containing both octahedral and tetrahedral metal clusters; the accurately exchange mechanism of the single octahedral coordination site between the primary SBU and the substituted SUB; fluorescent excitation and emission positions (λ_{ex} and λ_{em}) for two pairs of the MOFs. (a) SBU $Zn_2Zn(COO)_6$ for **ZnZn-tbip**, Symmetry codes: A (x, 1.5-y, 0.5-z), B (-0.5+x, y, 1-z), C (-0.5+x, 1.5-y, -0.5+z); (b) SBU $Zn_2Cd(COO)_6$ for **ZnCa-tbip**, Symmetry codes: A (x, 0.5-y, 1.5-z), B (0.5+x, y, 1-z), C (0.5+x, 0.5-y, 0.5+z); (c) SBU $Zn_2Ca(COO)_6$ for **ZnCa-mip**, Symmetry codes: A (1-x, 1-y,1-z); (d) SBU $Zn_2Cd(COO)_6$ for **ZnCd-mip**, Symmetry codes: A (1-x, 1-y,1-z).



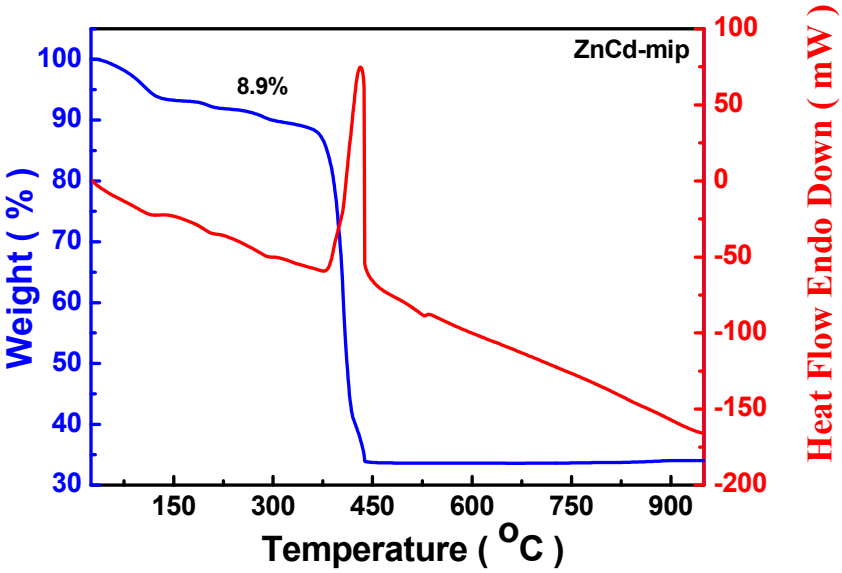
ESI. 2 TG-DTA for **ZnZn-tbip**



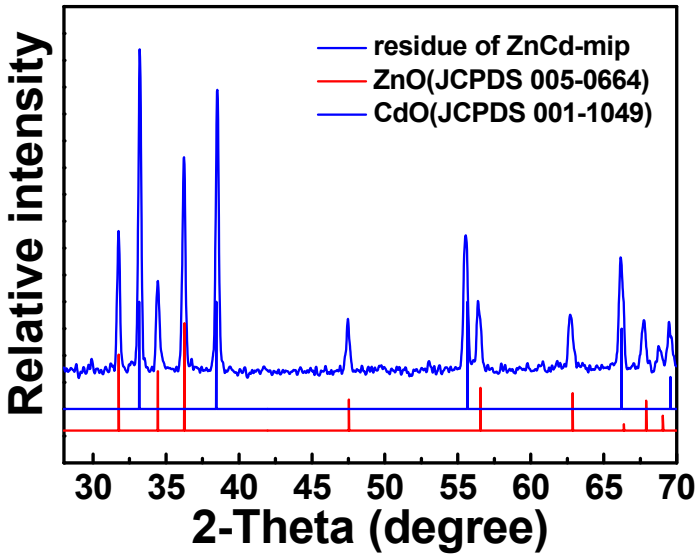
ESI. 3 TG-DTA for **ZnCa-tbip**



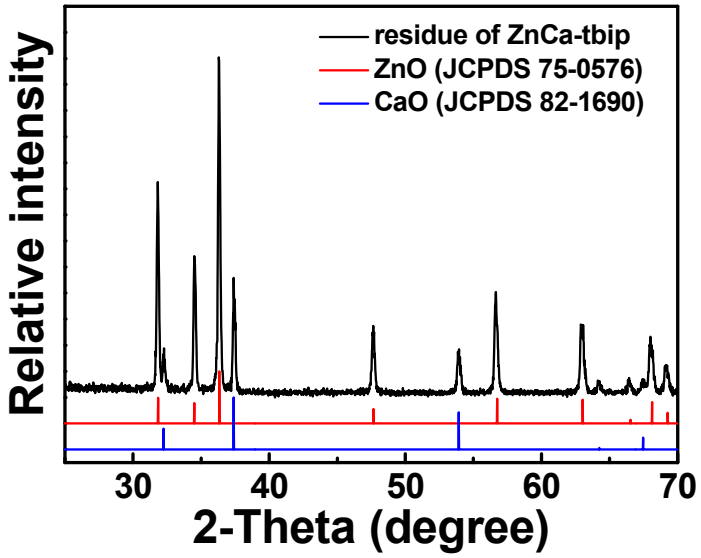
ESI. 4 TG-DTA for **ZnCa-mip.**



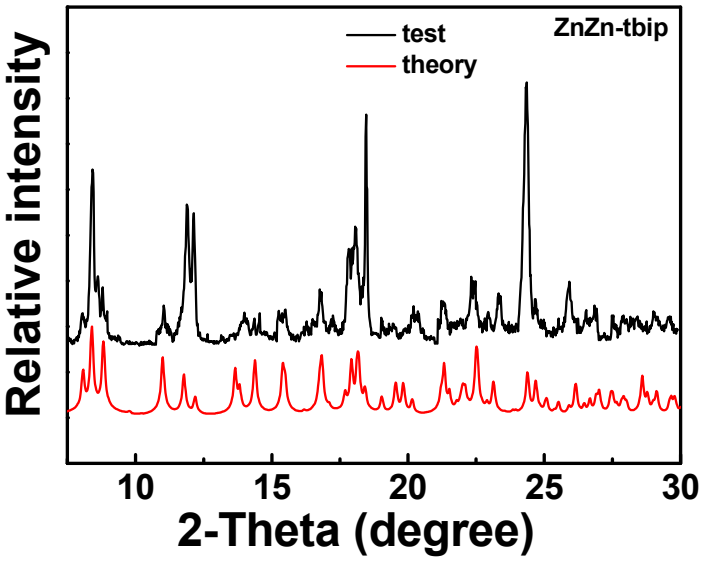
ESI. 5 TG-DTA for **ZnCd-mip**



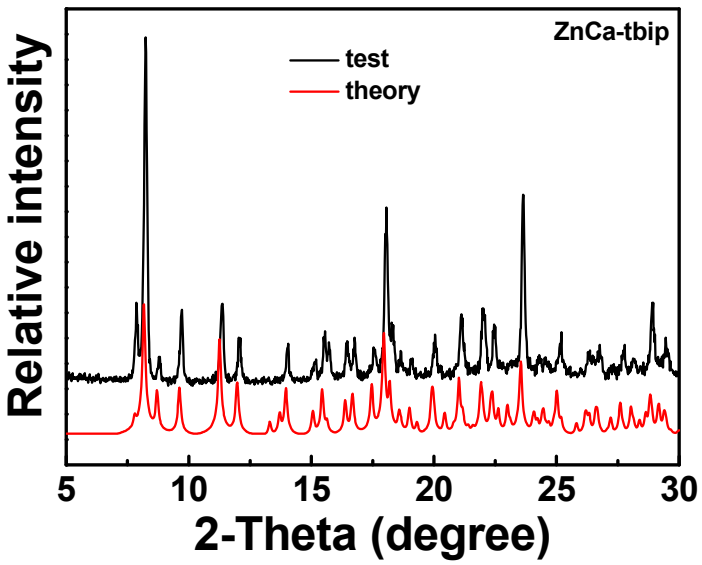
ESI. 6 The XRPD patterns of the burning residuals for **ZnCd-mip** and the referenced XRPD patterns for standard samples ZnO (JCPDS 005-0664) and CdO (JCPDS 001-1049).



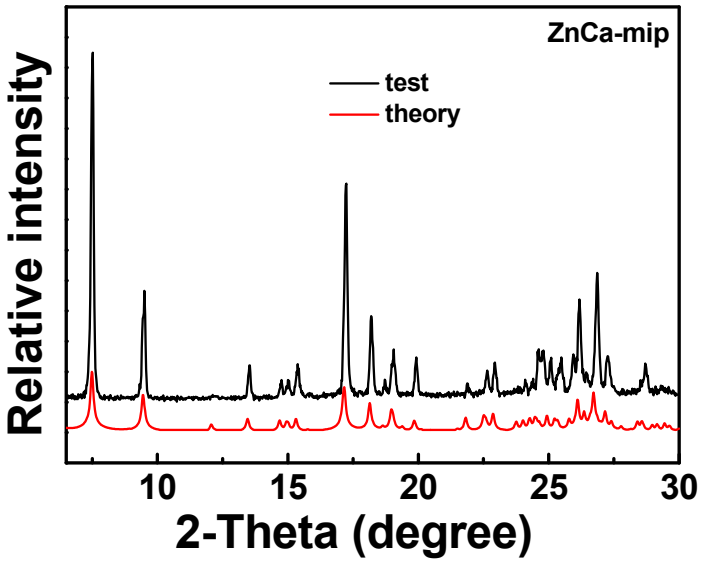
ESI. 7 The XRPD patterns of the burning residuals for **ZnCa-tbip** and the referenced XRPD patterns for standard samples ZnO (JCPDS 75-0576) and CaO (JCPDS 82-1690).



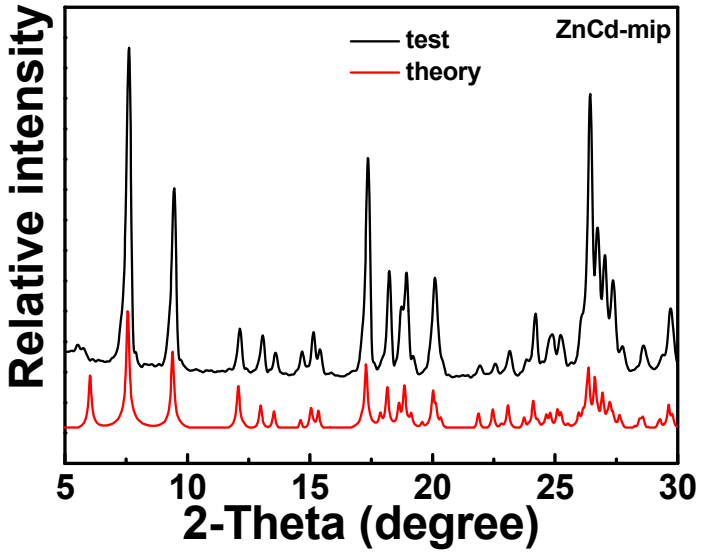
ESI. 8 The XRPD patterns of the simulated and as-synthesized MOFs for **ZnZn-tbip**.



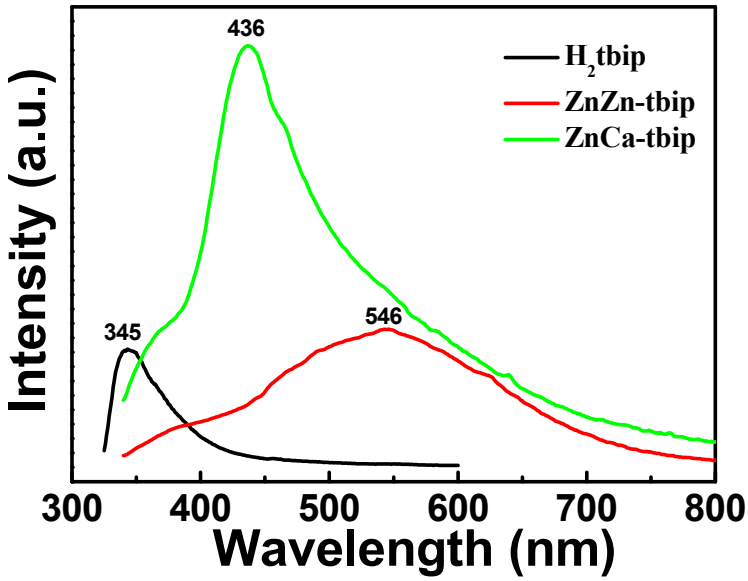
ESI. 9 The XRPD patterns of the simulated and as-synthesized MOFs for **ZnCa-tbip**.



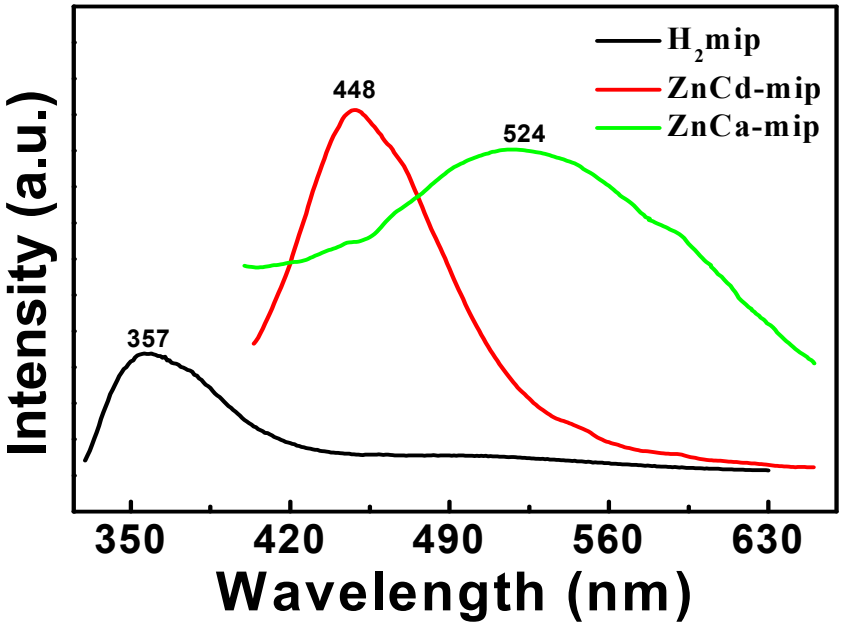
ESI. 10 The XRPD patterns of the simulated and as-synthesized MOFs for **ZnCa-mip**.



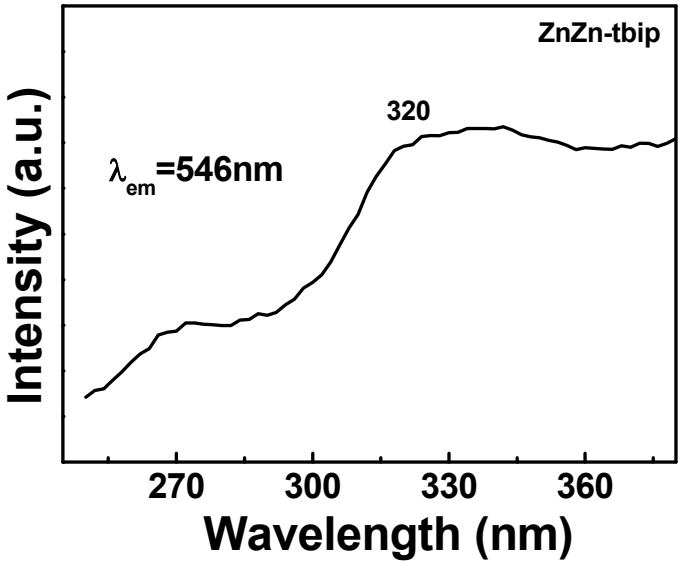
ESI. 11 The XRPD patterns of the simulated and as-synthesized MOFs for **ZnCd-mip**.



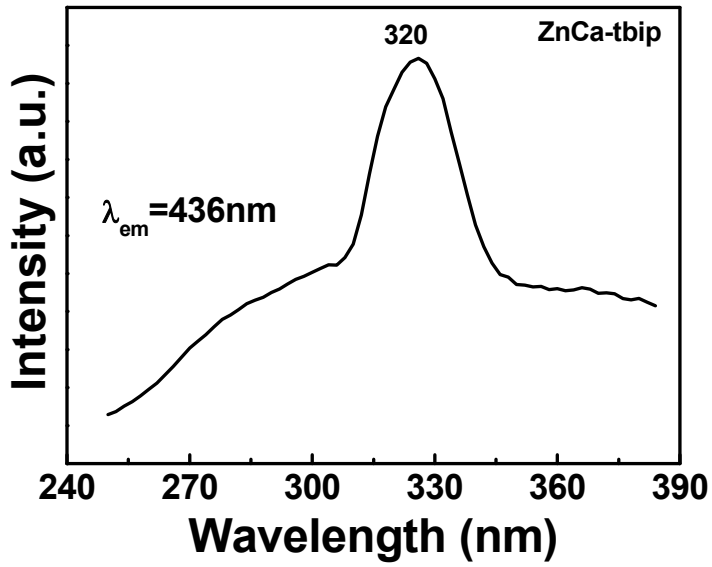
ESI. 12 The emission spectra excited at 315, 320 and 320 for **H_2tbip**, **ZnZn-tbip** and **ZnCa-tbip**, respectively.



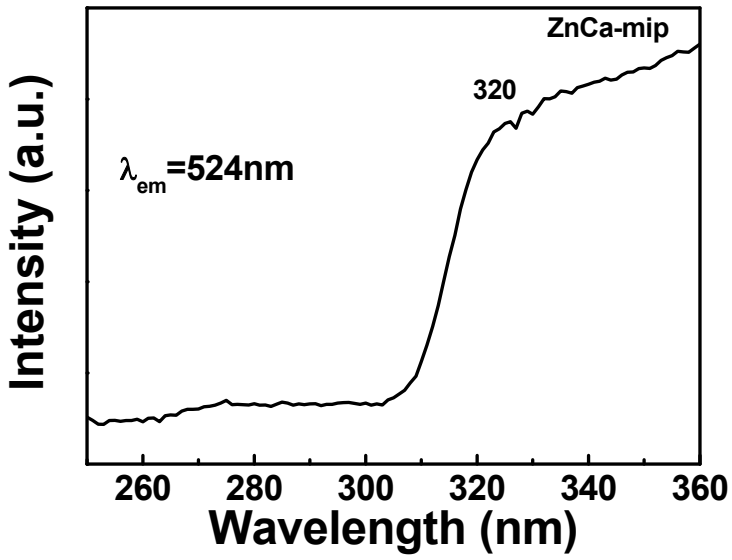
ESI. 13 The emission spectra excited at 315, 320 and 320 nm for **H_2mip**, **ZnCa-mip** and **ZnCd-mip**, respectively.



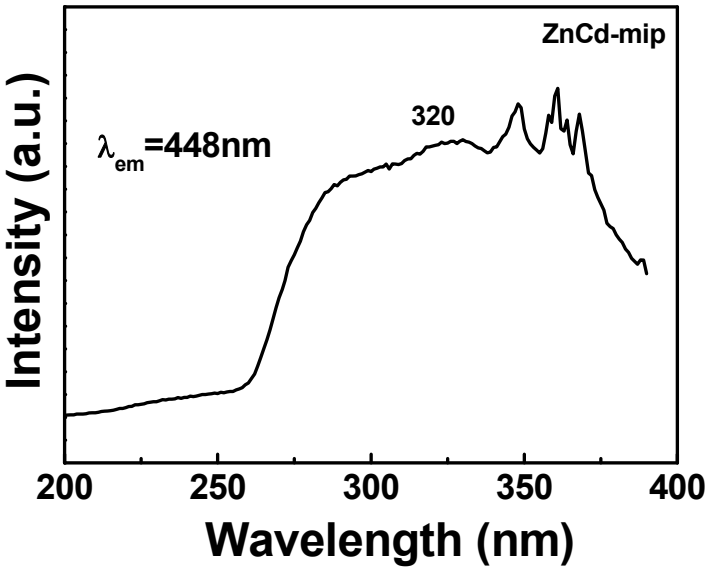
ESI. 14 The excitation spectrum for **ZnZn-tbip**



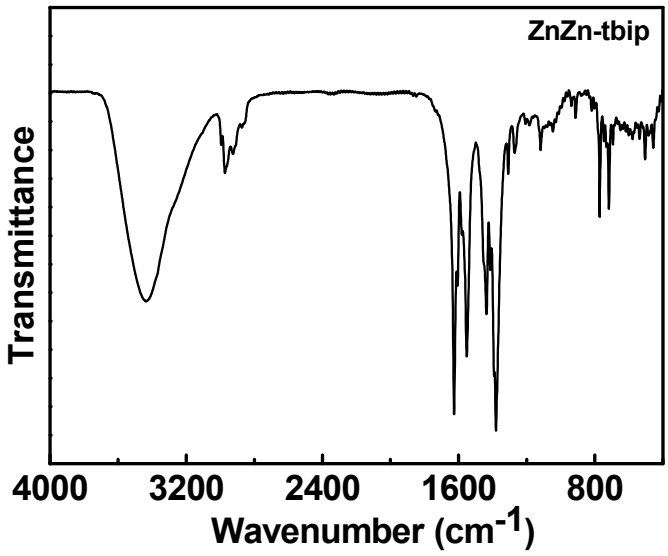
ESI. 15 The excitation spectrum for **ZnCa-tbip**



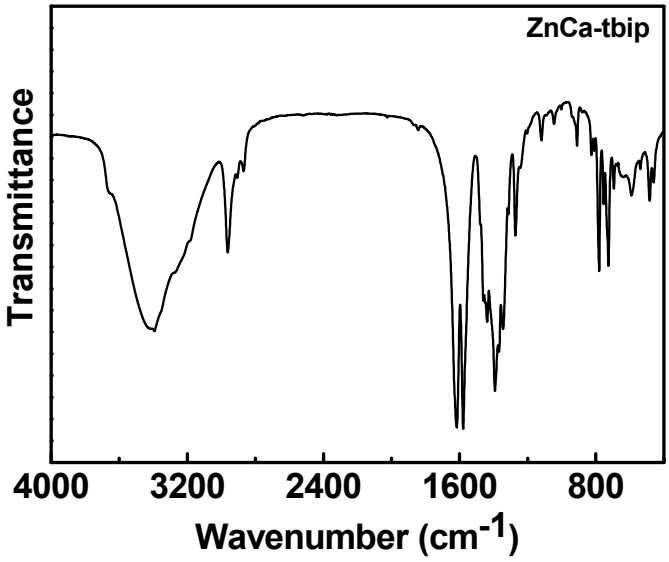
ESI. 16 The excitation spectrum for **ZnCa-mip**



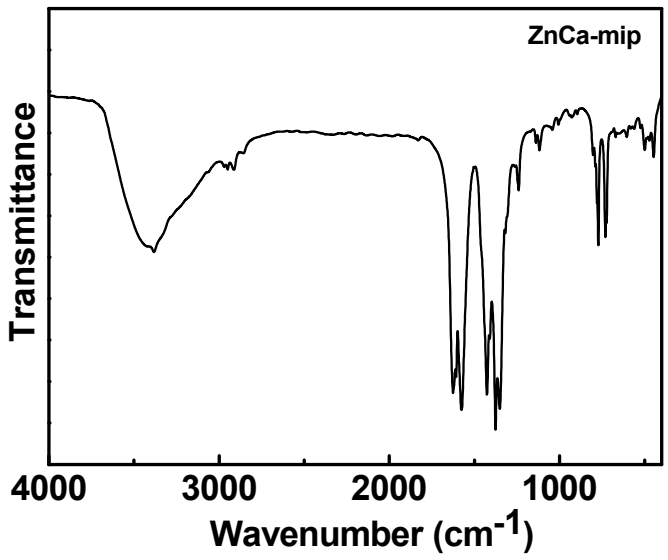
ESI. 17 The excitation spectrum for **ZnCd-mip**



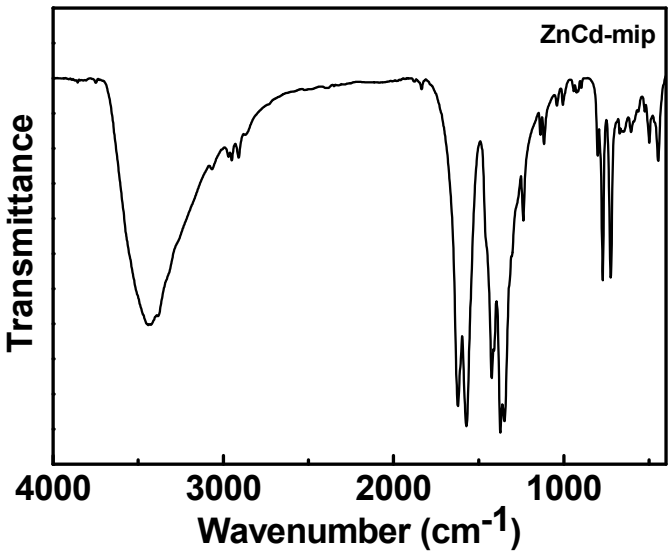
ESI. 18 FT-IR spectrum for **ZnZn-tbip.**



ESI. 19 FT-IR spectrum for **ZnCa-tbip.**



ESI. 20 FT-IR spectrum for **ZnCa-mip.**



ESI. 21 FT-IR spectrum for **ZnCd-mip.**