Supplementary Information for

Post-synthetic linker installation: an unprecedented strategy to enhance iodine adsorption in metal-organic frameworks

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S1. EXPERIMENTAL SECTION

S1.1 Materials and Synthesis

Caution! ^{232}Th used in this study is an α emitter with the daughter of radioactive Ra-228. All thorium compounds used and investigated were operated in an authorized laboratory designed for actinide element studies. Standard precautions for handling radioactive materials should be followed.

Materials. $Th(NO_3)_4·6H_2O$ (99%) were from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. 3,5-bis(3-carboxyphenyl)-1,2,4-triazole (98%) was from Zhengzhou Alfa Chemical Co., Ltd. 2,5-diaminoterephthalic acid (98%) were purchased from Jilin Chinese Academy of Sciences–Yanshen Technology Co., Ltd. 1,4-benzenedicarboxylic acid (99%), 2-aminoterephthalic acid (98%+), 2,5-pyridine-dicarboxylic acid (98%), *N,N'*-Dimethylformamide (DMF, 99%), dichloromethane (DCM, 99.5%), n-hexane (97%, SafeDry), and iodine were provided by Adamas. Concentrated hydrochloric acid (36.0~38.0%) and acetone (≥ 99.0%) were from Sinopharm Chemical Reagent Co., Ltd.

Synthesis

Th-BCPT. A mixture of $Th(NO_3)_4·6H_2O$ (23.5 mg, 0.04 mmol), 3,5-bis(3-carboxyphenyl)-1,2,4-triazole (H_2BCPT, 6.2 mg, 0.02 mmol), DMF (0.395 mL), concentrated hydrochloric acid (0.08 mL) and H_2O (0.06 mL)in a capped vial was heated at 120 ºC for 6 h. Colorless block crystals were filtered, washed with DMF and acetone, and dried at room temperature. Yield, 65% based on H_2BCPT. Anal. Calcd for $Th_6(\mu_3\text{-}O)_4(\mu_3OH)_4(C_{16}H_9N_3O_4)_4(HCOO)_4(H_2O)_6(C_3H_7NO)_{11}(H_2O)_9$, $C_{104}H_{174}N_{24}Th_6O_{67}$, C, 29.57%; H, 4.15%; N, 7.96%. Found: C, 29.71%; H, 4.32%; N, 8.15%. IR: 3379 (w), 2919 (w), 1649 (s), 1599 (vs), 1552 (s), 1500 (m), 1376 (vs), 1256 (m), 1175 (w), 1096 (w), 1016 (w), 978 (w), 873 (w), 837 (w), 795 (w), 744(s), 658 (w), 568 (w), 524 (m) cm^{-1}.

Th-BCPT-BDC. A mixture of fresh Th-BCPT (10 mg) and 1,4-benzenedicarboxylic acid (39.9 mg, 0.24 mmol) in DMF (1.5 mL) was heated to 80 ºC for 24 h. Fresh DMF (5 mL) was added once a day for three days, then washed with DMF and acetone, and to obtain **Th-BCPT-BDC**. Yield, 94%. Anal. Calcd for $Th_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(C_{16}H_9N_3O_4)_4(C_8H_4O_4)(HCOO)_2(H_2O)_6(C_3H_7NO)_{11}(H_2O)_9$, $C_{116}H_{164}N_{26}Th_6O_{56}$, C, 33.09%; H, 3.93%; N, 8.65%. Found: C, 32.92%; H, 4.07%; N, 8.57%. IR: 3386 (w), 2923 (w), 1647 (s), 1593 (vs), 1549 (s), 1507 (m), 1386 (vs), 1251 (m), 1092 (m), 1021 (w), 979 (w), 875 (w), 749 (s), 659 (w), 570 (w), 488 (m) cm^{-1}.

Th-BCPT-BDC-NH_2. A mixture of fresh Th-BCPT (10 mg) and 2-aminoterephthalic acid (43.5 mg, 0.24 mmol) in DMF (1.5 mL) was heated to 80 ºC for 24 h. Fresh DMF (5 mL) was added once a day for three days, then washed with DMF and acetone, and to obtain **Th-BCPT-BDC-NH_2**. Yield, 95%. Anal. Calcd for $Th_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(C_{16}H_9N_3O_4)_4(NC_8H_5O_4)(HCOO)_2(H_2O)_6(C_3H_7NO)_{13}(H_2O)_{10}$, $C_{113}H_{170}N_{26}Th_6O_{61}$, C, 31.85%; H, 4.02%; N, 8.55%. Found: C, 31.72%; H, 4.34%; N, 8.25%. IR: 3352 (w), 2929 (w), 1655 (s),

1593 (s), 1551 (vs), 1495 (m), 1386 (vs), 1243 (m), 1173 (w), 1092(w), 1007(w), 982 (w), 867 (w), 791 (w), 746 (m), 654 (w), 570 (w), 491 (s) cm^{-1}.

Th-BCPT-BDC-(NH_2)$_2$. A mixture of fresh Th-BCPT (10 mg) and 2,5-diaminoterephthalic acid (47.1 mg, 0.24 mmol) in DMF (1.5 mL) was heated to 80 ºC for 24 h. Fresh DMF (5 mL) was added once a day for three days, then washed with DMF and acetone, and to obtain **Th-BCPT-BDC-(NH_2)$_2$**. Yield, 91%. Anal. Calcd for $Th_6(\mu_3\text{-}O)_4(\mu_3OH)_4(C_{16}H_9N_3O_4)_4(N_2C_8H_6O_4)(HCOO)_2(H_2O)_6(C_3H_7NO)_{10}(H_2O)_{14}$, $C_{104}H_{158}N_{24}Th_6O_{62}$, C, 30.25%; H, 3.86%; N, 8.14%. Found: C, 30.51%; H, 4.02%; N, 3.75%. IR: 3363 (w), 2926 (w), 1649 (s), 1588 (s), 1551 (vs), 1504 (m), 1386 (vs), 1251 (m), 1170 (w), 1094 (w), 1013 (w), 990 (w), 881 (w), 797 (w), 746 (s), 659 (w), 572 (w), 499 (m) cm^{-1}.

Th-BCPT-PDC. A mixture of fresh Th-BCPT (10 mg) and 2,5-pyridine-dicarboxylic acid (40.1 mg, 0.24 mmol) in DMF (1.5 mL) was heated to 80 ºC for 24 h. Fresh DMF (20 mL) was added once a day for three days, then washed with DMF and acetone, and to obtain **Th-BCPT-PDC**. Yield, 90%. Anal. Calcd for $Th_6(\mu_3\text{-}O)_4(\mu_3OH)_4(C_{16}H_9N_3O_4)_4(NC_7H_3O_4)(HCOO)_2(H_2O)_6(C_3H_7NO)_{21}(H_2O)_{16}$, $C_{136}H_{236}N_{34}Th_6O_{75}$, C, 30.25%; H, 3.86%; N, 8.14%. Found: C, 30.51%; H, 4.02%; N, 3.75%. IR: 3378 (w), 3027 (w), 2760 (w), 2466 (w), 1649 (m), 1593 (s), 1549 (s), 1473 (w), 1383 (s), 1277 (m), 1243 (m), 1097 (m),1018 (m), 984 (w), 875 (w), 784 (w), 752 (s), 687 (w), 548 (w), 499 (s) cm^{-1}.

S1.2 Characterizations

X-ray Crystallography. Single-crystal X-ray diffraction data was collected on a Bruker D8-Venture single crystal X-ray diffractometer equipped with an IμS 3.0 microfocus X-ray source (Mo–Kα radiation, λ = 0.71073Å) and a CMOS detector. The data frames were collected using the APEX3 program and processed using the *SAINT* routine. The empirical absorption correction was applied using the SADABS program [1]. The structure was solved by Intrinsic Phasing with *ShelXT* [2] and refined with ShelXL [3] using *OLEX2* [4]. All the non-H atoms were subjected to anisotropic refinement by full-matrix program. Due to the disorder of PDC^{2-} in **Th-BCPT-PDC** and the amino groups can be distributed randomly in the benzene rings for **Th-BCPT-BDC-NH_2** and **Th-BCPT-BDC-(NH_2)$_2$**, the N atom of PDC^{2-} and the amino groups were assigned randomly. Crystal data and details of the data collection are given in Table S1. Powder X-ray diffraction (PXRD) data were collected on were collected from 2 to 40° with a step of 0.02° on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.54178 Å). The calculated PXRD pattern was produced from the CIFs using the *Mercury* 1.4.2 program.

CO_2 absorption and Langmuir surface area Analysis. The CO_2 adsorption isotherms were recorded at 273.15 K by using a micromeritics ASAP 2020 surface area and porosity analyser. Before the adsorption measurements, the freshly prepared sample was first exchange with DCM for 15 minutes three times and with n-hexane for 15 minutes three times. Then, the samples were activated with the "degas" port under the

vacuum at 30°C for 2 h.

X-ray photoelectron spectroscopy (XPS). The XPS data of iodine adsorbed samples were recorded on a Thermo Scientific ESCALAB 250Xi using monochromatic Al Kα (1486.8 eV) X-ray source with a spot size of 500 μm. The anode was operated at 15 kV and 10 mA.

Elemental Analysis. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) data were recorded on a Zeiss Merlin Compact LEO 1530 VP scanning electron microscope. The energy of the electron beam voltage was 10 keV for imaging and was 15 keV for quantitative identifications of elements. Elemental analyses of C, N, and O were performed with a Vario EL Cube.

S1.3 Iodine Vapor Adsorption Studies

Stable isotope (^{127}I) was used as a surrogate for the radioactive ^{129}I and ^{131}I as their chemical properties are identical. An open vial (20 mL) containing 50 mg samples was accurately weighted (m_0) and introduced into a glass vessel (150 mL) containing 500 mg iodine. The vessel was sealed and kept in an oven at 75 °C. After certain time intervals, the vial containing the sample was weighed periodically (m_t) until the mass of it did not change. The iodine adsorption capacity can be calculated as: $wt\% = (m_t - m_0)/m_0$. Sorption kinetics of iodine can be fitted to a pseudo second-order kinetics model, $t/q_t = 1/h + t/q_e$ (where q_t, q_e represent the amounts of adsorbate at certain time t or at equilibrium time, h is the initial adsorption rate, $h = kqe^2$, and k is the rate constant).

S2. FIGURES AND TABLES

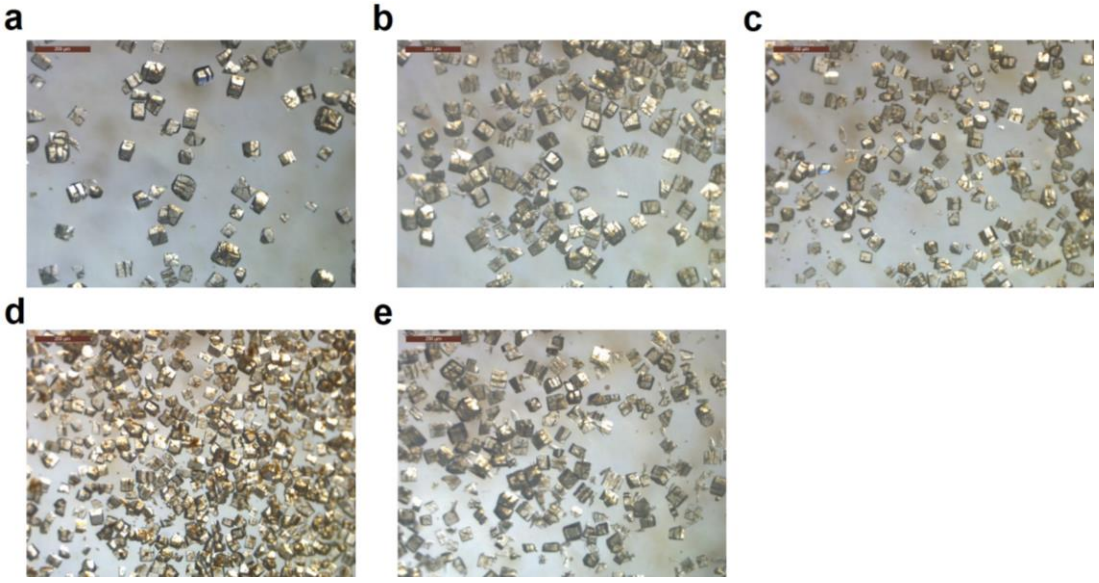

Fig. S1 Crystal images of (a) **Th-BCPT**, (b) **Th-BCPT-BDC**, (c) **Th-BCPT-BDC-NH_2**, (d) **Th-BCPT-BDC-$(NH_2)_2$**, and (e) **Th-BCPT-PDC**.

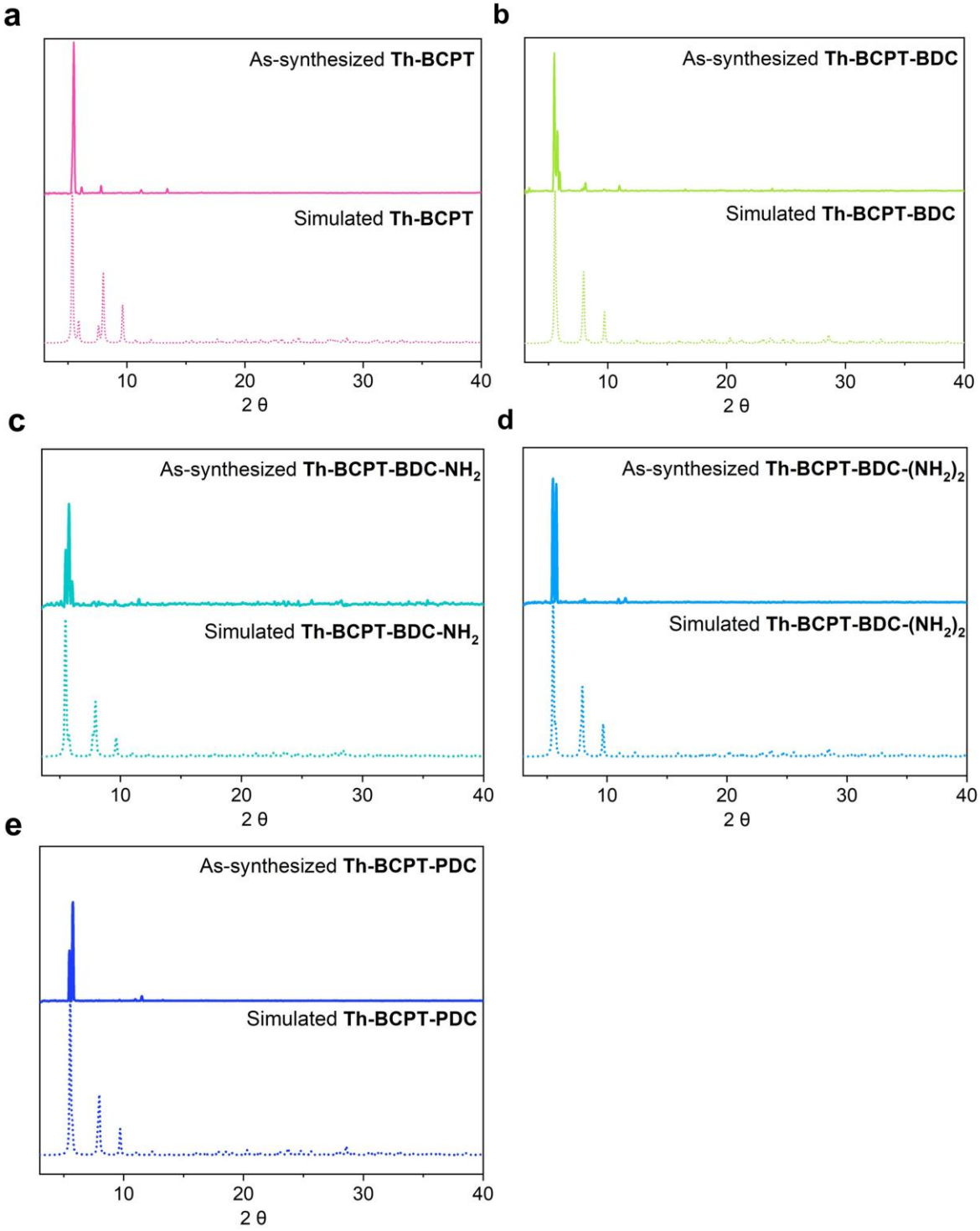

Fig. S2 Powder X-ray diffraction patterns of as-synthesized and simulated (a) **Th-BCPT**, (b) **Th-BCPT-BDC**, (c) **Th-BCPT-BDC-NH_2**, (d) **Th-BCPT-BDC-$(NH_2)_2$**, and (e) **Th-BCPT-PDC**.

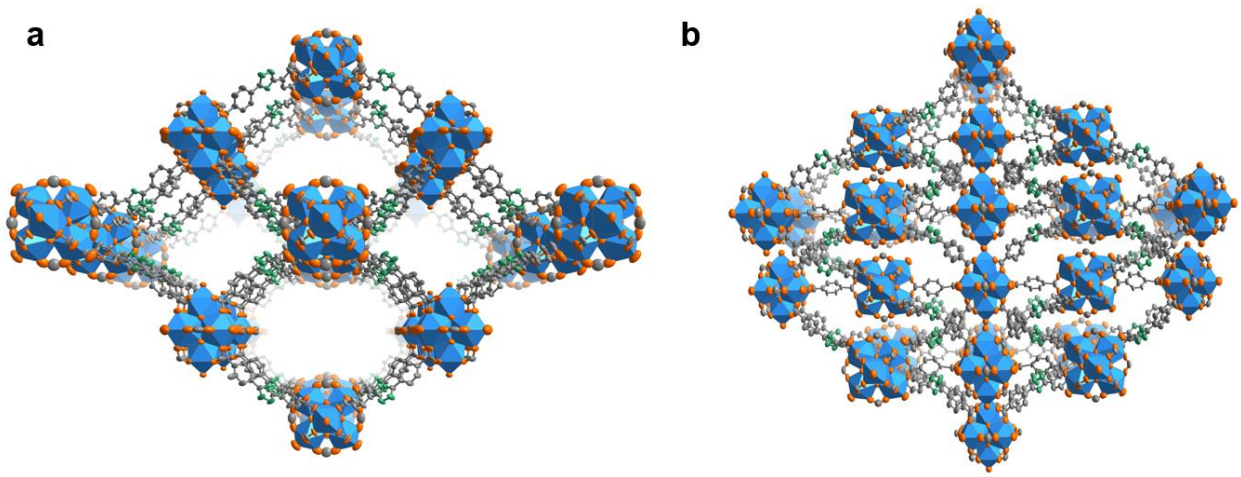

Fig. S3 Structural representation showing ADPs of (a) **Th-BCPT** and (b) **Th-BCPT-BDC**.

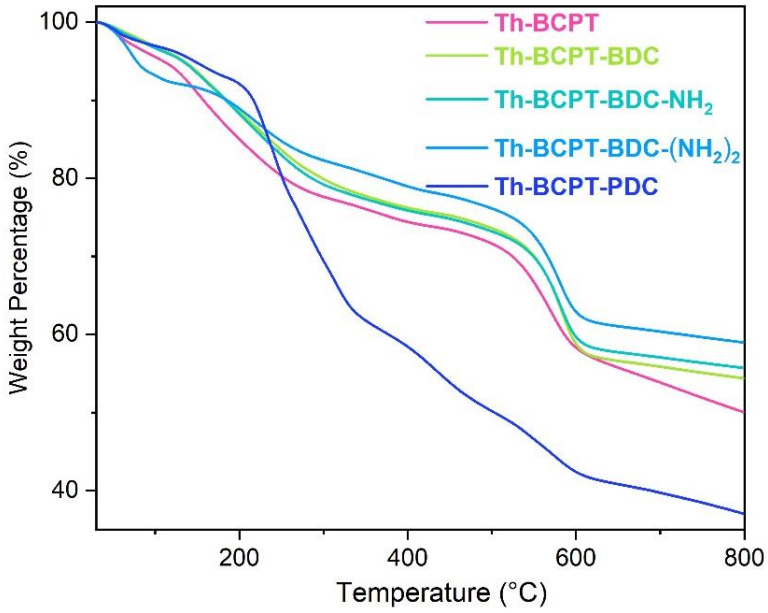

Fig. S4 Thermal gravimetric analysis (TGA) curves of **Th-BCPT**, **Th-BCPT-BDC**, **Th-BCPT-PDC**, **Th-BCPT-BDC-NH_2**, and **Th-BCPT-BDC-$(NH_2)_2$**.

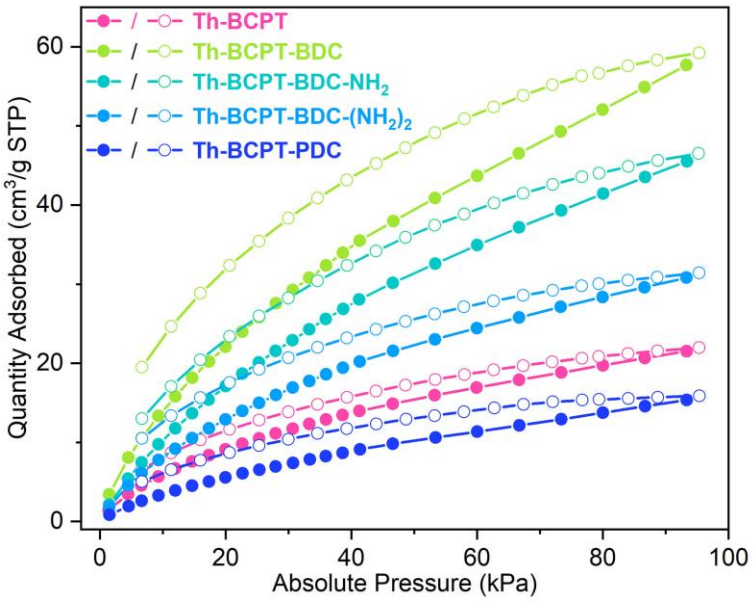

Fig. S5 CO_2 adsorption-desorption isotherms of **Th-BCPT**, **Th-BCPT-BDC**, **Th-BCPT-PDC**, **Th-BCPT-BDC-NH_2**, and **Th-BCPT-BDC-$(NH_2)_2$**.

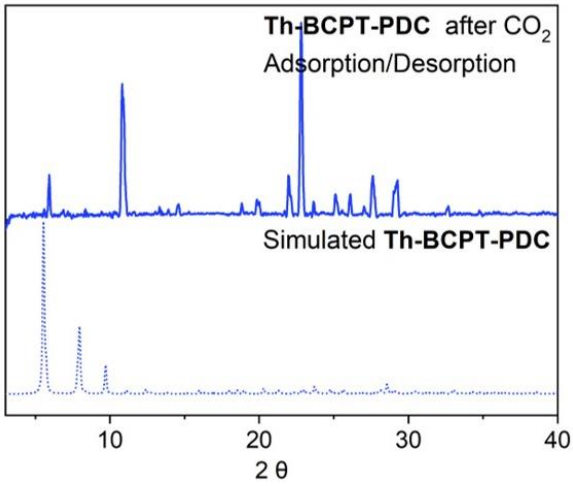

Fig. S6 Powder X-ray diffraction patterns of **Th-BCPT-PDC** before and after CO_2 adsorption/desorption process.

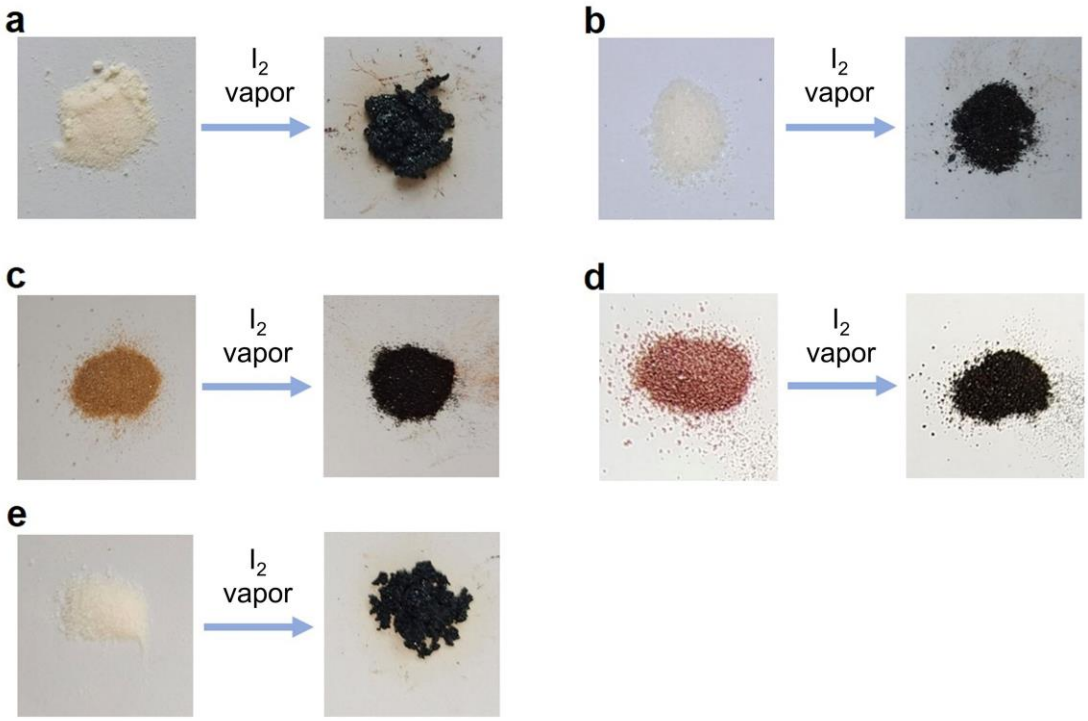

Fig. S7 Photographs of (a) **Th-BCPT**, (b) **Th-BCPT-BDC**, (c) **Th-BCPT-BDC-NH_2**, (d) **Th-BCPT-BDC-$(NH_2)_2$**, and (e) **Th-BCPT-PDC** powder before and after I_2 vapor adsorption.

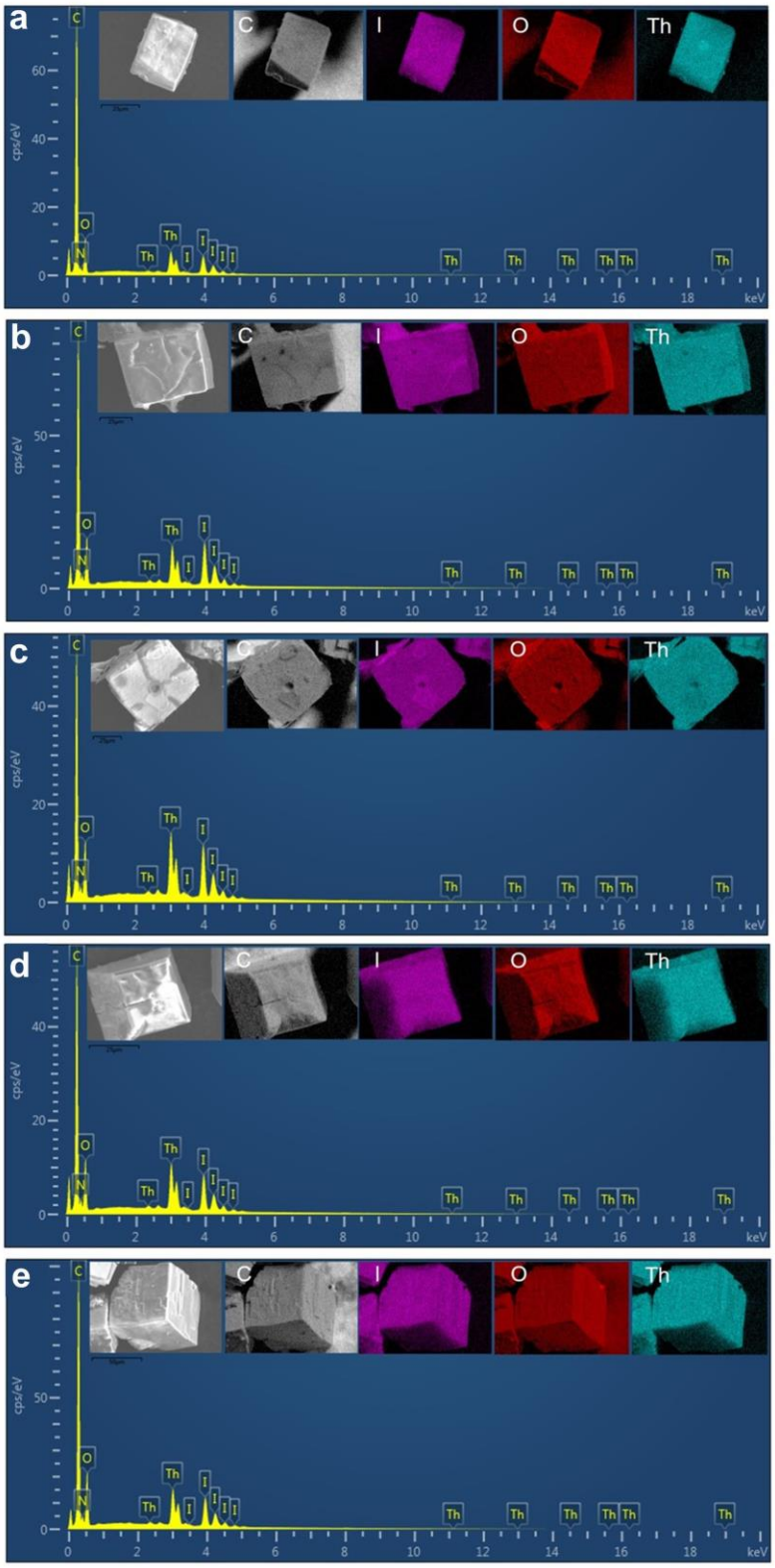

Fig. S8 SEM-EDS results of (a) **Th-BCPT**, (b) **Th-BCPT-BDC**, (c) **Th-BCPT-BDC-NH_2**, (d) **Th-BCPT-BDC-$(NH_2)_2$**, and (e) **Th-BCPT-PDC** after I_2 vapor absorption.

Table S1 Crystallographic data for **Th-BCPT**, **Th-BCPT-BDC**, **Th-BCPT-BDC-NH_2**, **Th-BCPT-BDC-$(NH_2)_2$**, and **Th-BCPT-PDC**

Code	**Th-BCPT**	**Th-BCPT-BDC**	**Th-BCPT-BDC-NH_2**	**Th-BCPT-BDC-$(NH_2)_2$**	**Th-BCPT-PDC**
CCDC No.	2235274	2235275	2235276	2235277	2235278
formula	$C_{52}H_{68}N_{12}O_{25}Th_3$	$C_{46}H_{48}N_9O_{22}Th_3$	$C_{169}H_{159}N_{33}O_{83}Th_{12}$	$C_{43}H_{42}N_9O_{21}Th_3$	$C_{85}H_{89}N_{17}O_{46}Th_6$
formula weight	1957.30	1775.05	6764.76	1716.97	3476.97
habit	block	block	block	block	block
space Group	$P4_2/mcm$	$P4_2/mcm$	$P4_2/mcm$	$P4_2/mcm$	$P4_2/mcm$
a (Å)	16.4434(13)	15.9061(17)	16.1705(12)	16.037(3)	15.939(2)
b (Å)	16.4434(13)	15.9061(17)	16.1705(12)	16.037(3)	15.939(2)
c (Å)	29.878(2)	30.979(3)	30.701(3)	30.899(8)	15.939(2)
α	90	90	90	90	90
β	90	90	90	90	90
γ	90	90	90	90	90
V (Å^3)	8078.5(14)	7837.7(18)	8027.8(14)	7947(4)	7852(3)
Z	4	4	1	4	2
T (K)	120	120	120	120	120
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Max. 2θ (°)	53.996	55.08	55.084	55.14	45.536
ρ_{calcd} (g cm^{-3})	1.609	1.504	1.399	1.435	1.471
μ (mm^{-1})	5.580	5.739	5.598	5.656	5.727
GoF on F^2	1.045	1.042	1.099	1.065	1.046
R_1, wR_2 [I > 2σ(I)]	0.0548, 0.1416	0.0610, 0.1817	0.0314, 0.1008	0.0519, 0.1600	0.0508, 0.1528
R_1, wR_2 (all data)	0.0577, 0.1437	0.1050, 0.2106	0.0386, 0.1064	0.0661, 0.1735	0.0651, 0.1718
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e (Å^{-3})	1.62/-1.58	1.05/-2.44	1.17/-1.12	2.56/-1.52	1.76/-1.73

Table S2 Parameters of the pseudo-second-order kinetic model for I_2 vapor adsorption.

Sample	pseudo-second-order kinetic model		
	q_e (wt%)	k (h^{-1})	R^2
Th-BCPT	44.35008	3.47871	0.99672
Th-BCPT-BDC	43.67005	1.45783	0.96824
Th-BCPT-BDC-NH_2	59.35265	2.69333	0.99436
Th-BCPT-BDC-$(NH_2)_2$	94.736	1.51659	0.98404
Th-BCPT-PDC	166.02254	0.6294	0.98711

S3. REFERENCES

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2. G. M. Sheldrick, *Acta Crystallographica Section A: Found. Adv.*, 2015, **71**, 3.
3. G. M. Sheldrick, *Acta Crystallogr. Sect. C: Struct. Chem.*, 2015, **71**, 3.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.