Electronic Supplementary Information

Defective MOF-74 with ancillary open metal sites for the enhanced adsorption of chemical warfare agent simulants

*Sujeong Lee, Sojin Oh, Gihyun Lee and Moonhyun Oh**

Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea
*Corresponding author.
E-mail: moh@yonsei.ac.kr

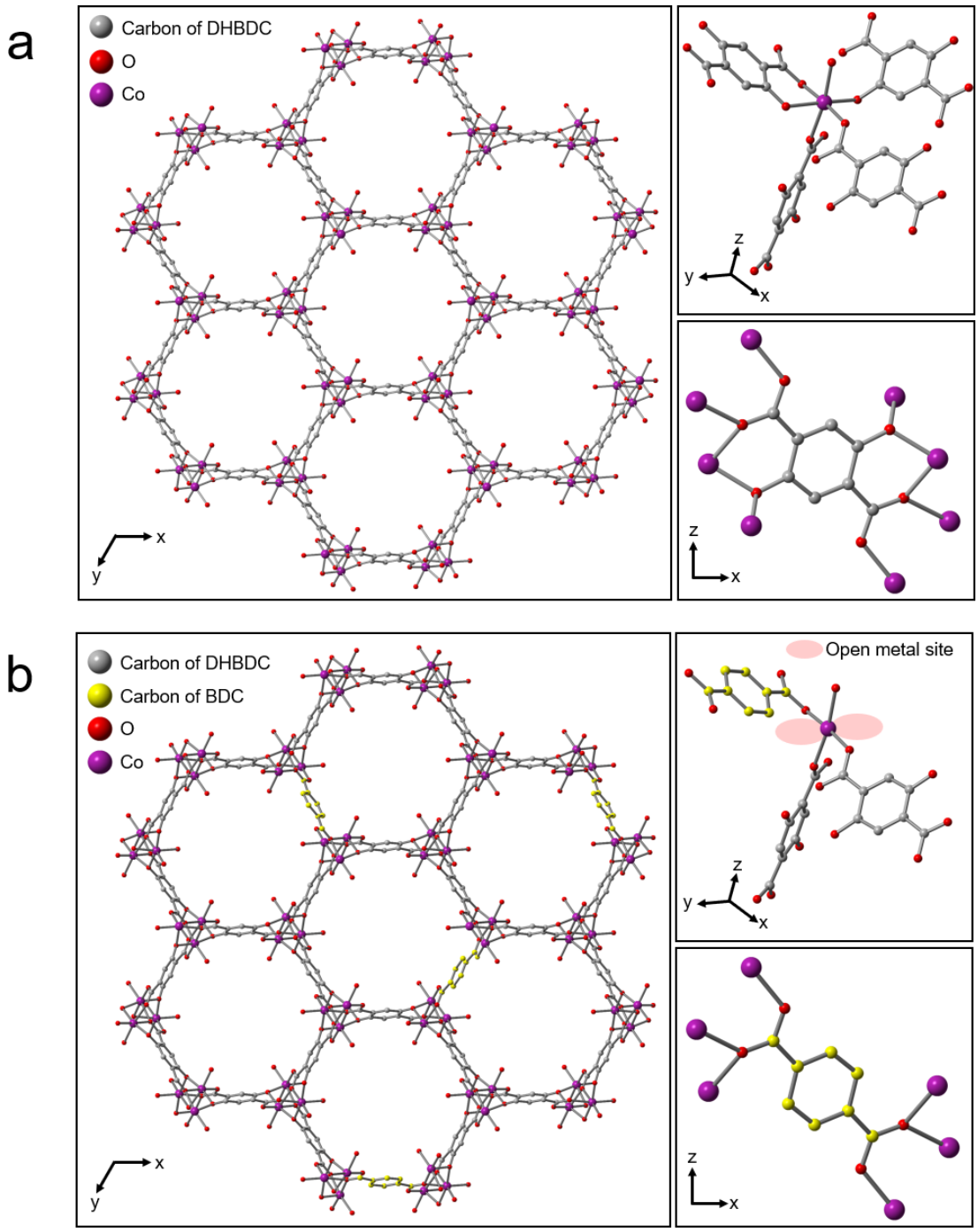

Fig. S1 Ball-and-stick representations of (a) MOF-74 and (b) D-MOF-74. Co: purple; C: gray for DHBDC or yellow for BDC; O: red. H atoms are omitted for clarity.

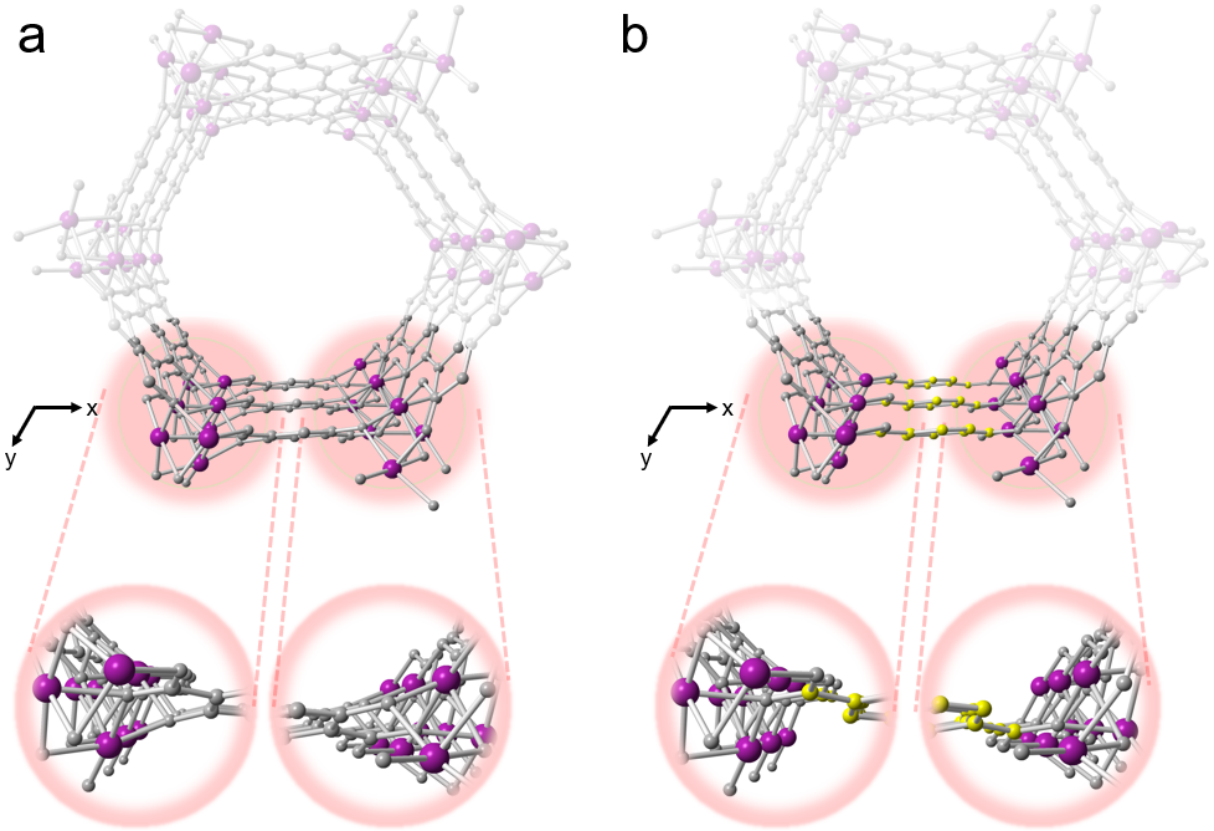

Fig. S2 Ball-and-stick representations of (a) MOF-74 and (b) D-MOF-74 showing the open metal sites generated due to the absence of bridged hydroxyl groups. Co: purple; C: grey for DHBDC or yellow for BDC; O: grey. H atoms and H_2O are omitted for clarity.

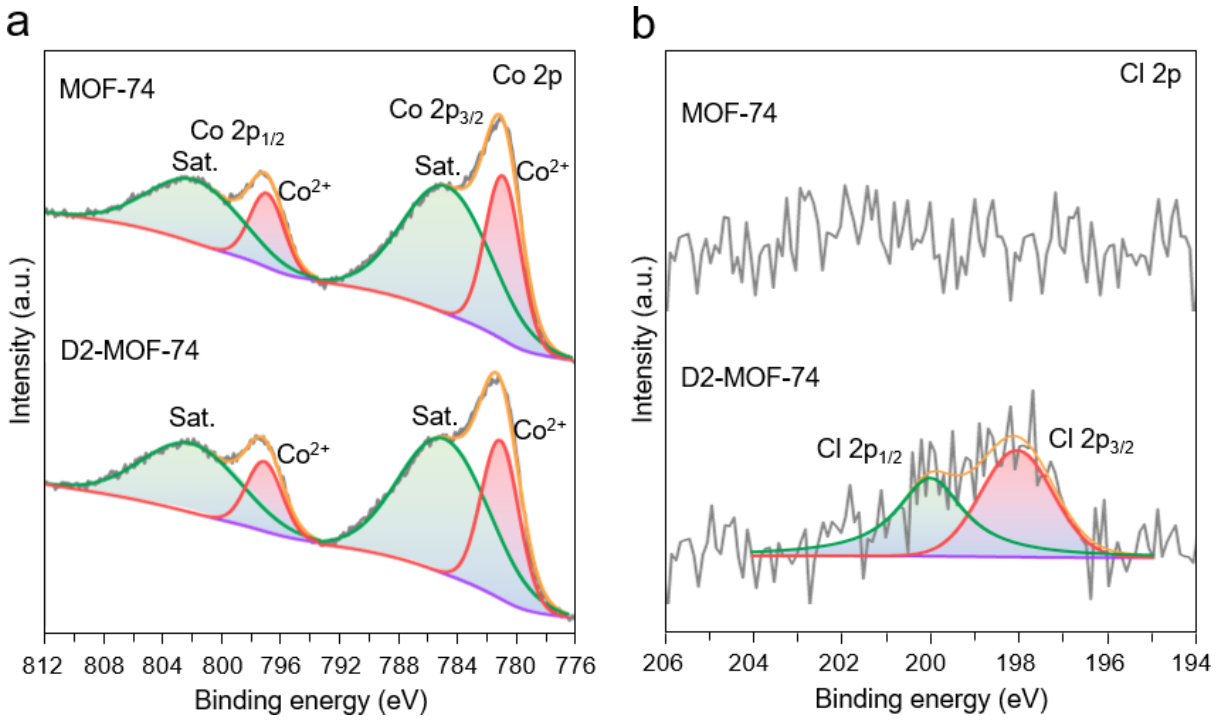

Fig. S3 High-resolution (a) Co 2p and (b) Cl 2p XPS spectra of pure MOF-74 and D2-MOF-74.

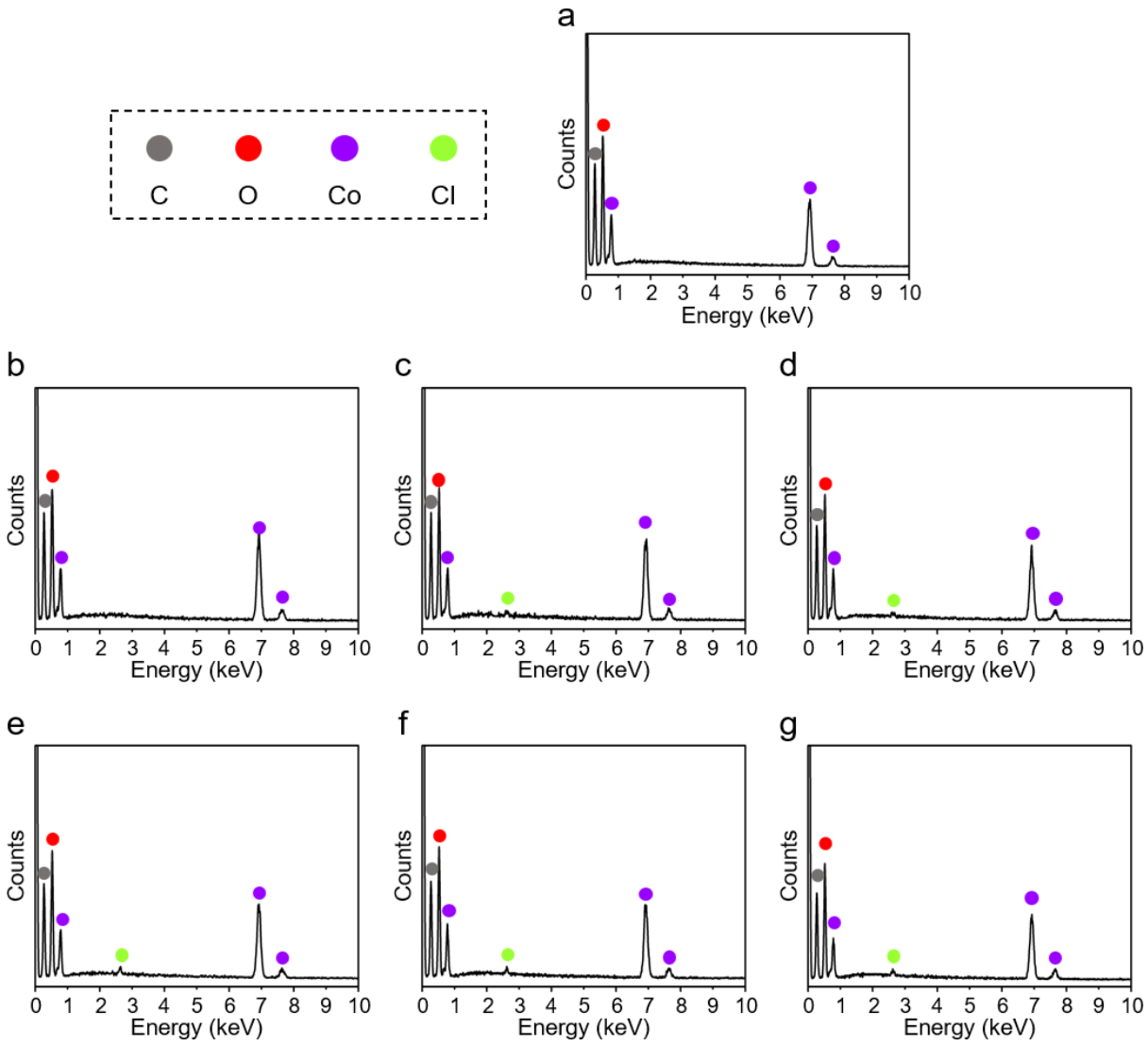

Fig. S4 EDX spectra of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74.

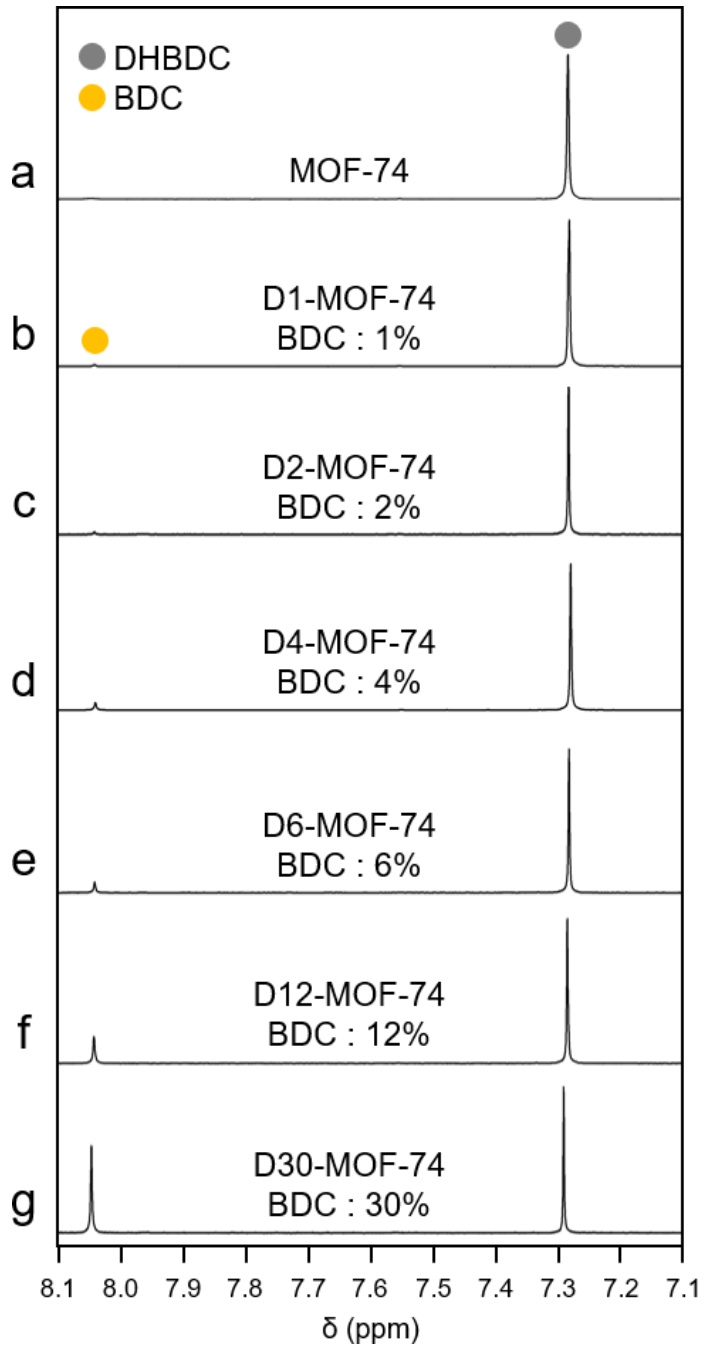

Fig. S5 ^{1}H NMR spectra of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74 showing the incorporated amounts of DHBDC and BDC. To determine the relative amounts of the two organic linkers, the integration of peaks corresponding to both DHBDC and BDC was utilized.

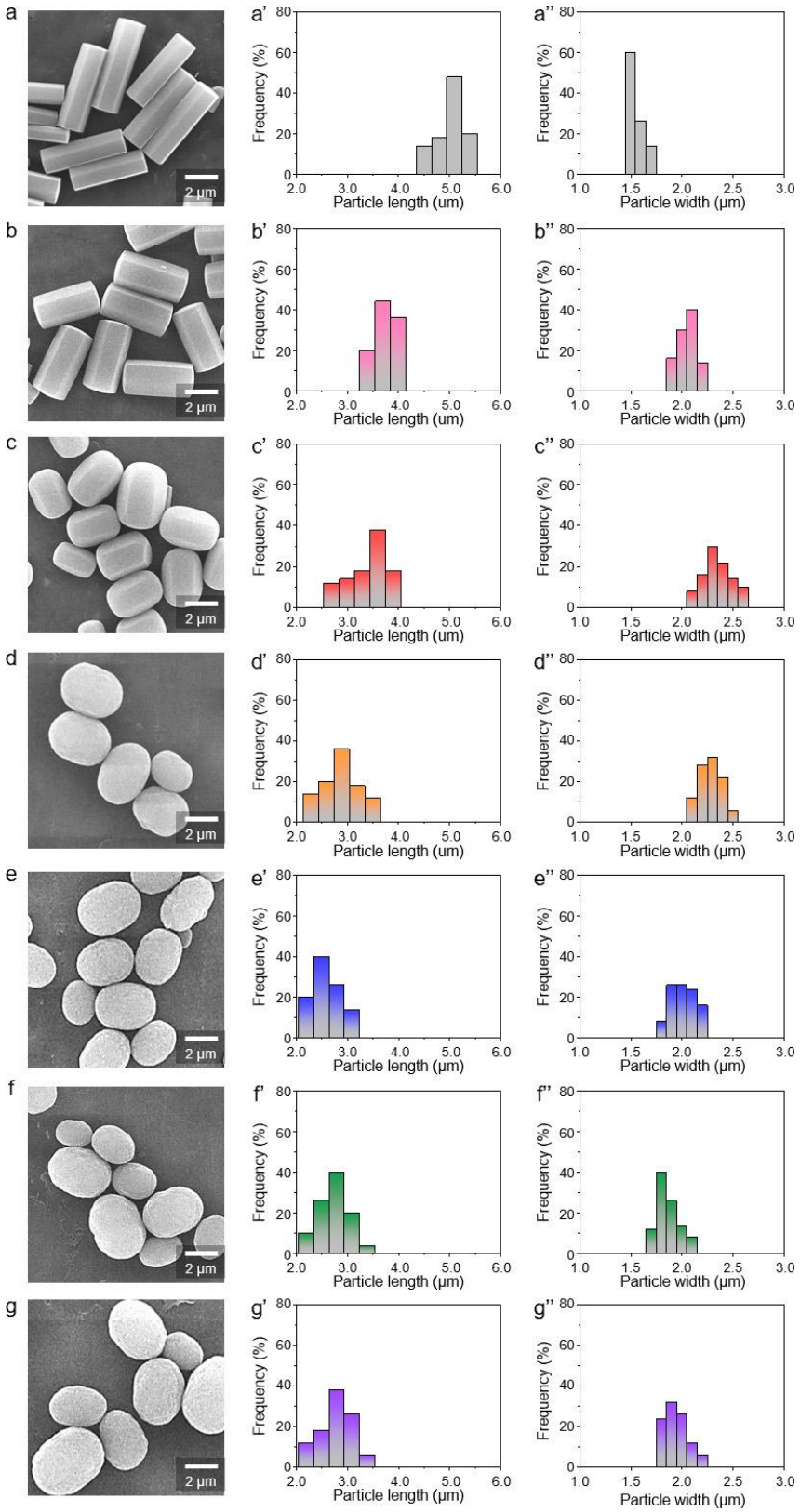

Fig. S6 (a–g) SEM images and size distributions of (a′–g′) length and (a″–g″) width of pure MOF-74 and a series of D-MOF-74 samples (n = 50).

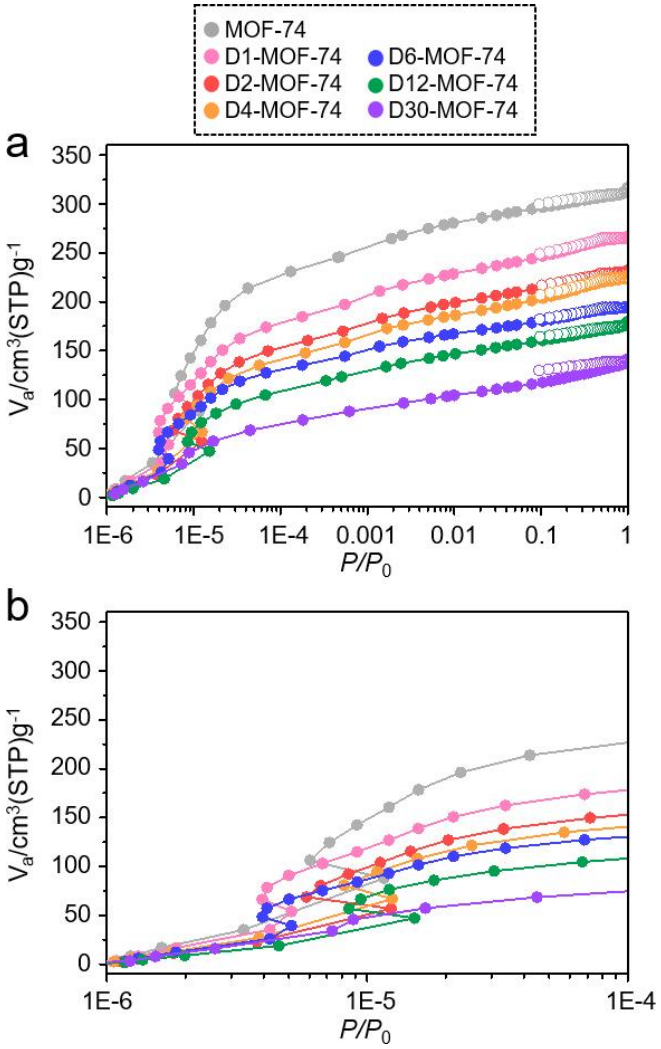

Fig. S7 (a, b) N_2 sorption isotherms of MOF-74 and a series of D-MOF-74 in the logarithmic scale.

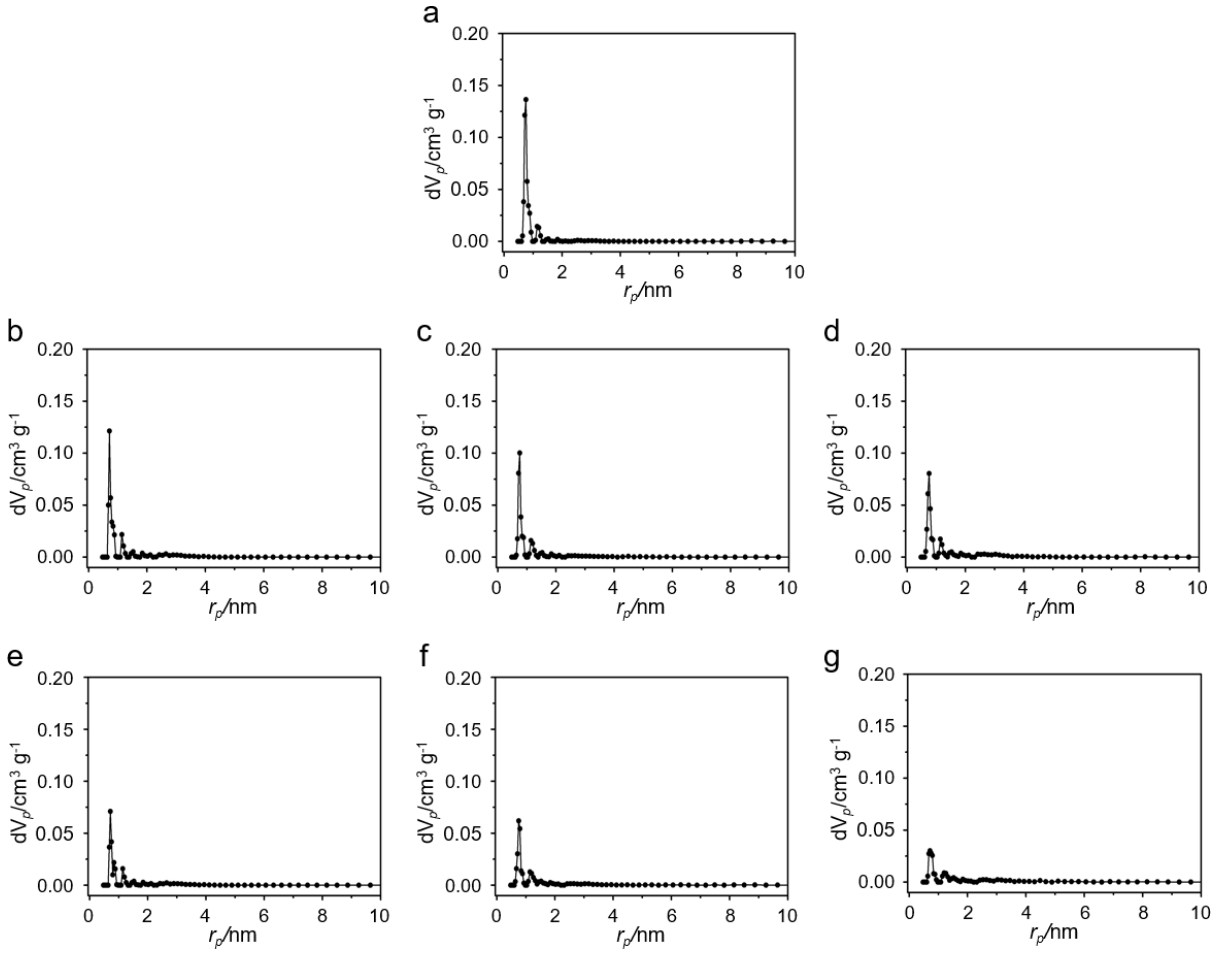

Fig. S8 Pore size distributions of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74 calculated using non-local density functional theory.

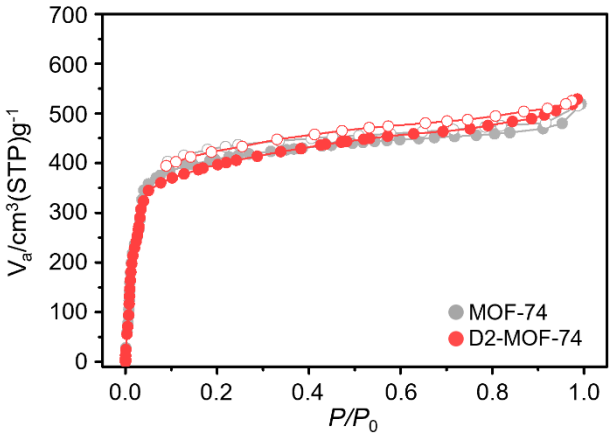

Fig. S9 Water vapor sorption isotherms of pure MOF-74 and D2-MOF-74.

`

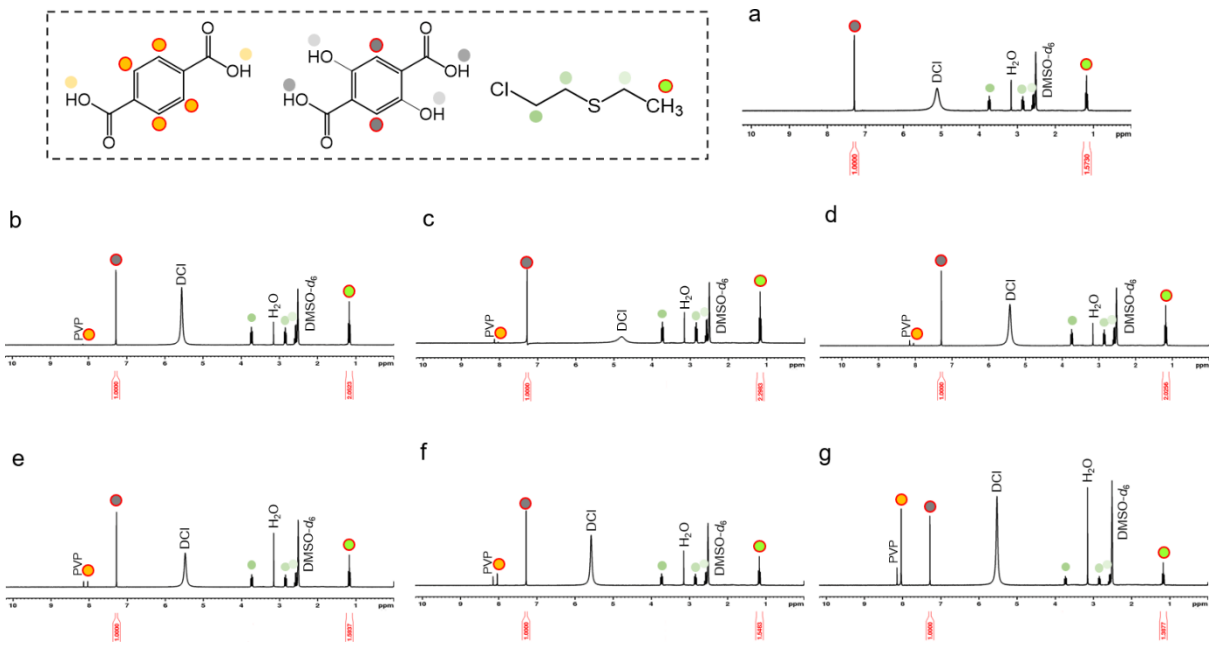

Fig. S10 ^{1}H NMR spectra showing the amounts of CEES adsorption on MOF-74 and a series of D-MOF-74. ^{1}H NMR spectra of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74 after exposure to CEES vapors for 4 h.

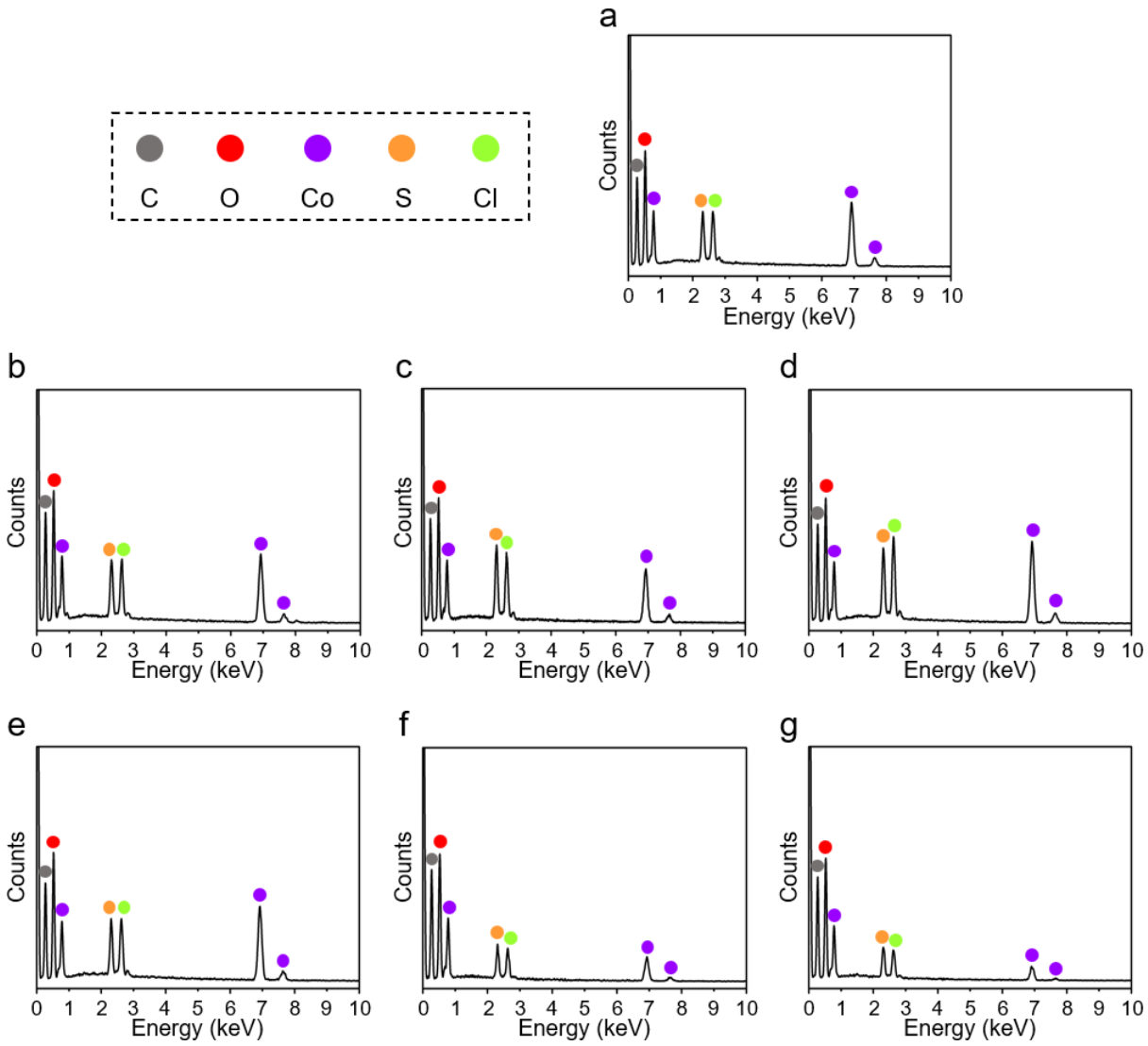

Fig. S11 EDX spectra of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74 measured after exposure to CEES vapors.

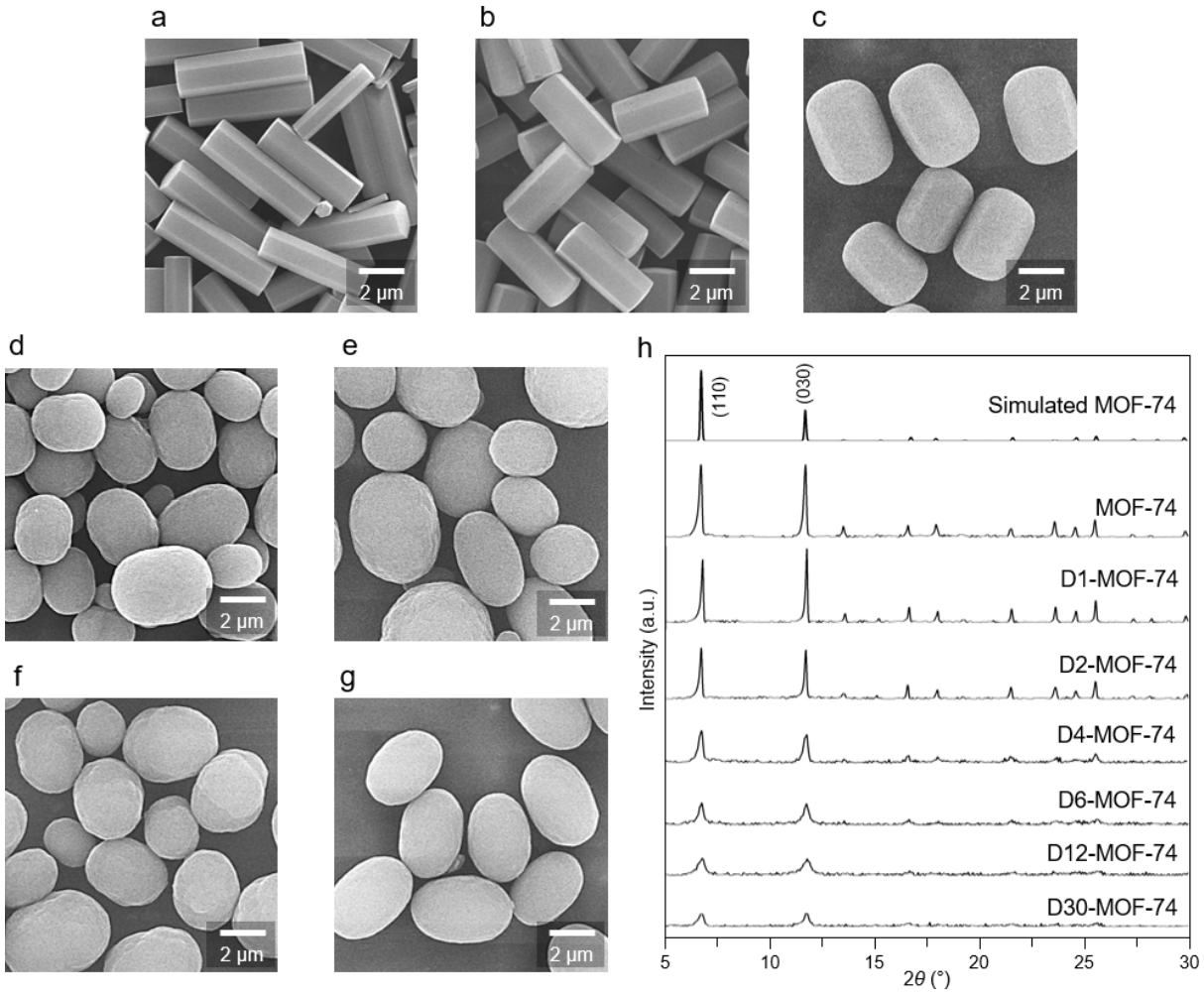

Fig. S12 SEM images of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74 measured after exposure to CEES vapors for 4 h. (h) PXRD patterns of pure and defective MOF-74 samples after exposure to CEES vapors for 4 h. The simulated PXRD pattern of MOF-74 is also shown at the top.

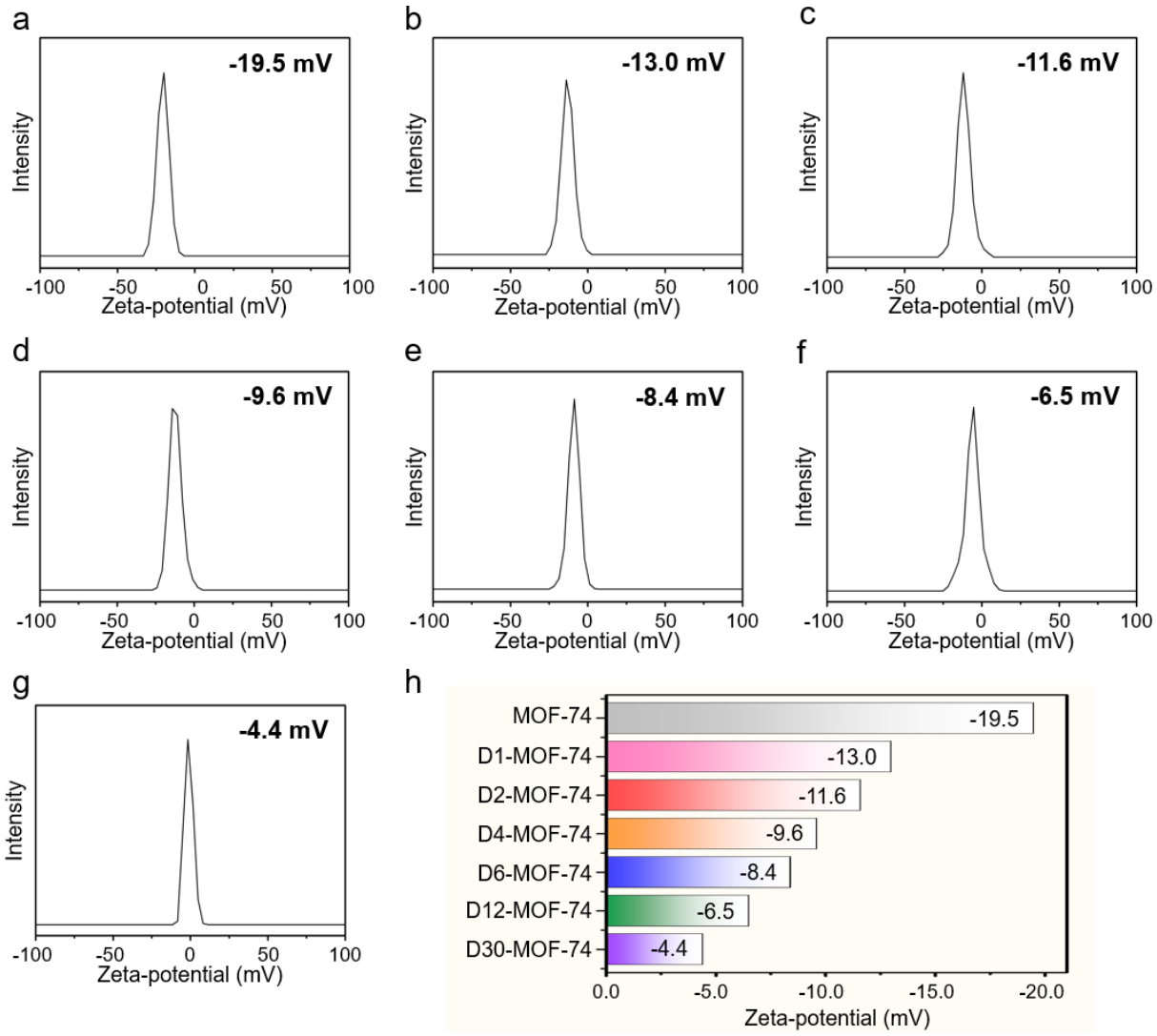

Fig. S13 Zeta-potentials of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74. (h) Summary of zeta-potential values of pure MOF-74 and a series of D-MOF-74 samples.

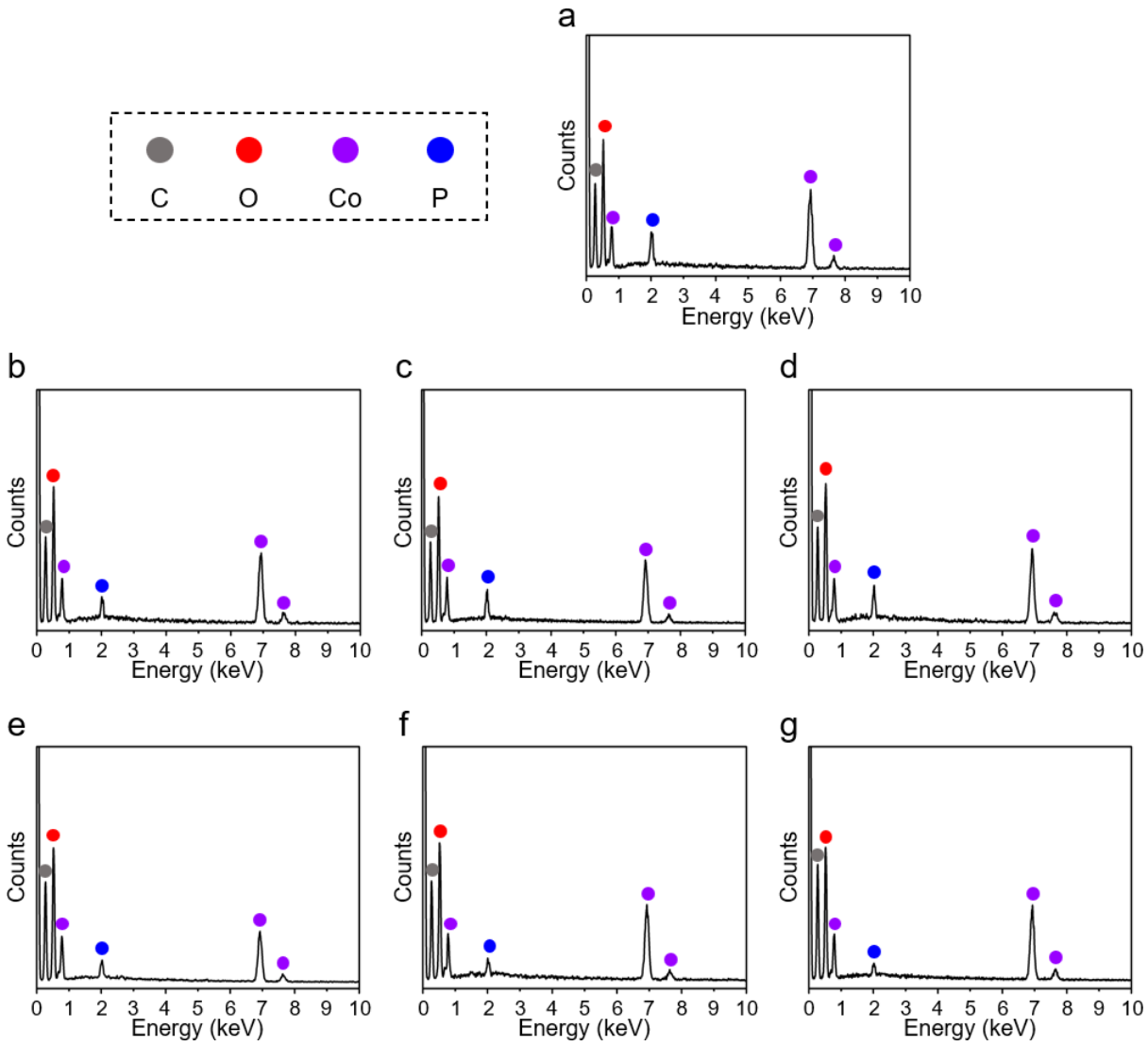

Fig. S14 EDX spectra of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74 measured after exposure to DMMP vapors.

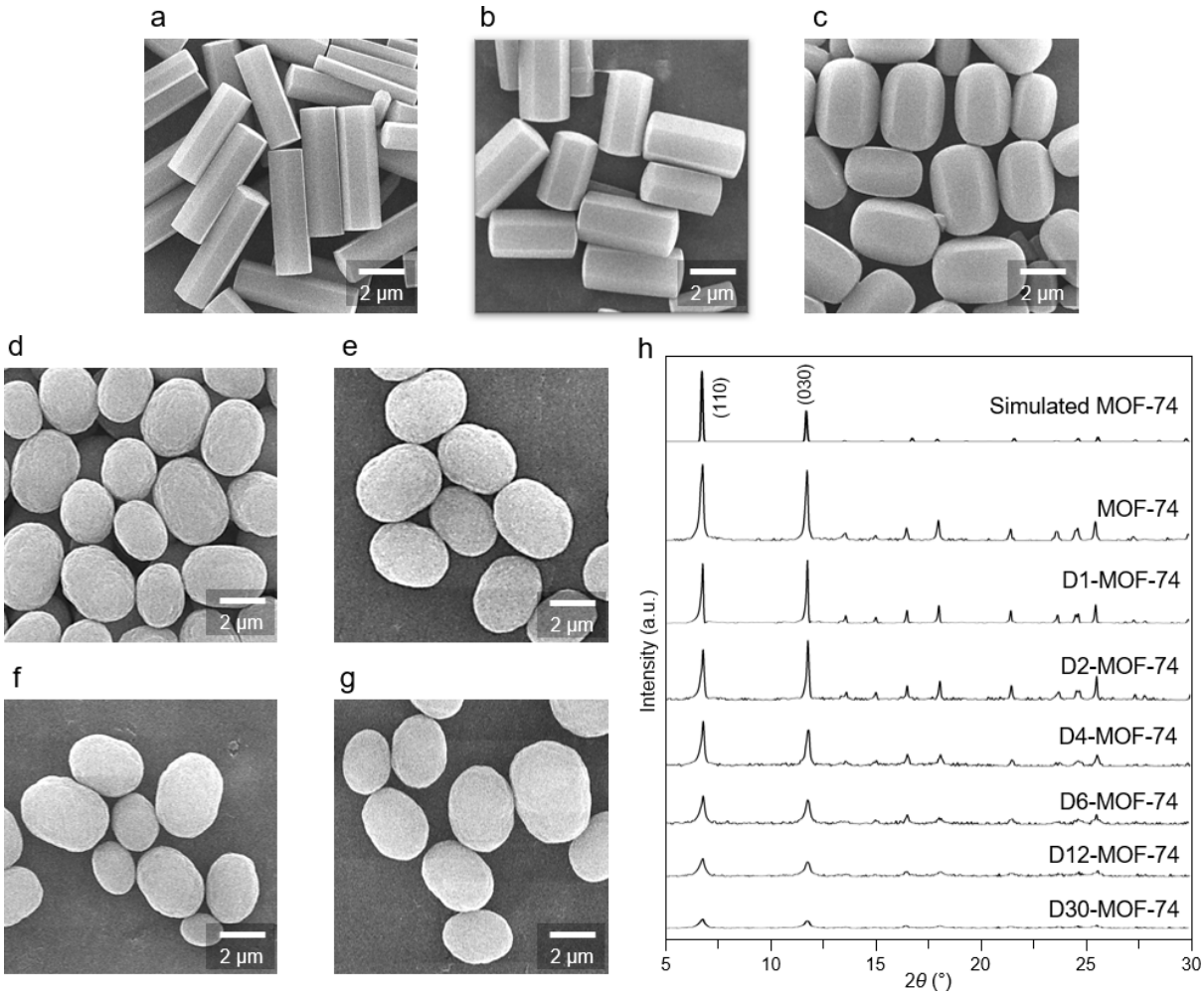

Fig. S15 SEM images of (a) pure MOF-74, (b) D1-MOF-74, (c) D2-MOF-74, (d) D4-MOF-74, (e) D6-MOF-74, (f) D12-MOF-74, and (g) D30-MOF-74 measured after exposure to DMMP vapors for 5 day. (h) PXRD patterns of pure and defective MOF-74 samples after exposure to DMMP vapors for 5 day. The simulated PXRD pattern of MOF-74 is also shown at the top.

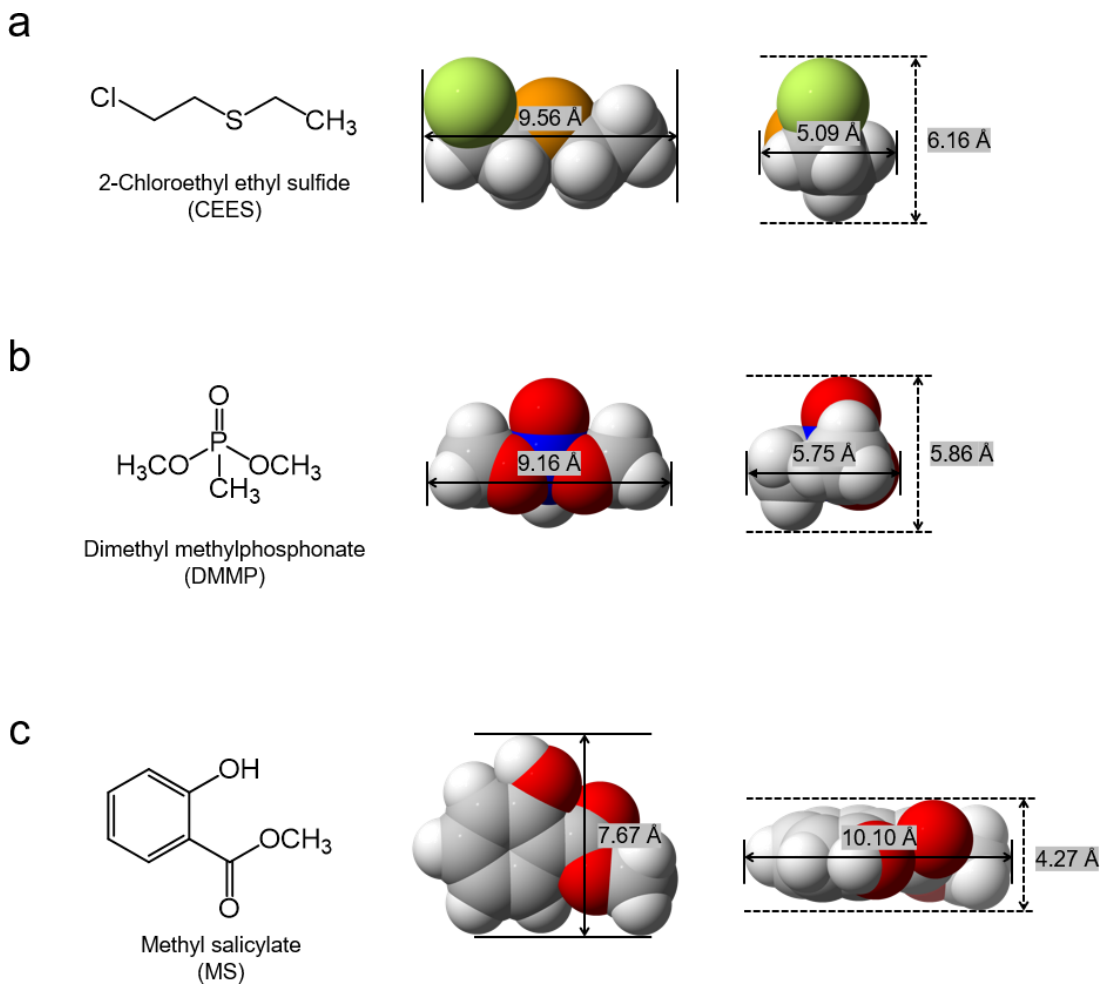

Fig. S16 Structures and van der Waals models of (a) CEES, (b) DMMP, and (c) MS. C: grey, S: yellow, Cl: green, H: white, O: red, P: blue.

Table S1 The length and width of pure MOF-74 and a series of D-MOF-74 samples (n = 50).

MOF	Particle length (μm)	Particle width (μm)
MOF-74	5.0 ± 0.28	1.6 ± 0.08
D1-MOF-74	3.8 ± 0.21	2.0 ± 0.09
D2-MOF-74	3.4 ± 0.38	2.3 ± 0.14
D4-MOF-74	2.9 ± 0.36	2.1 ± 0.33
D6-MOF-74	2.6 ± 0.29	2.0 ± 0.12
D12-MOF-74	2.7 ± 0.30	1.9 ± 0.11
D30-MOF-74	2.8 ± 0.32	1.9 ± 0.11

Table S2 BET surface areas and total pore volumes of pure MOF-74 and a series of D-MOF-74 samples.

MOF	Surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})
MOF-74	1210.6	0.49
D1-MOF-74	996.7	0.41
D2-MOF-74	868.5	0.36
D4-MOF-74	812.0	0.35
D6-MOF-74	729.4	0.30
D12-MOF-74	641.5	0.28
D30-MOF-74	466.8	0.22