Supplementary Materials

Synthesis, characterization, and impact of water on the stability of postmodified Schiff base containing metal-organic frameworks

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1. Preparation of the ligands L^1 and L^2

Synthesis of dimethyl-2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate (IIa)

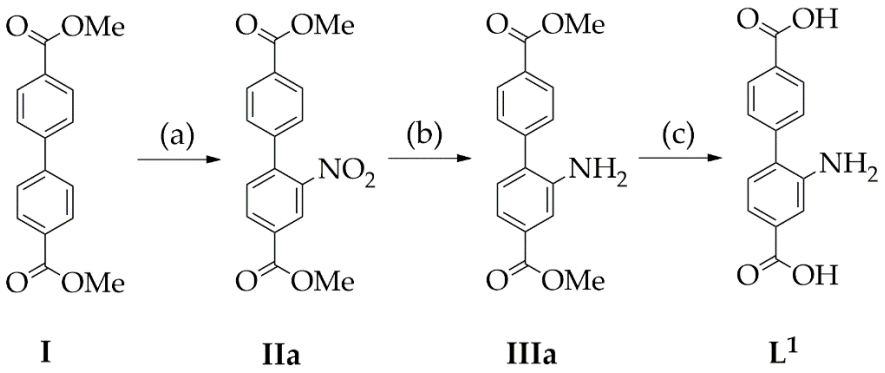
To a solution of 4 g (14.8 mmol) of biphenyl-4,4′-dicarboxylic acid dimethyl ester in 40 mL of conc. sulfuric acid was added 1 mL (14.8 mmol) of 65% HNO_3 in 3 mL of conc. H_2SO_4 dropwise at 15 °C under intense stirring. The reaction mixture was maintained at 15 – 20 °C for additional 2 h and then was carefully poured onto crushed ice. The precipitated solids were separated by filtration, washed with water, recrystallized from isopropanol, and air-dried. Yield 2.1 g, 45%. ν_{max}/cm^{-1} (ATR): 3436 w, 2956 w, 1727 s, 1620 m, 1530 s, 1483 w, 1437 m, 1348 s, 1311 s, 1289 s, 1254 m, 1195 w, 1154 w, 1118 s, 1007 w, 982 w, 906 w, 861 w, 822 w 757 m, 724 w, 703 w, 675 w, 486 w, 423 w.

Synthesis of dimethyl 2-amino-[1,1'-biphenyl]-biphenyl-4,4′-dicarboxylate (IIIa)

Dimethyl-2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate (500 mg, 1.58 mmol) dissolved in THF (14.03 mL) was added to a mixture of 1 % Pd/C catalyst (54.6 mg) in chilled MeOH (7.24 mL). Ammonium formate (454.8 mg, 7.21 mmol) was added portion-wise, and the mixture was heated at 60 °C for 2 h. After cooling to room temperature, the Pd/C was removed by filtration through Celite and MeOH and THF were removed by rotary evaporation. The resulting precipitate was taken up in EtOAc (25 mL), then washed with H_2O (3 × 25 mL), brine and dried over anhydrous Na_2SO_4. After removing the solvent by rotary evaporation, the crude product was recrystalized from EtOH. Yield 249 mg, 55%. ν_{max}/cm^{-1} (ATR): 3458 w, 3365 w, 3061 w, 2952 w, 1704 s, 1622 m, 1604 m, 1574 w, 1558 w, 1497 w, 1453 m, 1399 m, 1334 w, 1299 m, 1274 s, 1259 s, 1247 s, 1188 m, 1152 w, 1114 m, 1103 m, 1021 w, 998 m, 975 w, 908 m, 867 w, 828 w, 798 w, 779 m, 759 s, 733 w, 704 m, 637 w, 578 w, 562 w, 530 w, 475 w, 460 m, 444 w, 421 w, 414 w, 406 w.

Synthesis of 2-amino-[1,1'-biphenyl]-4,4'-dicarboxylic acid (L^1)

A mixture of dimethyl 2-aminobiphenyl-4,4′-dicarboxylate (206 mg, 0.72 mmol) in THF (4 mL) and aq. 1 M KOH (4 mL) was heated for reflux for 16 hours after cooling to room temperature the THF was removed *in vacuo* and the solution was acidified with 1M HCl. The resulting precipitate was separated by filtration washed with water then methanol and air-dried. Yield 141 mg, 76%. ^{1}H NMR (400 MHz, DMSO-d_6) 12.77 (br s, 2H, H7), 8.01 (d, J = 8.6 Hz, 2H, H6), 7.58 (d, J = 8.6 Hz, 2H, H5), 7.41 (d, J = 1.7 Hz, 1H, H4), 7.21 (dd, J = 7.8, 1.7, 7.8 Hz, 1H, H3), 7.12 (d, J = 7.8 Hz, 1H, H2), 5.16 (br s, 2H, H1). ν_{max}/cm^{-1} (ATR): 3497 w, 3405 w, 2980 w, 2833 w, 2659 w, 2544 w, 1679 s, 1622 s, 1604 s, 1574 m, 1557 m, 1517 w, 1496 w, 1436 m, 1418 m, 1401 m, 1315 s, 1289 s, 1244 s, 1184 m 1126 m 1109 m, 1018 w, 1004 m, 907 m, 896 s, 826 m, 808 m, 757 s, 732 m, 707 m, 666 m, 634 m, 573 m, 537 s 512 s, 467 s, 425 s, 406 m.



Scheme S1. Synthesis of **L**[1]. Reagents and conditions: (a) ccH_2SO_4, 65% HNO_3 (1 eq), 15 °C, 2 h; (b) Pd/C, MeOH, THF, 60 °C, 2 h (c) 1 M KOH, THF/H_2O, reflux, 16 h, then 1M HCl.

Synthesis of dimethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate (IIb)

To a solution of 4 g (14.8 mmol) of biphenyl-4,4′-dicarboxylic acid dimethyl ester in 40 mL of conc. sulfuric acid was added 2 mL (29.6 mmol) of 65% HNO_3 in 3 mL of cc H_2SO_4 dropwise at 15 °C under intense stirring. The reaction mixture was maintained at 15 – 20 °C for additional 2 h and then was carefully poured onto crushed ice. The precipitated solids were separated by filtration, washed with water, recrystallized from isopropanol, and air-dried. Yield 3.2 g, 60 %. ν_{max}/cm^{-1} (ATR): 3430 w, 3095 w, 3007 w, 2956 w, 2849 w, 1722 s, 1616 m, 1567 w, 1525 s, 1481 m, 1450 w, 1435 m, 1343 s, 1306 s, 1284 s, 1251 m, 1195 m, 1157 m, 1113 s, 1097 s, 1005 m, 983 m, 964 m, 936 m, 916 m, 906 m, 897 m, 873 m, 860 s, 823 m, 774 s, 768 s, 762 s, 753 s, 724 s, 708 m, 694 s, 676 m, 654 m, 603 m, 560 w, 515 w, 483 m, 419 m.

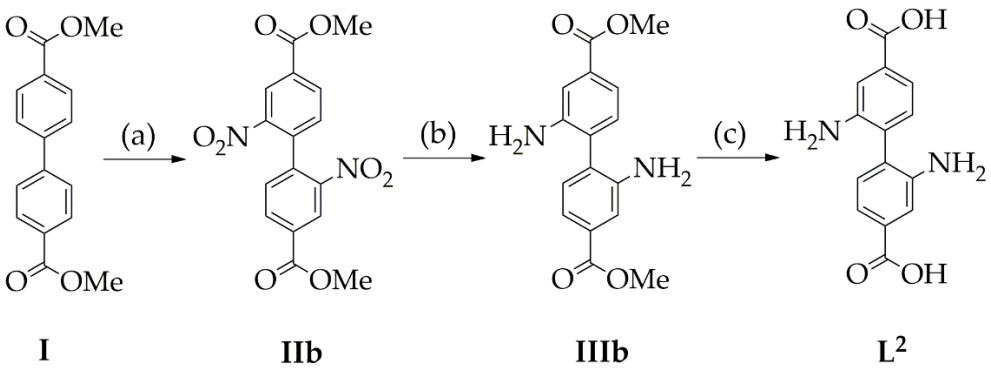
Synthesis of dimethyl 2, 2'-diamino-[1,1'-biphenyl]-4,4′-dicarboxylate (IIIb)

Dimethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate (0.5 g, 1.39 mmol) dissolved in THF (28 mL) was added to a mixture of 1 % Pd/C catalyst (109.9 mg) in chilled MeOH (14.4 mL). Ammonium formate (799.8 mg, 12.68 mmol) was added portion-wise, and the mixture was heated at 60 °C for 2 h. After cooling to room temperature, the Pd/C was removed by filtration through Celite and MeOH and THF were removed by rotary evaporation. The resulting precipitate was taken up in EtOAc (25 mL), then washed with H_2O (3 × 25 mL), brine and dried over anhydrous Na_2SO_4. After removing the solvent by rotary evaporation, the crude product was recrystallized from EtOH. Yield 358 mg, 86%. ν_{max}/cm^{-1} (ATR): 3449 w, 3358 m, 3232 w, 3065 w, 2999 w, 2949 w, 2846 w, 2100 w, 1784 w, 1696 s, 1614 m, 1564 m, 1515 w, 1495 w, 1436 m, 1418 s, 1373 w, 1297 s, 1280 m, 1233 s, 1195 s, 1158 m, 1112 s, 1045 m, 999 m, 986 m, 893 m, 829 w, 795 m, 762 s, 750 s, 731 s, 669 m, 584 m, 555 s, 523 s, 487 m, 453 s, 425 s, 406 m, 402 m.

Synthesis of 2,2'-diamino-[1,1′-biphenyl]-4,4′-dicarboxylic acid (L[2])

A mixture of dimethyl 2,2'-diamino-[1,1'-biphenyl]-4,4′-dicarboxylate (350 mg, 1.17 mmol) in THF (11.7 mL) and aq. 2 M KOH (4 mL) was heated for reflux for 16 hours. After cooling to room temperature the THF was removed by rotary evaporation and the solution was acidified with 2 M HCl. The resulting yellow precipitate was separated by filtration washed with water then methanol

and air-dried. Yield 286 mg, 90%. ^{1}H NMR (400 MHz, DMSO-d_6) 12.68 (br s, 2H, H5), 7.43 (d, J = 1.7 Hz, 2H, H4), 7.23 (dd, J = 9.5 Hz, 2H, H3), 7.06 (d, J = 7.8 Hz, 2H, H2), 4.94 (br s, 4H, H1). ν_{max}/cm^{-1} (ATR): 3421 w, 3359 w, 2798 w, 2527 w, 2285 w, 1687 m, 1615 w, 1547 m, 1506 m, 1412 m, 1389 w, 1302 m, 1281 m, 1264 m, 1228 s, 1139 w, 1113 w, 920 m, 882 m, 837 m, 786 s, 764 s, 754 s, 715 m, 660 s, 610 m, 579 m, 554 s, 458 s, 430 s.



I **IIb** **IIIb** **L^2**

Scheme S2. Synthesis of **L^2**. Reagents and conditions: (a) cc H_2SO_4, 65% HNO_3 (2 eq), 15–20 °C, 2 h; (b) Pd/C, MeOH, THF, 60 °C, 2 h (c) 2M KOH, THF/H_2O, reflux, 16 h, then 2M HCl.

2. NMR Spectra of L^1 and L^2

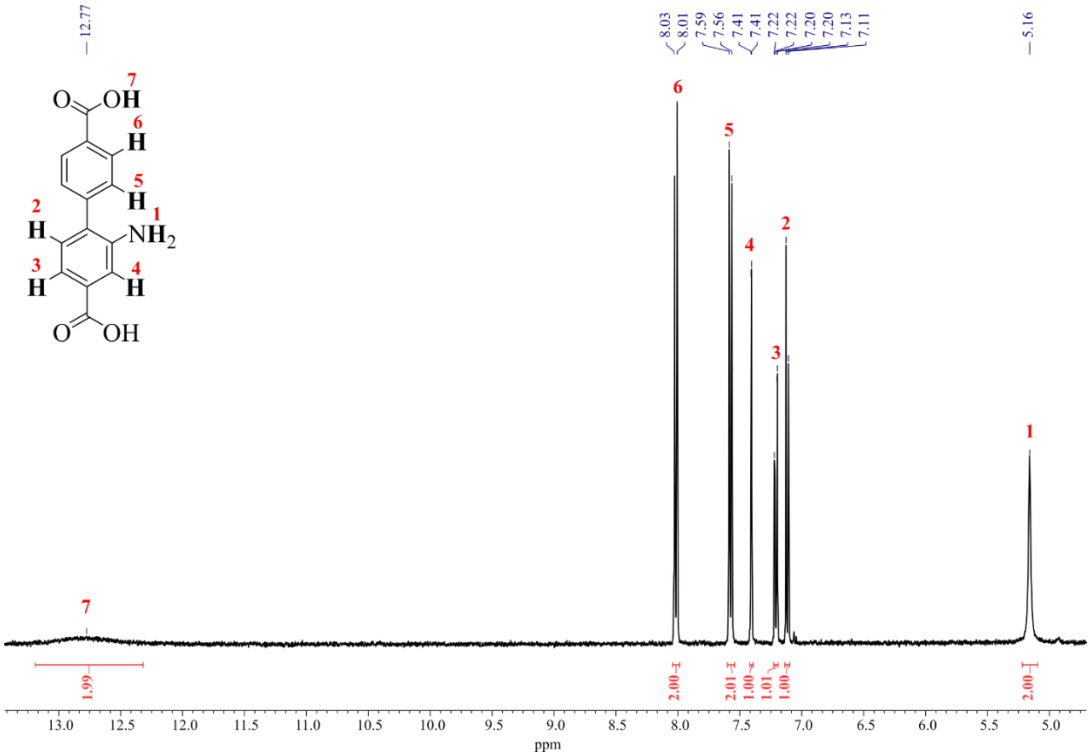


Figure S1. The ^{1}H NMR spectrum (400MHz, DMSO-d_6) of **L^1**.

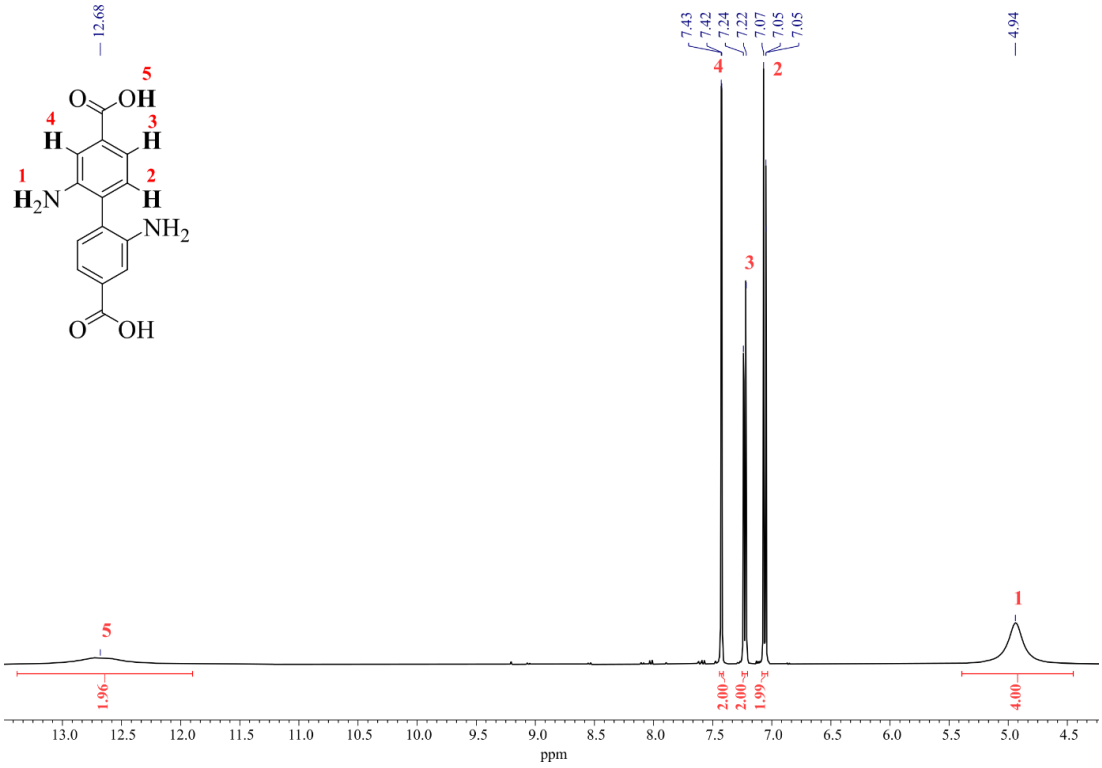


Figure S2. The ^{1}H NMR spectrum (400MHz, DMSO-d_6) of **L^2**.

3. FTIR spectra of L^1 and L^2

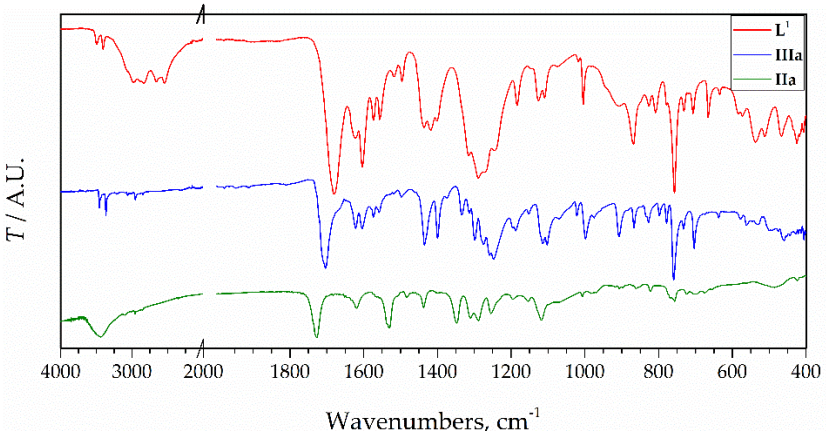


Figure S3. FT-IR Spectra of ligand (**L^1**) and intermediates (**IIa** and **IIIa**) of three-step synthetic pathway for comparison.

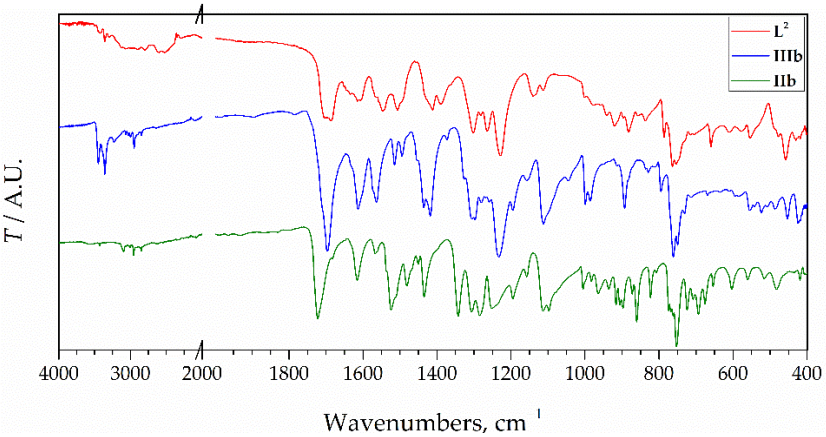


Figure S4. FT-IR Spectra of ligand (**L^2**) and intermediates (**IIb** and **IIIb**) of three-step synthetic pathway for comparison.

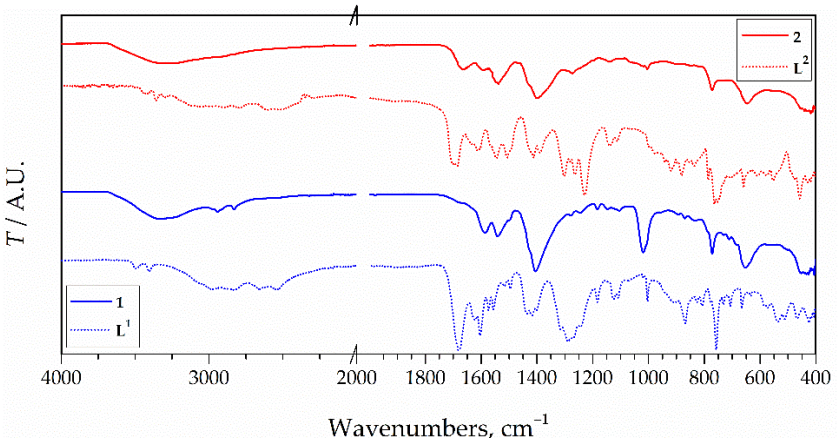


Figure S5. FT-IR spectra of **1**, **2** and corresponding ligands for comparison.

4. Thermogravimetric Analysis

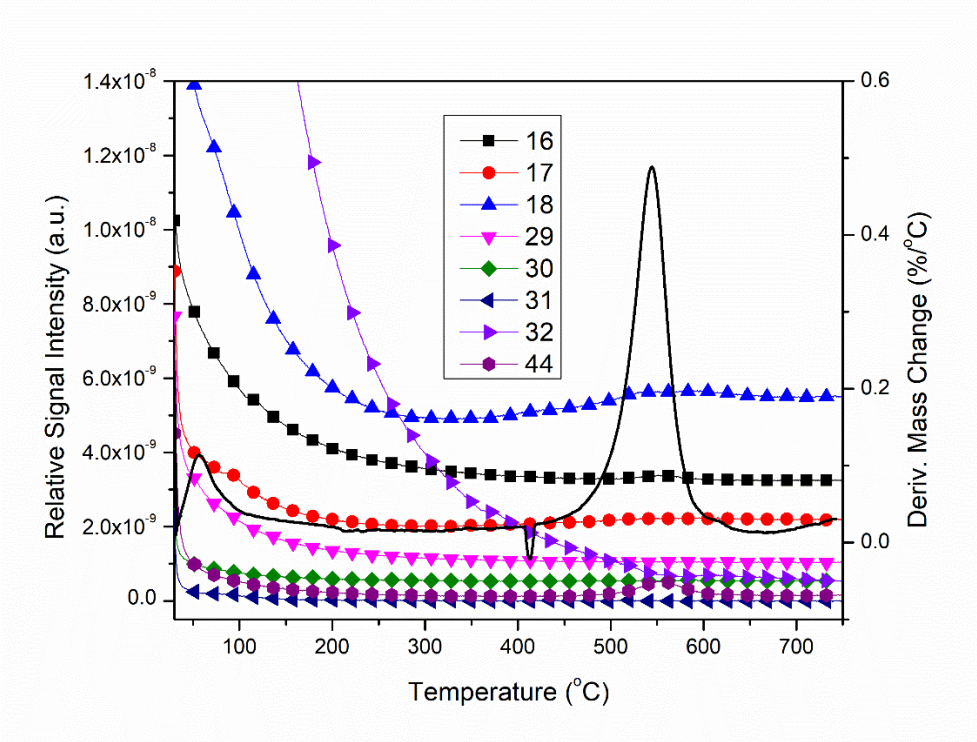


Figure S6. TG–MS signals of fragments evolved from **1a** during heating in argon.

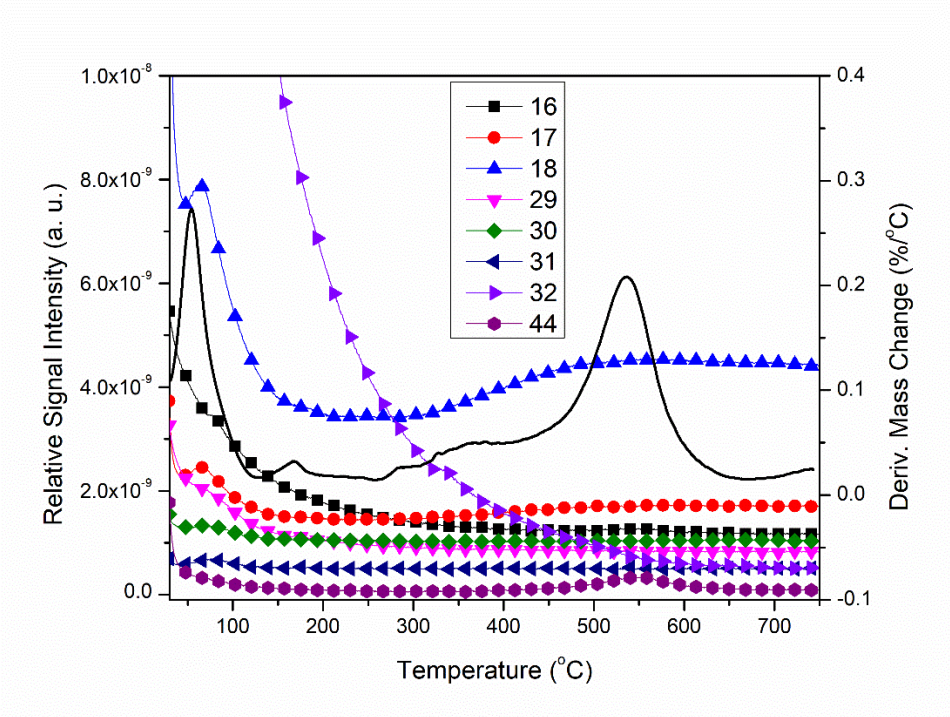


Figure S7. TG–MS signals of fragments evolved from **2a** during heating in argon.

5. Gas Adsorption Figures and Data

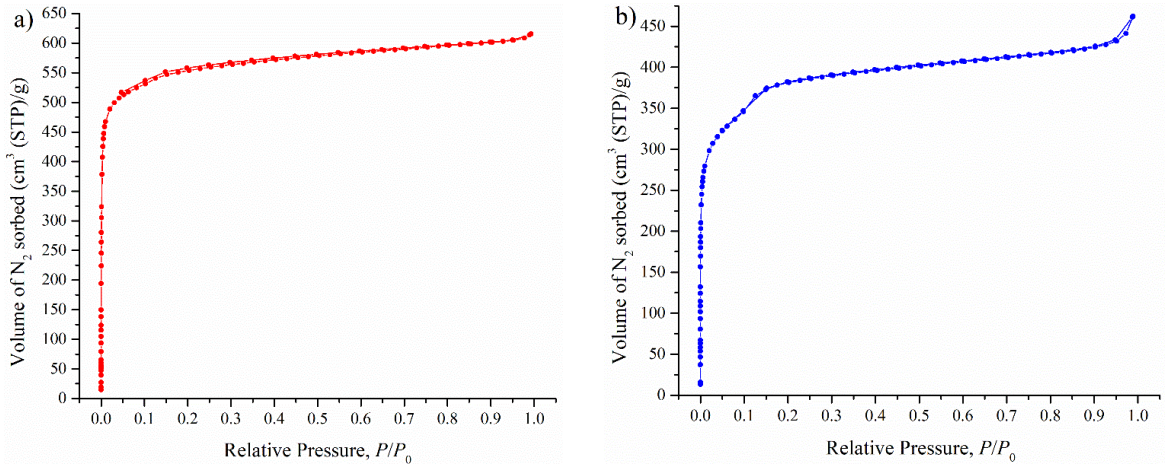


Figure S8. N_2 sorption isotherms for **1a** (a) and **2a** (b).

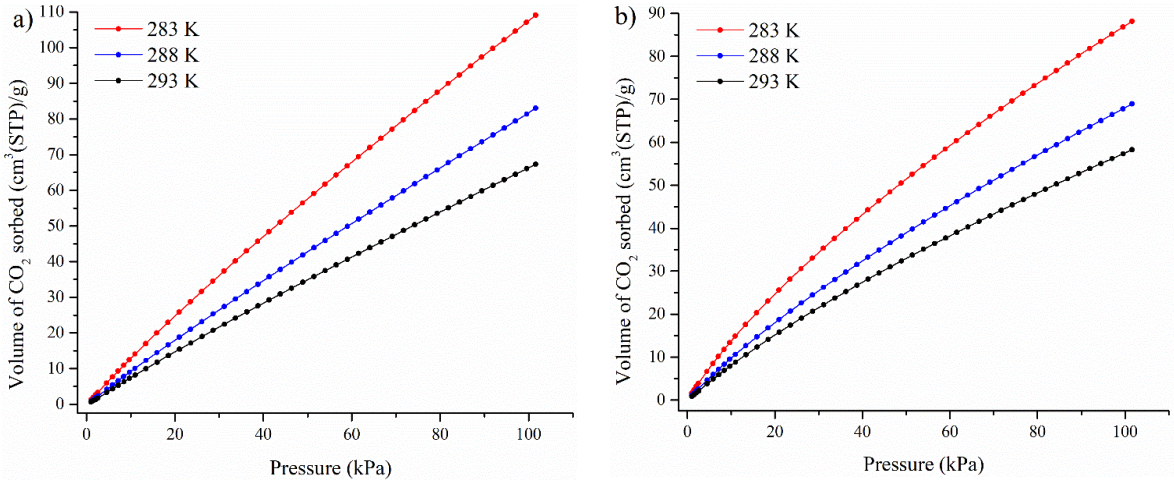


Figure S9. CO_2 sorption isotherms for **1a** (a) and **2a** (b) at 283, 288 and 293K.

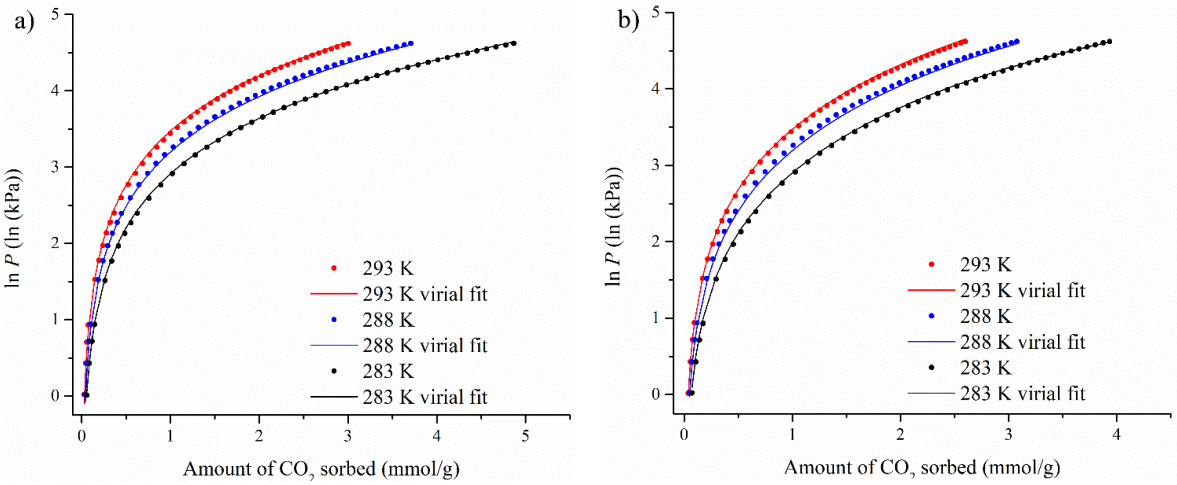


Figure S10. Virial fit of CO_2 adsorption data for **1a** (a) and **2a** (b) at 283, 288 and 293K.

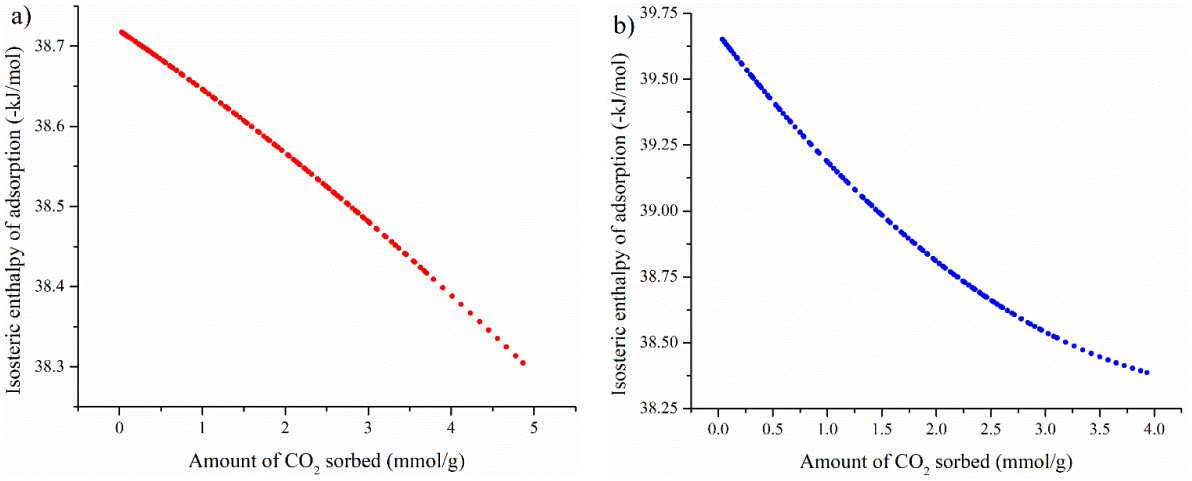


Figure S11. Isosteric enthalpy of adsorption obtained from virial fit for **1a** (a) and **2a** (b).

Table S1. gas sorption investigation data.

Parameter	**1a**	**2a**
BET surface [m^2/g]	2091	1381
Average pore size [Å]	12.7	8.2
Pore volume [cm^3/g]	0.892	0.623
CO_2 uptake at 293 K and 1 atm [cm^3/g]	67.1	58.2
Isosteric enthalpy of CO_2 adsorption [– kJ/mol]	38.6	39.0

Table S2. Obtained virial parameters.

Parameter	**1a**	**2a**
A_0	– 4656.86	– 4771.36
A_1	8.4240	64.7921
A_2	0.3742	– 6.4849
B_0	19.3296	19.5485

6. UV-Vis spectra

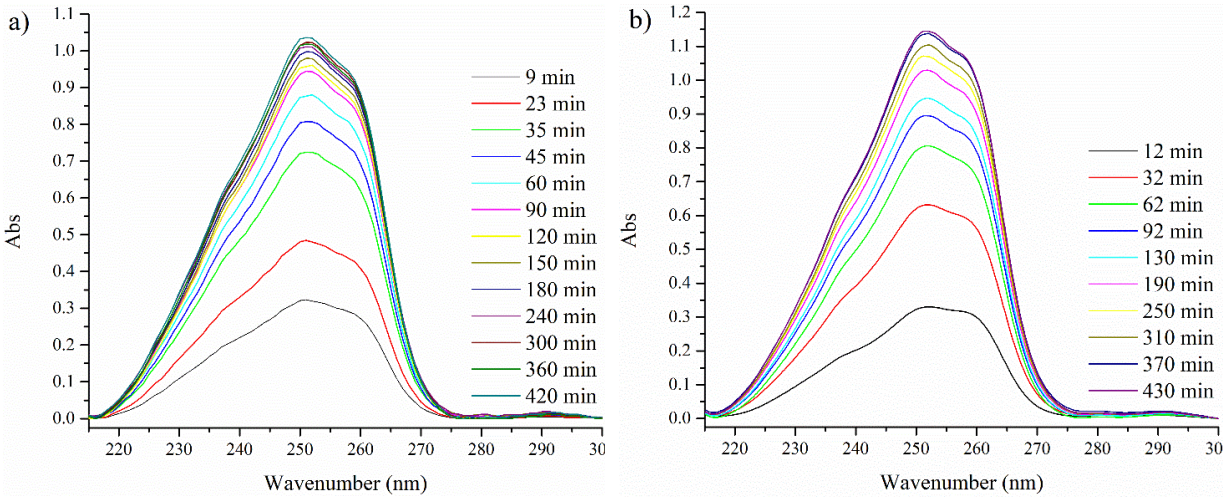


Figure S12. UV spectra of water samples containing **1a** (a) and **2a** (b) collected at different time intervals.

7. EDS spectra and SEM micrographs of 1a and 2a

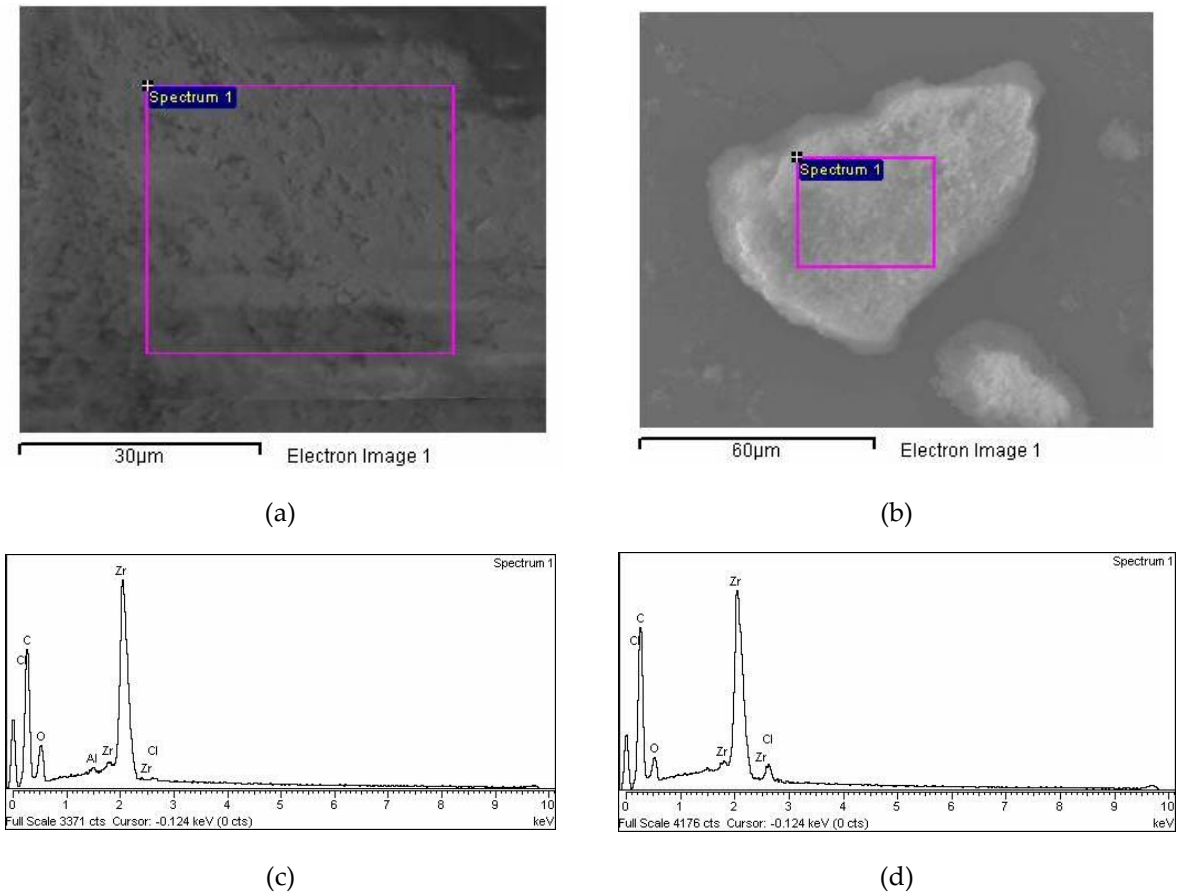


Figure S13. Selected surfaces of **1a** (a) and **2a** (b) for EDS analysis and their spectra (c and d).

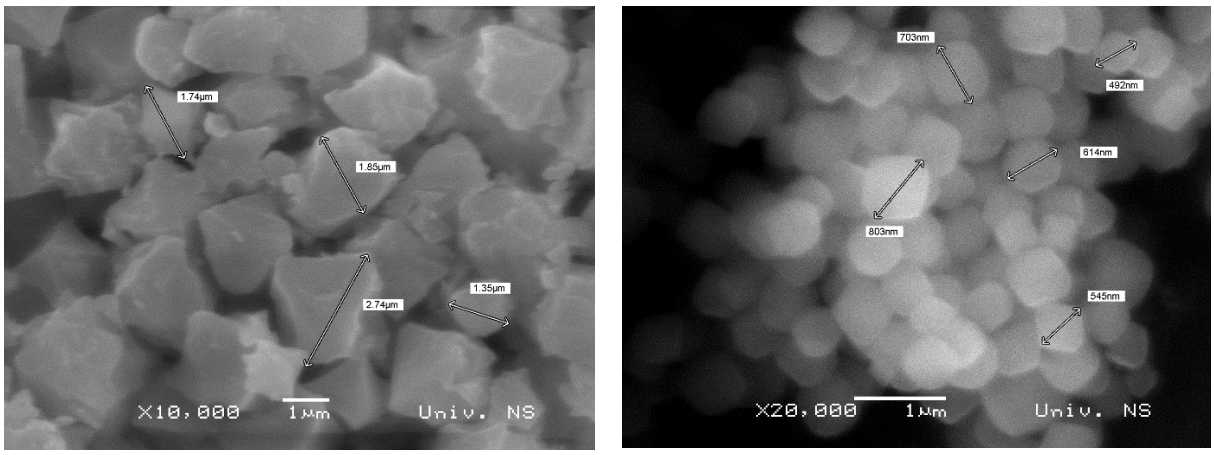


Figure S14. SEM micrographs of **1a** (a) and **2a** (b) that show the variety of crystal sizes.

8. PXRD of 1a and 2a after exposure to water

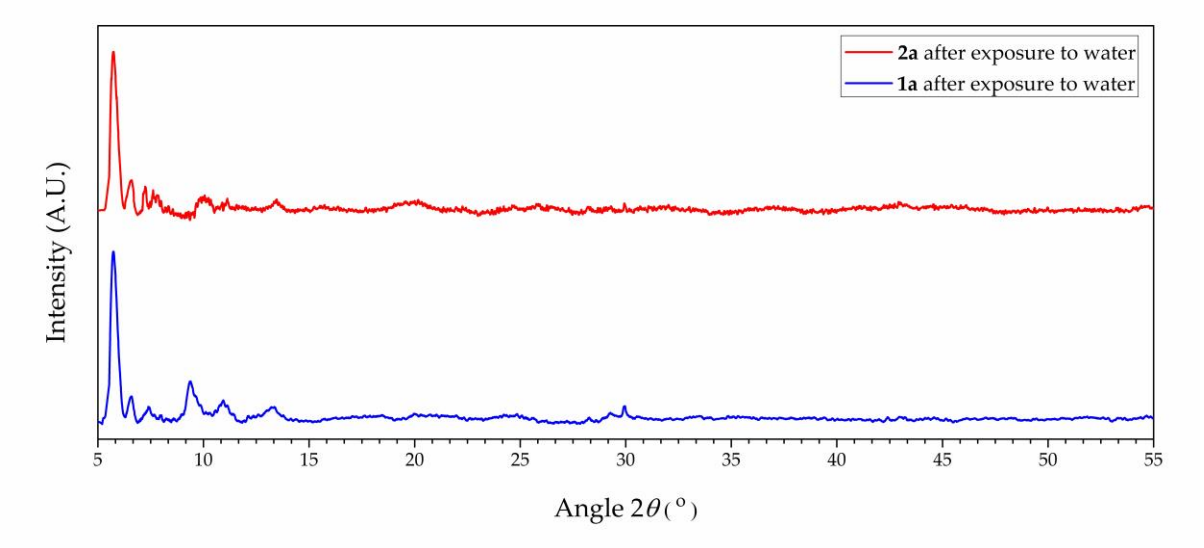


Figure S15. X-ray powder diffraction data for **1a** and **2a** after exposure to water.