Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATIONS

Upscale study of a binary pillared layered MOF for hydrocarbon gas storage and separation

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General information

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Materials

All chemicals were used as received without any further purification. 2,3-pyrazinedicarboxylic acid, pyrazine, copper nitrate hemipentahydrate and copper perchlorate were purchased from Aldrich. Copper hydroxide and sodium hydroxide were purchased Wako pure chemicals. Ethanol (EtOH) and other materials were purchased from either Nacalai Tesque or Wako pure chemicals.

General

Thermogravimetric analyses (TGA) were performed on a Rigaku model Thermo plus EVO with a heating rate of 5 °C/min under N_2 flow. Powder X-ray diffraction data were collected at ambient temperature with a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation. Gas adsorption experiments were carried at 298 K using BELSORP-mini volumetric gas adsorption instrument equipped with a thermostatic bath. CPL-1 powder (*ca.* 70mg) was introduced in a glass sample cell and activated on a BELPREP-vac II under vacuum (≤ 10^{-1} Pa) at 393 K for 12 h prior to acetylene volumetric gas adsorption at 298K using BELSORP-mini. High-pressure adsorption experiments were performed using BEL-HP (MicrotracBEL, Japan) gas adsorption instrument with adsorption temperatures maintained by custom made thermostatic bath. A mass of 200 mg of CPL-1 is required to performed high pressure measurements.

Stability tests

An exact mass of the product (100 mg) is placed in a sealed flask with a large excess of solvent. Different temperatures are applied depending of the solvent boiling point and the temperature used for shaping processes. Stirring is required for all the experiment time to homogenize the mixture. After cooling at room temperature, the product is washed and collected by filtration. After drying under reduced pressure, the product's mass is checked and characterization measurements (PXRD, TGA, adsorption isotherms…) are studied to confirm or not the stability of the product.

Thermogravimetric analysis (TGA)

The TG analyses of CPL-1 material showed a continuous weight loss with increase in temperature until 100°C, corresponding to the loss of guest solvent molecules. The decomposition of CPL-1 beyond 250 °C is confirmed by the sharp weight loss in the TGA curves.

Volumetric acetylene (C_2H_2) gas adsorption at 298K

The adsorption profile of CPL-1 for acetylene showed a flexible behavior at the low pressures (10kPa) corresponding to the adaptation of the acetylene molecule by the material. The maximum capacity of acetylene at 298K for CPL-1 is 42 $cm^3.g^{-1}$.

Field-emission scanning electron microscope analysis (FESEM)

Microstructures of the as-synthesized MOF crystals were observed under a Hitachi SU5000 field-emission scanning electron microscope (FESEM). Samples were sonicated for 1h in acetone solution before spin coating on conductive copper tape to avoid aggregation.

Synthetic procedure

Best conditions with the use of base

$Cu(OH)_2$ (51.2 mmol, 1eq), pyrazine (51.2 mmol, 1 eq) and 2,3-pyrazine-dicarboxylic acid (51.2 mmol, 1 eq) were mixed in 100 mL of water. pH is adjusted with a solution of NaOH 2N to pH = 6.4. A clear blue precipitate is formed after 30 min at room temperature. The crude solid is collected via centrifugation and washed with 2 x 40 mL of water and 3 x 40 mL of EtOH. The blue powder is dried under vacuum at 50°C overnight. (Yield = 95%). All the other synthetic procedures follow the same addition process and the same reaction treatment.

Best conditions with the use of an excess of pillar

Metal salt (1eq), pyrazine (>12eq) and 2,3-pyrazine-dicarboxylic acid (1eq) were mixed in water. A clear blue precipitate is formed after 30 min at room temperature. The crude solid is collected via centrifugation and washed with 2 x 40 mL of water and 3 x 40 mL of EtOH. The blue powder is dried under vacuum at 50°C overnight. (Yield = 95%).

All the other synthetic procedures follow the same addition process and the same reaction treatment.

Synthesis of **CPL-2** material

The first synthesis was done by the use of base (NaOH, 2N) to adjust the pH solution at 6.4. $Cu(OH)_2$ (1 g, 10.2 mmol), 2,3-pyrazinedicarboxylic acid (1.72 g, 10.2 mmol) and bipyridine (0.8 g, 5.12 mmol) were mixed in water ([Cu(II)] = 0.5M). A solution of NaOH (2N) was added to adjust the pH solution to 6.4. After 8 hours, a blue precipitate was collected via centrifugation and washed with 3 x 20 mL of EtOH. **CPL-2** material was dried under vacuum overnight, yield 96%.

The second synthesis involves an excess of 4,4´-bipyridine ligand. $Cu(OH)_2$ (1 g, 10.2 mmol), 2,3-pyrazinedicarboxylic acid (1.72 g, 10.2 mmol) and bipyridine (4 g, 26 mmol) were mixed in water ([Cu(II)] = 0.5M). After 8 hours, a blue precipitate was collected via centrifugation and washed with 3 x 20 mL of EtOH. **CPL-2** material was dried under vacuum overnight, yield 95%.

Table S1. List of all the combinations used for the CPL-1 synthesis

Entry	Metal source	Pyrazine	Concentration	Base (NaOH)	Reaction time	Desired product
1	$Cu(ClO_4)_2.6H_2O$	12.5 eq	0.01 M	2 eq	12 h	Yes 95-100%
2	$Cu(ClO_4)_2.6H_2O$	12.5 eq	0.33 M	2 eq	12 h	Yes 95-100%
3	$Cu(ClO_4)_2.6H_2O$	12.5 eq	0.5 M	2 eq	12 h	Yes 95-100%
4	$Cu(ClO_4)_2.6H_2O$	12.5 eq	0.01 M	2 eq	1 h	Yes 95-100%
5	$Cu(ClO_4)_2.6H_2O$	12.5 eq	0.33 M	2 eq	1 h	Yes 95-100%
6	$Cu(ClO_4)_2.6H_2O$	12.5 eq	0.5 M	2 eq	1 h	Yes 95-100%
7	$Cu(ClO_4)_2.6H_2O$	8 eq	0.5 M	2 eq	1 h	Yes

						95-100%
8	$Cu(ClO_4)_2.6H_2O$	6 eq	0.5 M	2 eq	1 h	Yes 95-100%
9	$Cu(ClO_4)_2.6H_2O$	4 eq	0.5 M	2 eq	1 h	Yes 95-100%
10	$Cu(ClO_4)_2.6H_2O$	2 eq	0.5 M	2 eq	1 h	Yes 95-100%
11	$Cu(ClO_4)_2.6H_2O$	equimolar	0.5 M	2 eq	1 h	Yes 95-100%
12	$Cu(ClO_4)_2.6H_2O$	Excess (>20 eq)	0.5 M	No base	1 h	Failed
13	$Cu(NO_3)_2.2.5H_2O$	12.5 eq	0.01M	2 eq	12 h	Yes 95-100%
14	$Cu(NO_3)_2.2.5H_2O$	12.5 eq	0.33M	2 eq	1 h	Yes 95-100%
15	$Cu(NO_3)_2.2.5H_2O$	12.5 eq	0.5 M	2 eq	1 h	Yes 95-100%
16	$Cu(NO_3)_2.2.5H_2O$	8 eq	0.5 M	2 eq	1 h	Yes 95-100%
17	$Cu(NO_3)_2.2.5H_2O$	6 eq	0.5 M	2 eq	1 h	Yes 95-100%
18	$Cu(NO_3)_2.2.5H_2O$	4 eq	0.5 M	2 eq	1 h	Yes 95-100%
19	$Cu(NO_3)_2.2.5H_2O$	2 eq	0.5 M	2 eq	1 h	Yes 95-100%
20	$Cu(NO_3)_2.2.5H_2O$	equimolar	0.5 M	2 eq	1 h	Yes 95-100%
21	$Cu(NO_3)_2.2.5H_2O$	Excess (>20 eq)	0.5 M	No base	1 h	Yes 95-100%
22	$Cu(OH)_2$	12.5 eq	0.01M	2 eq	12 h	Yes 95-100%
23	$Cu(OH)_2$	12.5 eq	0.33M	2 eq	1 h	Yes 95-100%
24	$Cu(OH)_2$	12.5 eq	0.5 M	2 eq	1 h	Yes 95-100%
25	$Cu(OH)_2$	8 eq	0.5 M	2 eq	1 h	Yes 95-100%
26	$Cu(OH)_2$	6 eq	0.5 M	2 eq	0.5 h	Yes 95-100%
27	$Cu(OH)_2$	4 eq	0.5 M	2 eq	0.5 h	Yes 95-100%
28	$Cu(OH)_2$	2 eq	0.5 M	2 eq	0.5 h	Yes 95-100%
29	$Cu(OH)_2$	equimolar	0.5 M	Adjustment	0.5 h	Yes

				at pH = 6.4		95-100%
30	$Cu(OH)_2$	equimolar	0.5 M	2 eq	0.5 h	Yes 95-100%
31	$Cu(OH)_2$	Excess (>20 eq)	0.5 M	No base	0.5 h	Yes 95-100%
32	$Cu(OH)_2$	2 eq	0.5 M	2 eq	0.1 h	Failed

- **Figures S1-S3** - Impact of the **<u>metal source</u>** on the CPL-1 synthesis

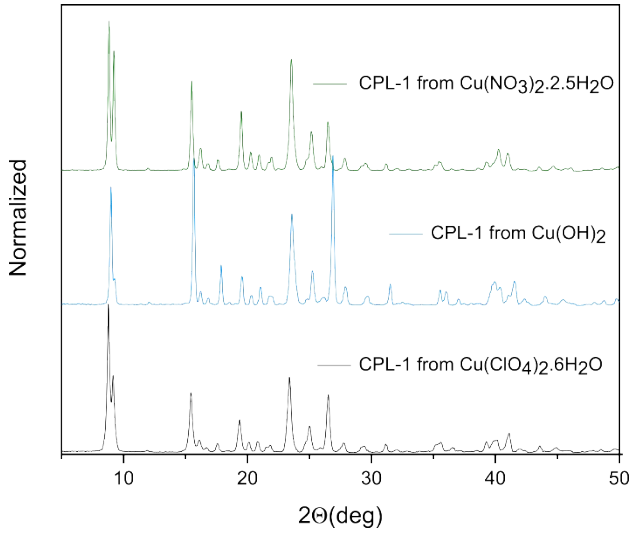


Figure S1. Comparison of PXRD patterns of as-synthesized **CPL-1** materials prepared from different metal sources: $Cu(ClO_4)_2.6H_2O$ (black), $Cu(OH)_2$ (blue) and $Cu(NO_3)_2.6H_2O$ (green).

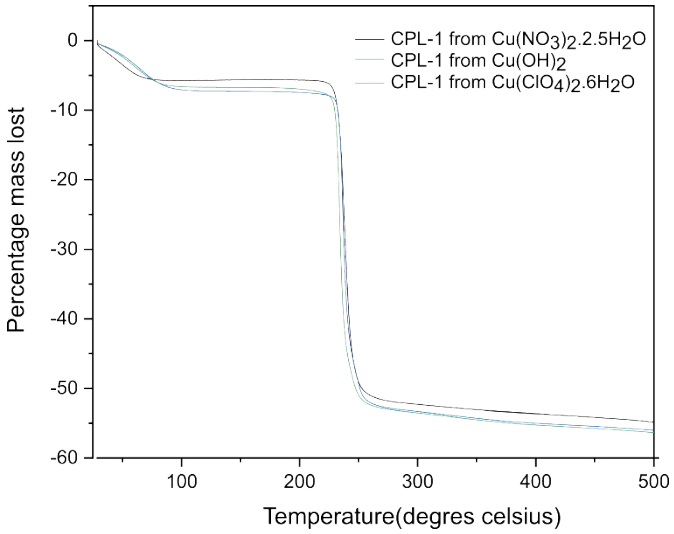


Figure S2. TGA of as-synthesized **CPL-1** materials prepared from different metal sources: $Cu(ClO_4)_2.6H_2O$ (black), $Cu(OH)_2$ (blue) and $Cu(NO_3)_2.6H_2O$ (green).

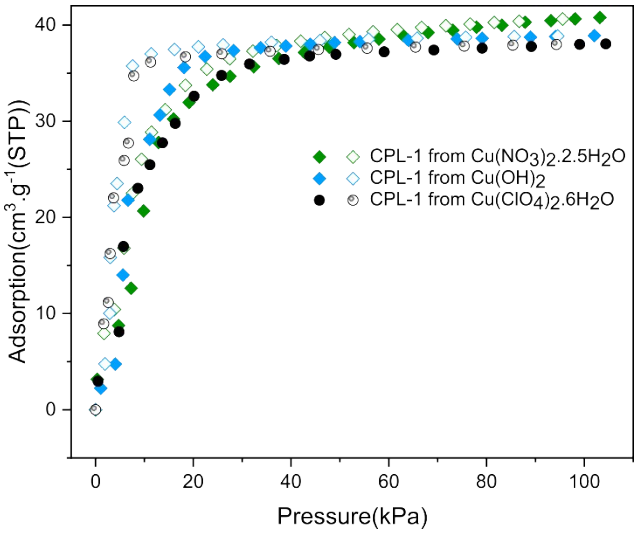


Figure S3. C_2H_2 gas adsorption/desorption isotherms of **CPL-1** materials at 298K prepared from different metal sources: $Cu(ClO_4)_2.6H_2O$ (black), $Cu(OH)_2$ (blue) and $Cu(NO_3)_2.6H_2O$ (green).

- **Figures S4-S6** Impact of the **<u>pyrazine equivalent reduction</u>** on the CPL-1 synthesis

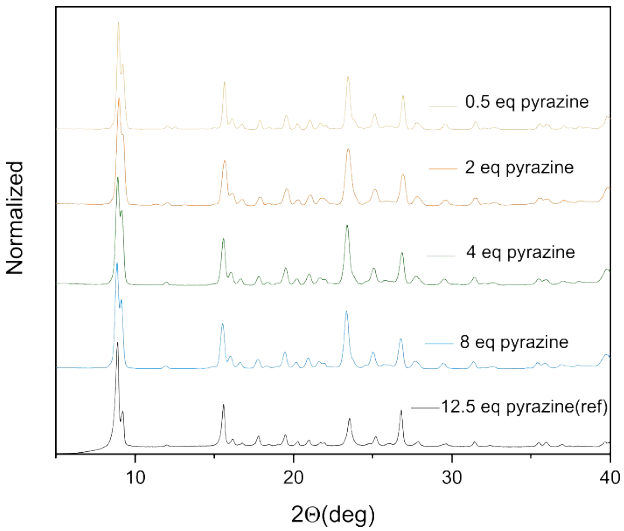


Figure S4. Comparison of PXRD patterns of as-synthesized **CPL-1** materials prepared with different equivalent amount of pyrazine pillar ligand: 12.5eq (black), 8eq (blue), 4eq (green), 2eq (orange) and 0.5eq (yellow).

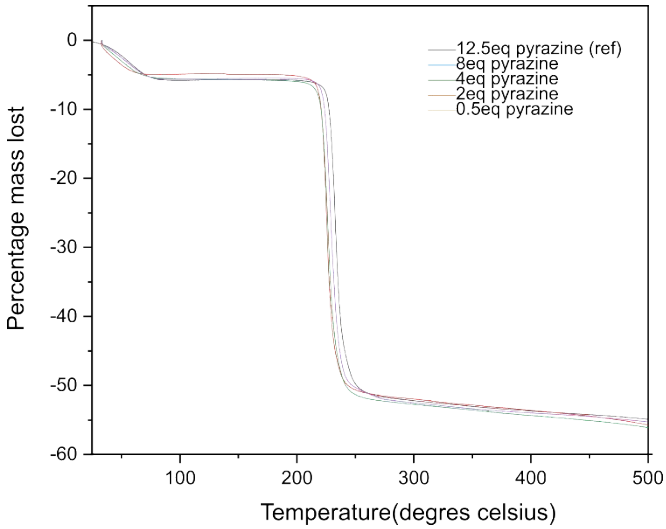


Figure S5. TGA of as-synthesized **CPL-1** materials prepared with different equivalent amount of pyrazine pillar ligand: 12.5eq (black), 8eq (blue), 4eq (green), 2eq (orange) and 0.5eq (yellow).

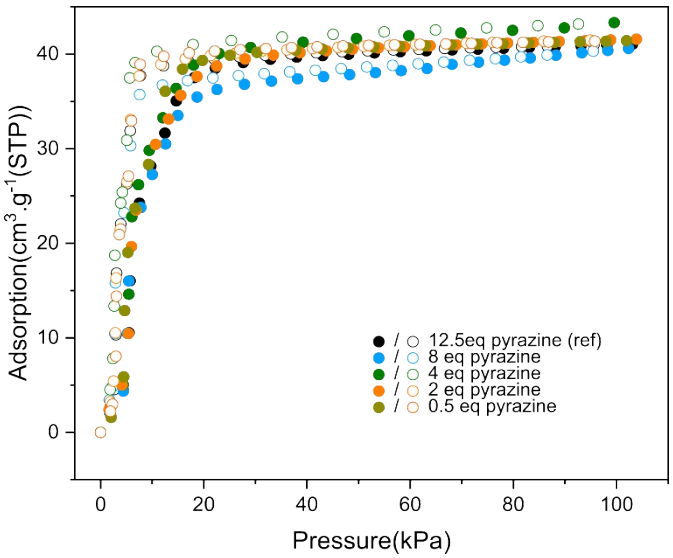


Figure S6. C_2H_2 gas adsorption/desorption isotherms of **CPL-1** materials prepared with different equivalent amount of pyrazine pillar ligand: 12.5eq (black), 8eq (blue), 4eq (green), 2eq (orange) and 0.5eq (yellow).

- **Figures S7**&**S8** Impact of the **base** on the **CPL-1** synthesis

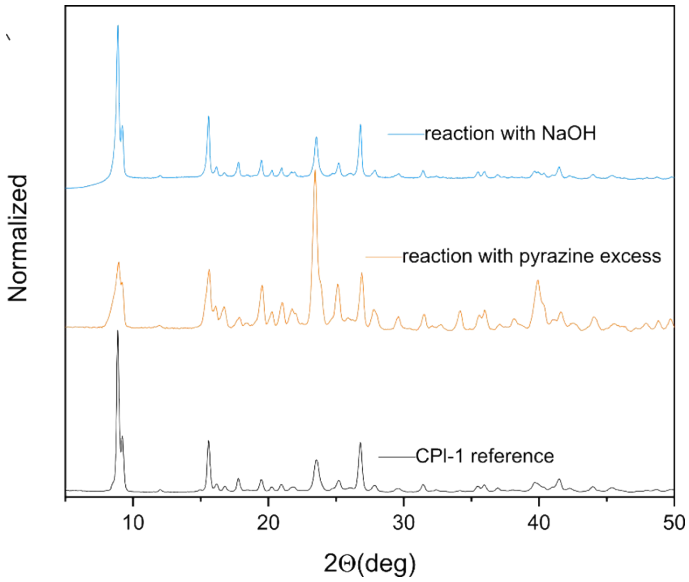


Figure S7. Comparison of PXRD patterns of **CPL-1** materials prepared with NaOH (blue) and excess of pyrazine (orange). PXRD pattern of CPL-1 reference is noted in black.

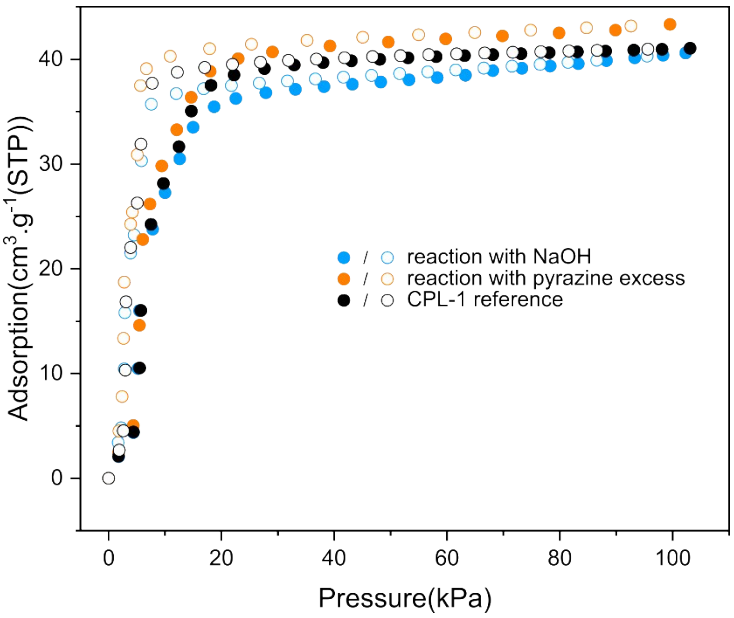


Figure S8. C_2H_2 gas adsorption/desorption isotherms of **CPL-1** materials prepared with base (blue) or with excess of pyrazine (orange). CPL-1 reference is noted in black.

- **Figures S9&S10** Impact of the **<u>water quality</u>** on the **CPL-1** synthesis

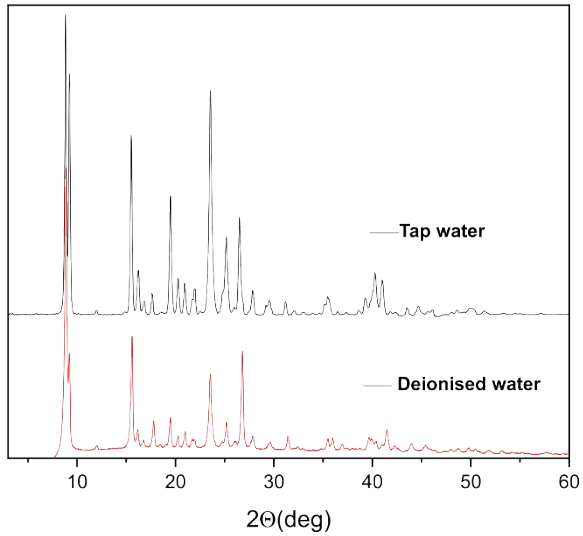


Figure S9. Comparison of PXRD patterns of **CPL-1** materials synthesized with deionized water (red) and tap water (black).

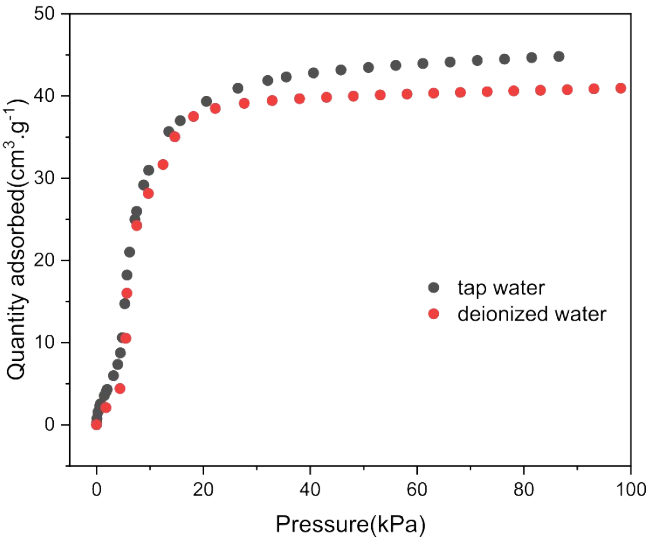


Figure S10. C_2H_2 gas adsorption isotherms of **CPL-1** materials prepared with tape water (black) or with deionized water (red).

- **Figures S11-S13** Impact of the **<u>concentration</u>** on the **CPL-1** synthesis

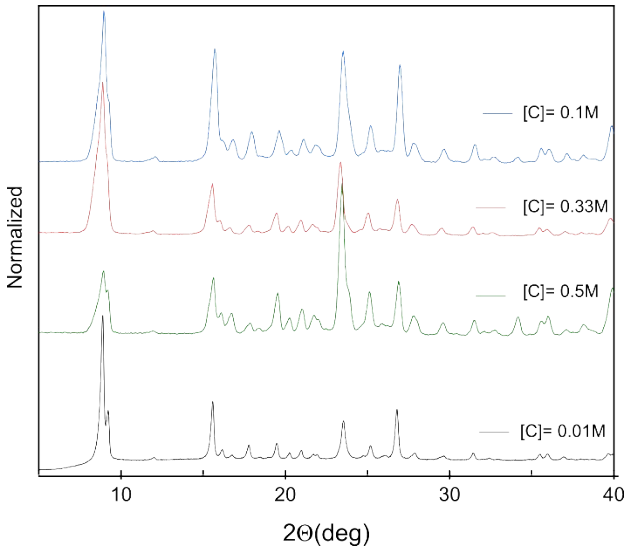


Figure S11. Comparison of PXRD patterns of as-synthesized **CPL-1** materials prepared at different concentrations: [C]=0.01M (black), [C]=0.5M (green), [C]=0.33M (red) and [C]=0.1M (blue).

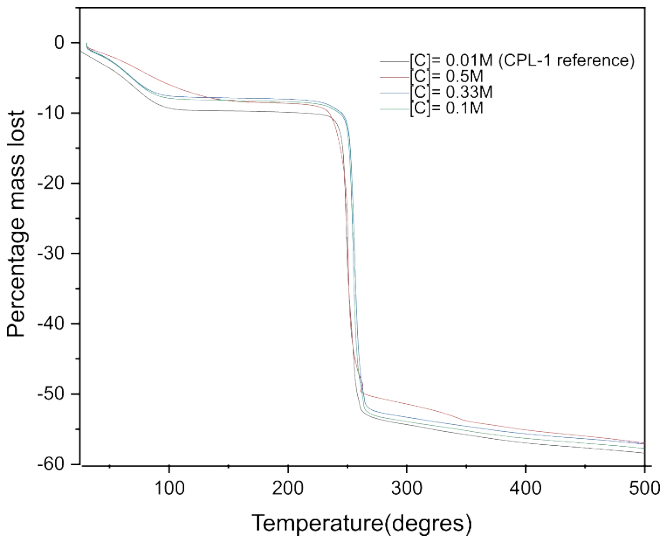


Figure S12. TGA of as-synthesized **CPL-1** materials prepared at different concentrations: [C]=0.01M (black), [C]=0.5M (green), [C]=0.33M (red) and [C]=0.1M (blue).

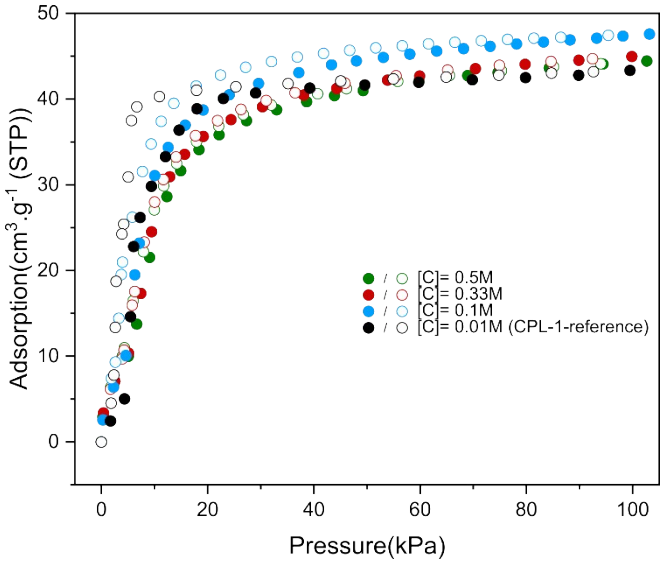
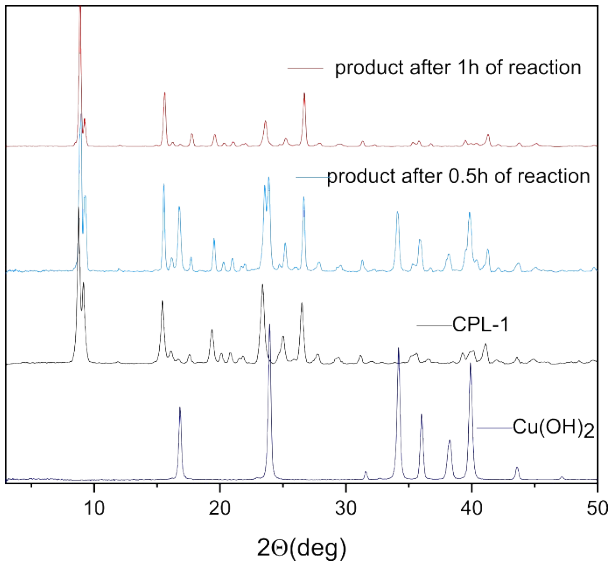


Figure S13. C_2H_2 gas adsorption/desorption isotherms of **CPL-1** materials prepared at different concentrations: [C]=0.01M (black), [C]=0.5M (green), [C]=0.33M (red) and [C]=0.1M (blue).

- **Figures S14&S15** Impact of the **reaction time** on the **CPL-1** synthesis



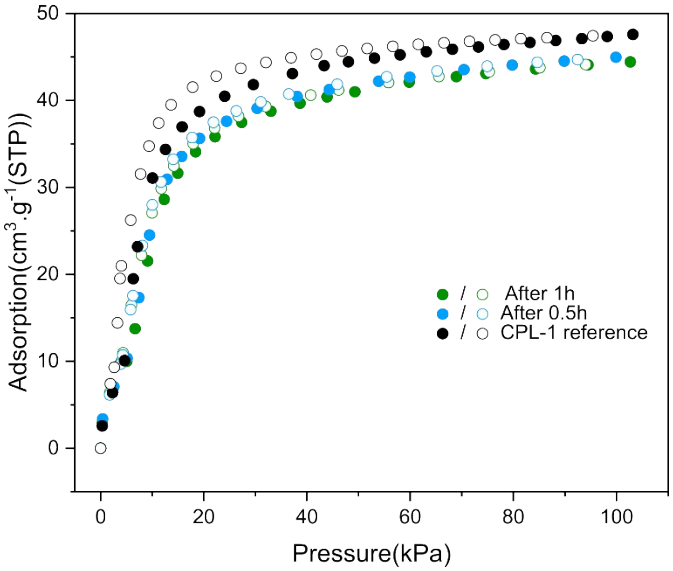


Figure S14. Comparison of PXRD patterns of **CPL-1** materials at different reaction time: 0.5h (red), 1h (blue), CPL-1 reference (black) $Cu(OH)_2$ (navy).

Figure S15. C_2H_2 gas adsorption/desorption isotherms of **CPL-1** materials at different reaction time: 0.5h (red), 1h (blue), **CPL-1** reference (black).

- **Figures S16**&**S17** Field-emission scanning electron spectroscopy (FESEM) of **CPL-1** materials and size distribution

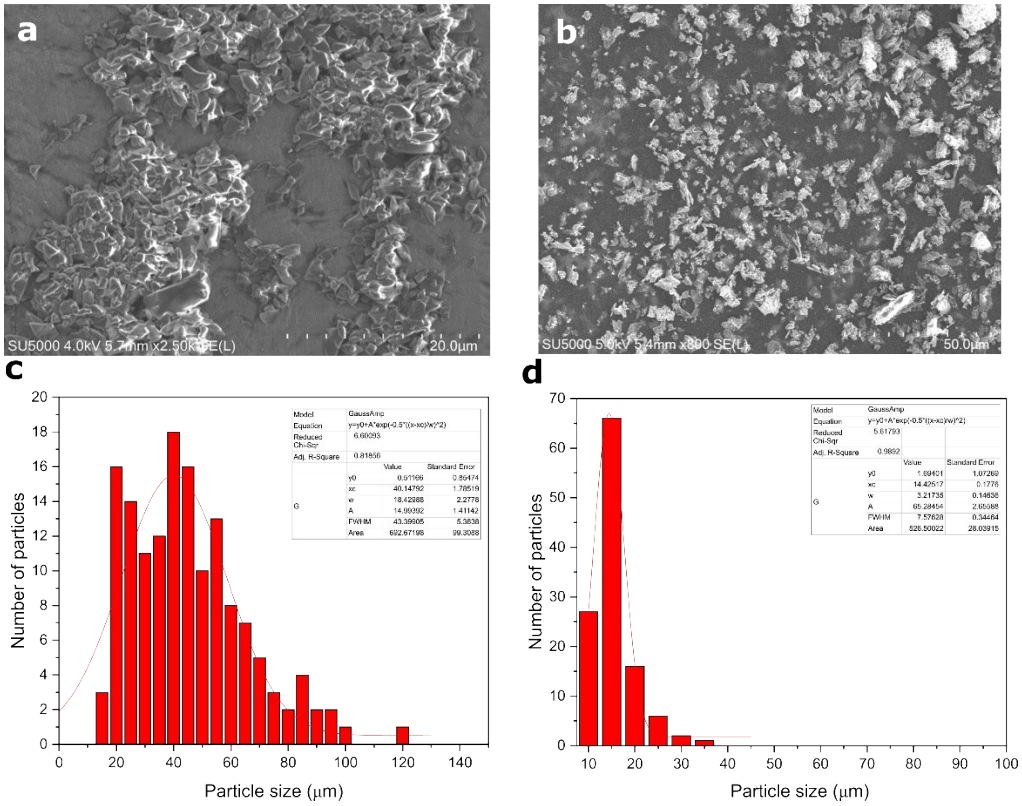


Figure S16. Top: FESEM images of **CPL-1** material synthesized with $Cu(OH)_2$ and without base (a) before sonication and (b) after sonication. Bottom: size distribution of **CPL-1** particles (c) before sonication and (d) after sonication. The size distributions were obtained from the measurement of around 160 particle sizes, using imageJ software, from the FESEM images of each sample.

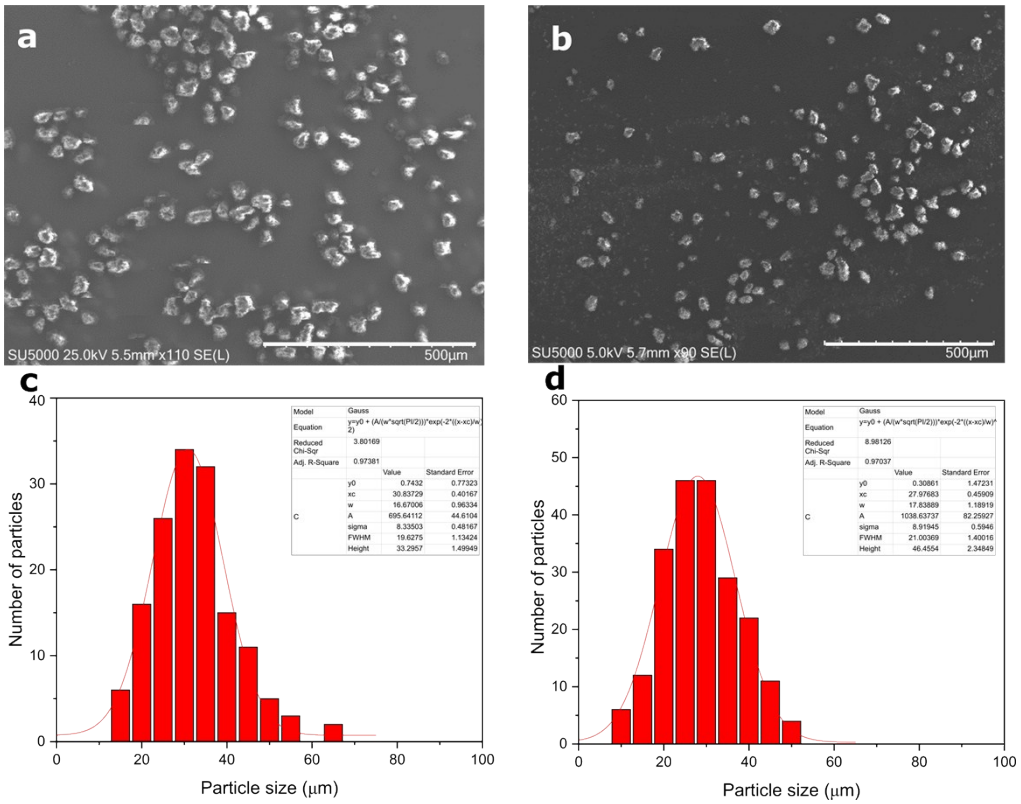


Figure S17. Top: FESEM images of **CPL-1** material synthesized with $Cu(NO_3)_2.2.5H_2O$ and with base (a) before sonication and (b) after sonication. Bottom: size distribution of **CPL-1** particles (c) before sonication and (d) after sonication. The size distributions were obtained from the measurement of around 160 particle sizes, using imageJ software, from the FESEM images of each sample (scale 500 μm).

- **Figures S18-S21 <u>Stability tests</u>** on the CPL-1 synthesis

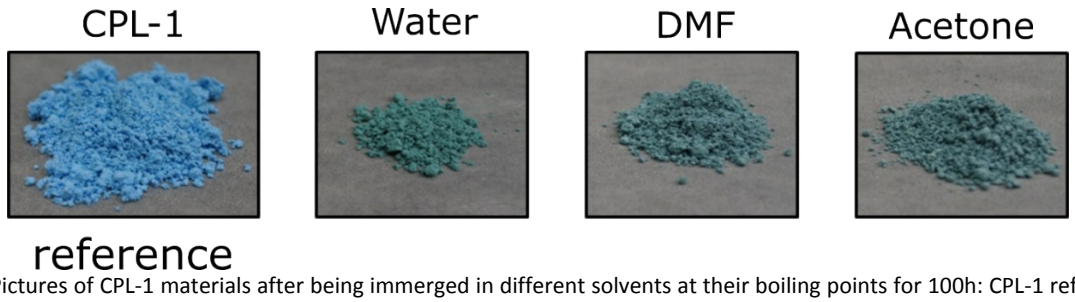


Figure S18. Pictures of CPL-1 materials after being immerged in different solvents at their boiling points for 100h: CPL-1 reference, water, DMF and acetone.

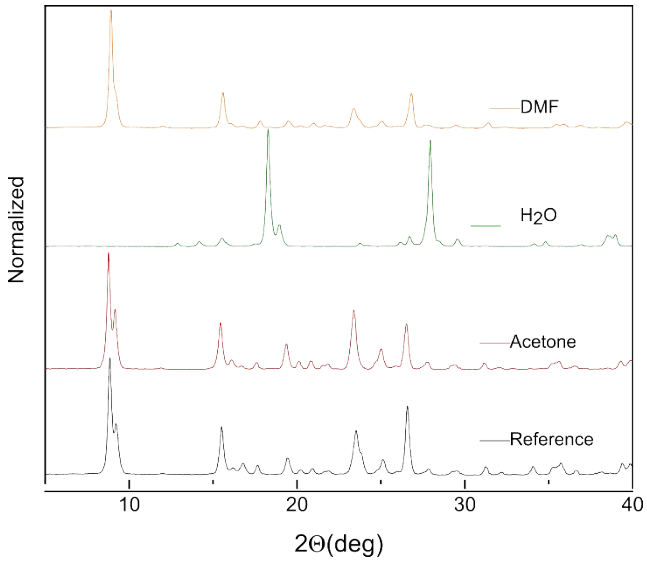


Figure S19. Comparison of PXRD patterns of **CPL-1** materials immerged in different solvents at their boiling points for 100h: CPL-1 reference (black), acetone (red), water (green) and DMF (orange).

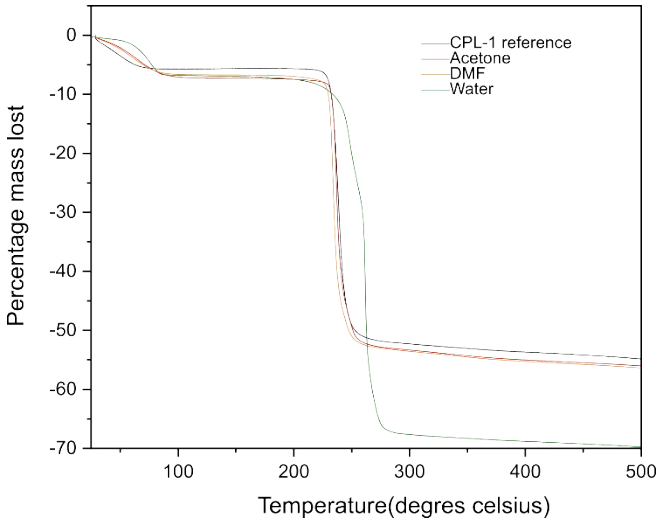


Figure S20. TGA of **CPL-1** materials immerged in different solvents at their boiling points for 100h: CPL-1 reference (black), water (green), DMF (orange) and acetone (red).

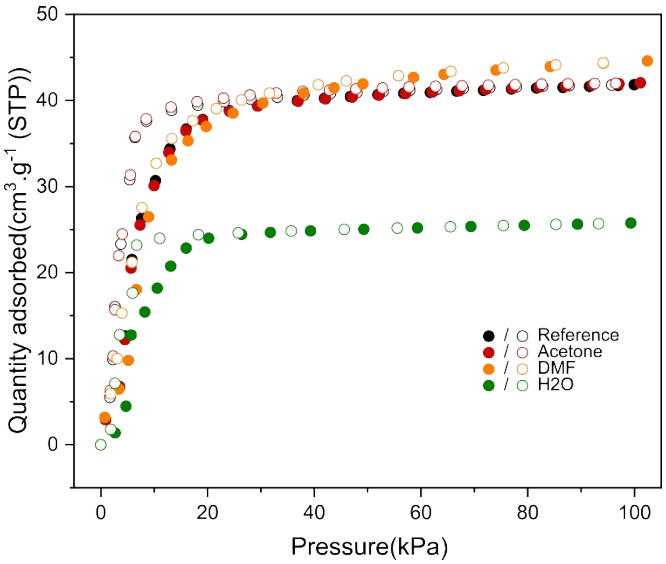


Figure S21. C_2H_2 gas adsorption/desorption isotherms of **CPL-1** materials immerged in different solvents at their boiling points for 100h: CPL-1 reference (black), water (green), DMF (orange) and acetone (red).

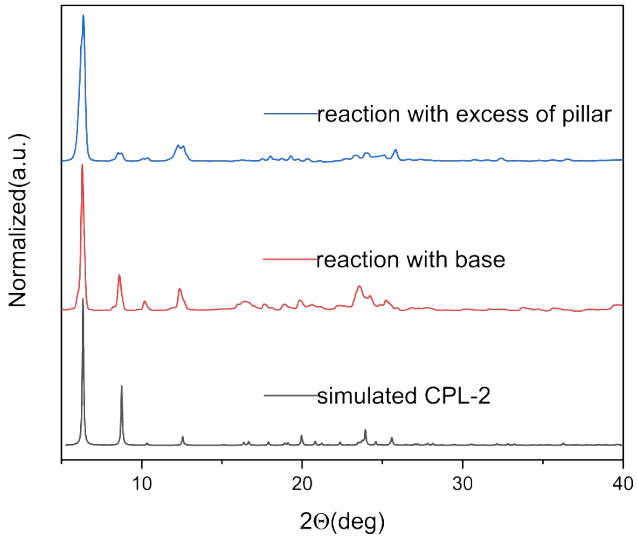


Figure S22. Comparison of PXRD patterns of simulated **CPL-2** (black) material and **CPL-2** material synthesized with base (red) or with an excess of pillared ligand (blue)

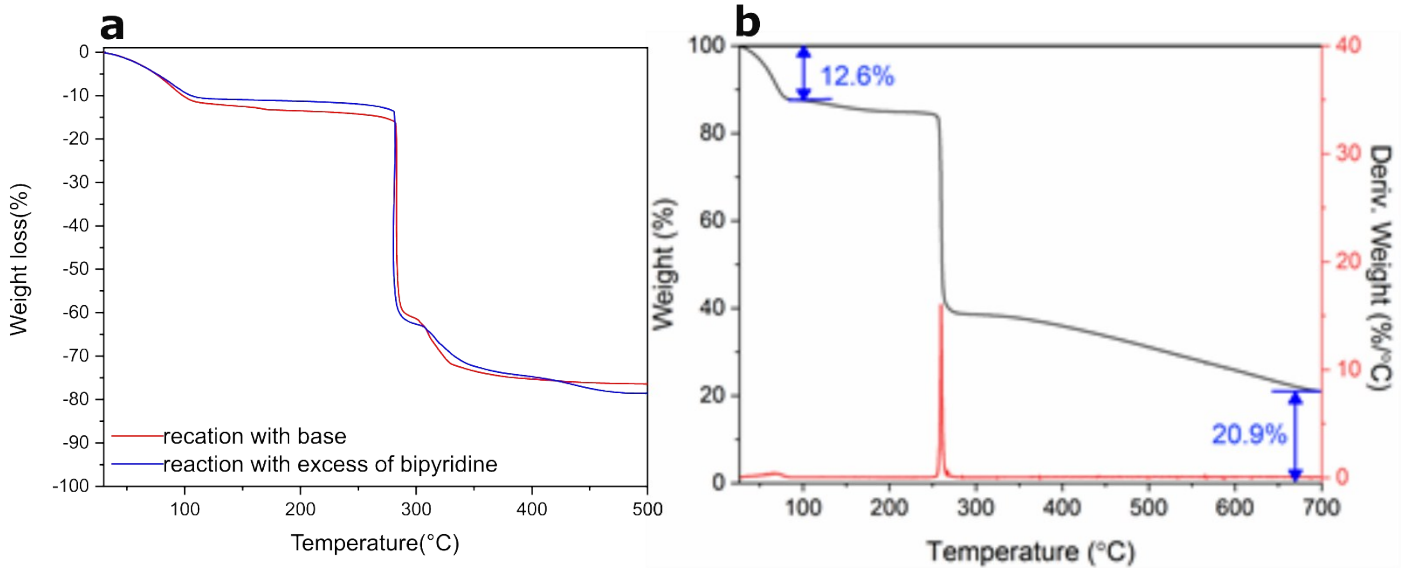
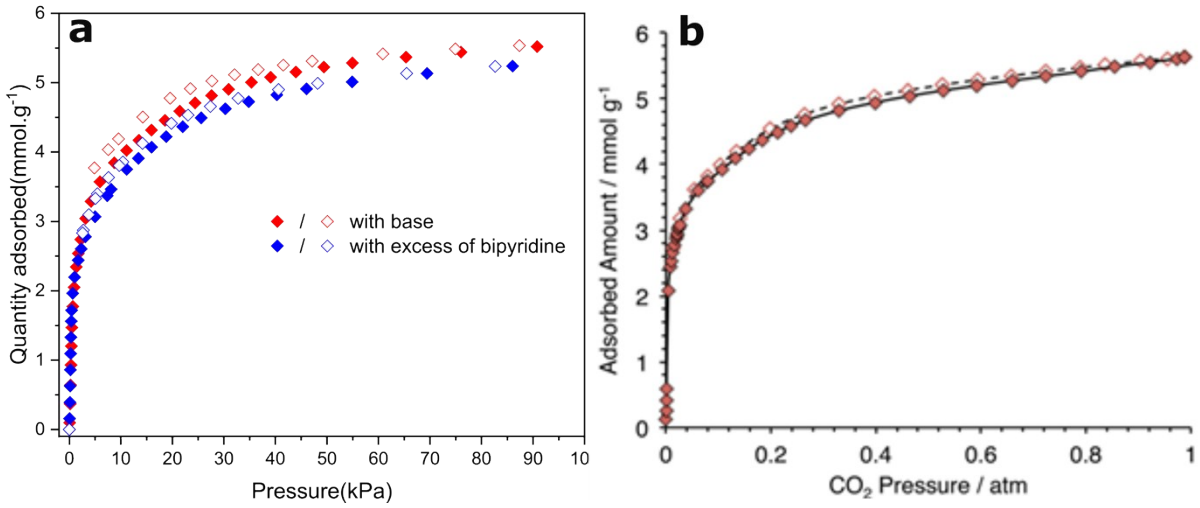


Figure S23. TGA of (**a**) **CPL-2** materials synthesized with base (red) and with an excess of bipyridine ligand (blue) (b) Reported **CPL-2** from the literature [1]



Firgure S24. CO_2 gas adsorption/desorption isotherms at 195K of (**a**) **CPL-2** material synthesized with base (red) and with an excess of bipyridine ligand (blue) (b) Reported **CPL-2** from the literature [2]

1. H. Xiang, A. Ameen, J. Shang, Y. Jiao, P. Gorgojo, F. R. Siperstein and X. Fan, *Microporous Mesoporous Mater.*, 2019, DOI: https://doi.org/10.1016/j.micromeso.2019.109784, 109784.
2. K. Riascos-Rodríguez, A. J. Schroeder, M. R. Arend, P. G. Evans and A. J. Hernández-Maldonado, *Dalton Transactions*, 2014, **43**, 10877-10884.