

Electronic Supplementary Information

MOFs side chains as sources of supramolecular interactions: organic pollutants extraction from water

Nizami Israfilov^a, Karel Soukup^b, Benoît Louis^{*c}, Jean-Marc Planeix^{*a}

^a CNRS, CMC UMR 7140, Université de Strasbourg, 4 rue Blaise Pascal, F-67000 Strasbourg, France. E-mail: planeix@unistra.fr

^b Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Rozvojová 135, 16502 Prague 6, Czech Republic.

^c CNRS, ICPEES UMR 7515, Université de Strasbourg, 25 rue Becquerel, F-67087 Strasbourg, France. E-mail: blouis@unistra.fr

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1. Synthesis and characterization of ligands

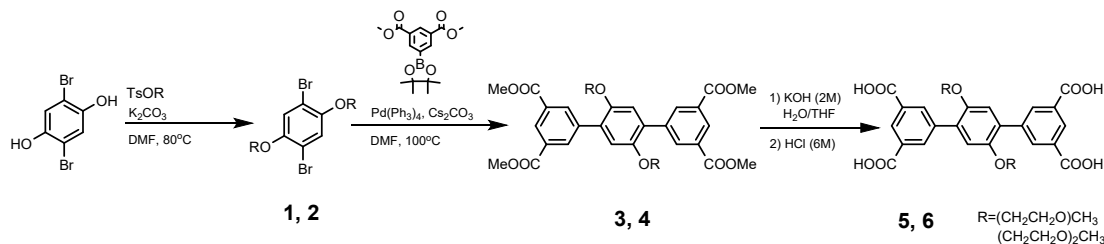


Fig. 1 Synthesis scheme of substituted terphenyl tetracarboxylate ligands

Compound 1 and 2

Double necked flask dried oven before reaction. Dibromohydroquinone (4.48 mmol), TsOR (11.22 mmol) and potassium carbonate (26.88 mmol) added to flask. Then flask evacuated and filled 3 times with Argon. Finally, DMF added. Reaction continued overnight (18 h). Reaction mixture quenched with 120 ml water, white precipitation obtained. Small amount of benzoquinone gives brownish color. Product recrystallized to eliminate this color. Yield for compound 4: 53,6%. Compound 5: 71%

Compound 3 and 4

Double necked flask dried oven before reaction. 3,5-Bis(methoxycarbonyl)benzeneboronic Acid Pinacol Ester (6.25 mmol) and compound 1 or 2 (2.08 mmol) tared, then 40 ml DMF added under Argon atmosphere. After 20 min mixing under argon, Cesium carbonate (6.25 mmol) and Tetrakis(triphenylphosphine)palladium (0) (0.054 mmol) added and mixture heated. Reaction continued overnight.

Reaction mixture dried under reduced pressure, extracted with chloroform and purified with column. White solid obtained. Yield for compound 6; 79%, compound 7; 90%

Compound 3:

^1H NMR (500 MHz, CDCl_3) δ 8.67 (d, $J = 1.7$ Hz, 2H), 8.49 (d, $J = 1.7$ Hz, 4H), 7.07 (s, 2H), 4.13 (t, $J = 4.7$ Hz, 4H), 3.98 (s, 12H), 3.66 (t, $J = 4.7$ Hz, 4H), 3.34 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 166.38, 150.39, 138.61, 134.90, 130.47, 129.71, 129.44, 116.28, 71.01, 69.32, 59.23, 52.47.

LRMS (ESI⁺) for compound 6 calculated: $\text{C}_{32}\text{H}_{34}\text{O}_{12}$, 610.21 found: $\text{C}_{28}\text{H}_{25}\text{O}_{12}\text{Na}$, 633.19

Elemental analysis (%) for $\text{C}_{32}\text{H}_{34}\text{O}_{12}$ calculated: C 62.95, H 5.61; found: C 60.52, H 5.54

Compound 4:

^1H NMR (500 MHz, CDCl_3) δ 8.64 (t, $J = 1.7$ Hz, 2H), 8.44 (d, $J = 1.7$ Hz, 4H), 7.02 (s, 2H), 4.12 (t, $J = 4.9$ Hz, 4H), 3.96 (s, 13H), 3.74 (t, $J = 4.9$ Hz, 4H), 3.58 – 3.53 (m, 4H), 3.46 – 3.41 (m, 4H), 3.29 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 166.32, 150.28, 138.69, 134.88, 130.45, 129.65, 129.40, 116.06, 71.88, 70.79, 69.68, 69.42, 59.02, 52.47.

LRMS (ESI⁺) for compound 7 calculated: $\text{C}_{36}\text{H}_{42}\text{O}_{14}$, 698.26, found $\text{C}_{36}\text{H}_{42}\text{O}_{14}\text{Na}$, 721.25

Elemental analysis (%) for calculated: C 61.88, H 6.06; found C 58.95, H 5.82

Compound 5 and 6

Compound 3 or 4 (1.64 mmol) dissolved in the mixture 100 ml THF and 100 ml aq. KOH (2M). Mixture heated to 90°C overnight. Once, reaction mixture reached RT, THF evaporated under reduced pressure. Aqueous solution treated with 6M HCl to pH1. Precipitation filtered and washed with water. Dried under vacuum overnight. Yield for compound 5; 89%, compound 6; 95%

Compound 5:

^1H NMR (300 MHz, DMSO) δ 13.29 (s, 4H), 8.46 (t, $J = 1.6$ Hz, 2H), 8.42 (d, $J = 1.6$ Hz, 4H), 7.25 (s, 2H), 4.24 – 4.15 (m, 4H), 3.63 – 3.54 (m, 4H), 3.22 (s, 6H).

^{13}C NMR (126 MHz, DMSO) δ 167.12, 150.23, 138.70, 134.67, 131.67, 129.22, 129.08, 116.25, 70.93, 69.07, 58.68.

LRMS (ESI⁺) for compound 8 calculated: $\text{C}_{28}\text{H}_{26}\text{O}_{12}$, 554.14 found: $\text{C}_{28}\text{H}_{25}\text{O}_{12}$, 553.14

Elemental analysis (%) for $\text{C}_{28}\text{H}_{26}\text{O}_{12}$ calculated: C 60.65, H 4.46; found: C 52.46, H 4.73.

Compound 6:

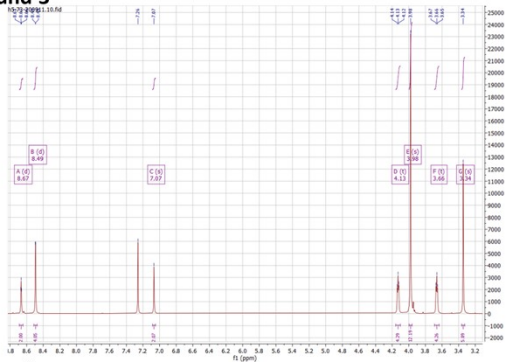
^1H NMR (500 MHz, DMSO) δ 13.31 (s, 4H), 8.45 (t, $J = 1.7$ Hz, 2H), 8.38 (d, $J = 1.6$ Hz, 4H), 7.23 (s, 2H), 4.20 – 4.15 (m, 4H), 3.67 – 3.62 (m, 4H), 3.46 (dd, $J = 5.8, 3.8$ Hz, 4H), 3.33 (d, $J = 2.1$ Hz, 4H), 3.14 (s, 6H).

^{13}C NMR (126 MHz, DMSO) δ 167.13, 150.24, 138.75, 134.66, 131.62, 129.33, 129.07, 116.33, 71.60, 70.18, 69.48, 69.46, 58.37.

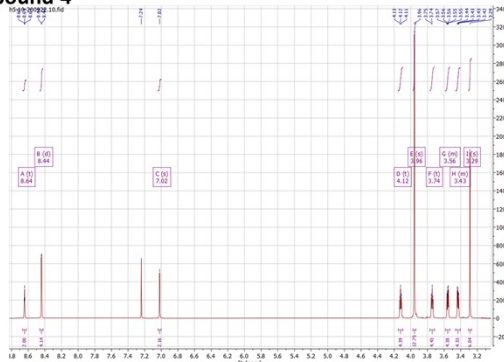
LRMS (ESI⁺) for compound 9 calculated: $\text{C}_{32}\text{H}_{34}\text{O}_{14}$ 642.19 found: $\text{C}_{32}\text{H}_{34}\text{O}_{14}\text{K}$ 681.16 (one K atom plus)

Elemental analysis (%) for $\text{C}_{32}\text{H}_{34}\text{O}_{14}$ calculated: C 59.81, H 5.33; found: C 58.13, H 5.18

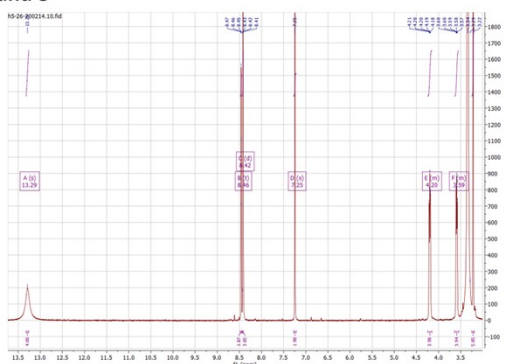
Compound 3



Compound 4



Compound 5



Compound 6

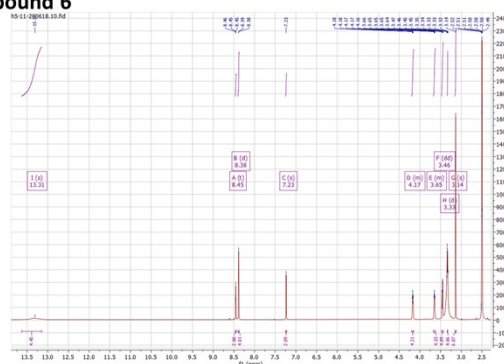
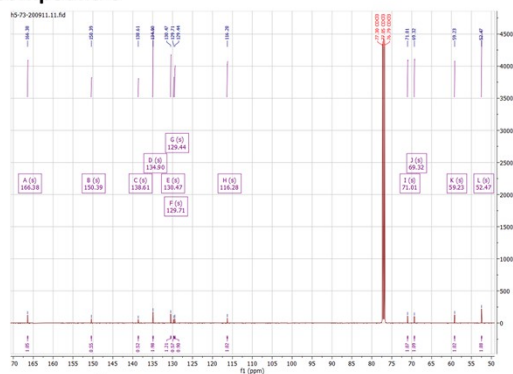
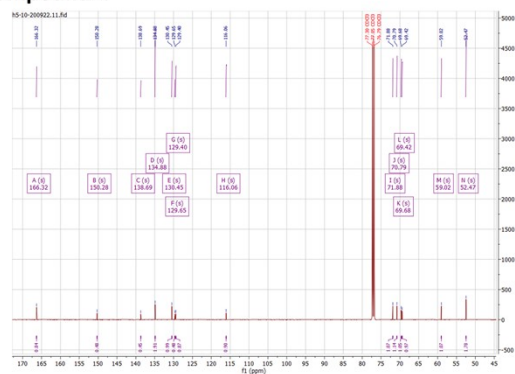


Fig. 2 Proton NMR spectra of substituted terphenyl tetraester (3, 4) and substituted terphenyl tetracarboxylate ligands (5, 6)

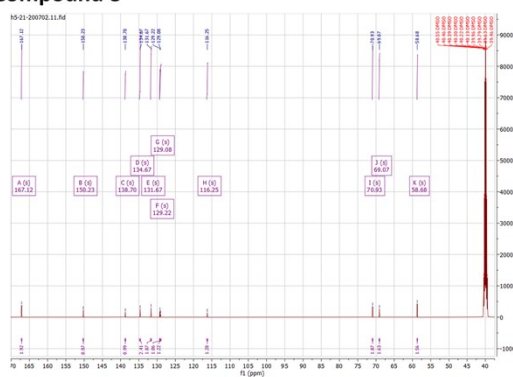
Compound 3



Compound 4



Compound 5



Compound 6

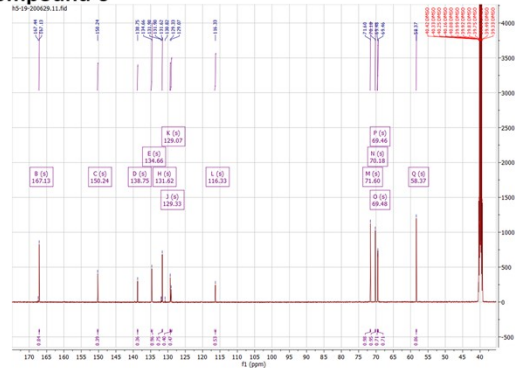


Fig. 3 Carbon NMR spectra of substituted terphenyl tetraester (3, 4) and substituted terphenyl tetracarboxylate ligands (5, 6)

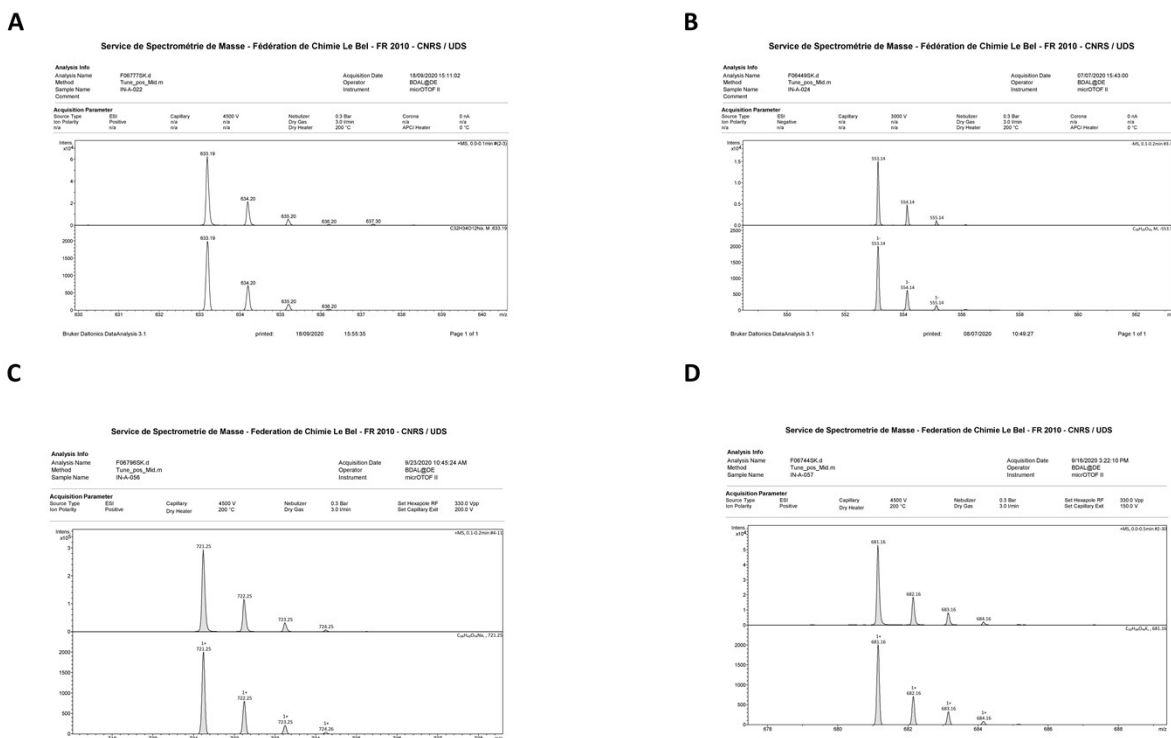


Fig. 4 LR-MS of compound 3 = A spectra, compound 4 = B spectra, compound 5 = C spectra, compound 6 = D spectra.

2. Synthesis of MOF's

In 10 ml dram vial, 0.018 mmol ligand (11,6 mg of H4L(diglyme)₂, 10 mg of H4L(glyme)₂ tared and dissolved in 4 ml DMF and 1,3 ml water. Then, 0,072 mmol (17,5 mg) of Cu(NO₃)₂·3H₂O added to the solution and dissolved in the solution. Finally, 33 μl of concentrated HCl added, vial is closed and put into dry bath at 80°C. After 24h, microcrystalline powder is filtered and washed with DMF. 14 mg (48% yield) of SUM-103 and 12.5 mg (45% yield) of SUM-102.

3. Characterization of MOF's

Crystal Structure Report for e4763

A specimen of C14H15CuO7 was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a trigonal unit cell yielded a total of 36566 reflections to a maximum θ angle of 27.48° (0.77 Å resolution), of which 3224 were independent (average redundancy 11.342, completeness = 99.7%, Rint = 8.84%, Rsig = 4.26%) and 2575 (79.87%) were greater than 2 σ (F₂). The final cell constants of a = 18.5565(7) Å, b = 18.5565(7) Å, c = 38.7407(16) Å, volume = 11552.9(10) Å³, are based upon the refinement of the XYZ-centroids of reflections above 20 σ (I).

The final anisotropic full-matrix least-squares refinement on F₂ with 107 variables converged at R1 = 8.65%, for the observed data and wR2 = 26.80% for all data. The goodness-of-fit was 0.882. The largest peak in the final difference electron density synthesis was 1.440 e-/Å³ and the largest hole was -1.076 e-/Å³ with an RMS deviation of 0.326 e-/Å³. On the basis of the final model, the calculated density was 0.103 g/cm³ and F(000), 368 e-.

Table 1. Crystal data for SUM-102.

Identification code	e4763	
Chemical formula	C ₁₄ H ₁₅ CuO ₇	
Formula weight	358.80 g/mol	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	trigonal	
Space group	R -3 m	
Unit cell dimensions	a = 18.5565(7) Å	α = 90°
	b = 18.5565(7) Å	β = 90°
	c = 38.7407(16) Å	γ = 120°
Volume	11552.9(10) Å ³	
Z	2	
Density (calculated)	0.103 g/cm ³	
Absorption coefficient	0.097 mm ⁻¹	
F(000)	368	
Theta range for data collection	1.37 to 27.48°	
Index ranges	-23 ≤ h ≤ 24, -22 ≤ k ≤ 23, -50 ≤ l ≤ 50	
Reflections collected	36566	
Independent reflections	3224 [R(int) = 0.0884]	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	Σ w(F _o ² - F _c ²) ²	
Data / restraints / parameters	3224 / 2 / 107	
Goodness-of-fit on F²	0.882	
Δ/σ_{max}	0.004	
Final R indices	2575 data; I > 2σ(I)	R1 = 0.0865, wR2 = 0.2479
	all data	R1 = 0.1040, wR2 = 0.2680
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.1962P) ² + 111.3399P] where P = (F _o ² + 2F _c ²)/3	
Extinction coefficient	0.0061(6)	
Largest diff. peak and hole	1.440 and -1.076 eÅ ⁻³	
R.M.S. deviation from mean	0.326 eÅ ⁻³	

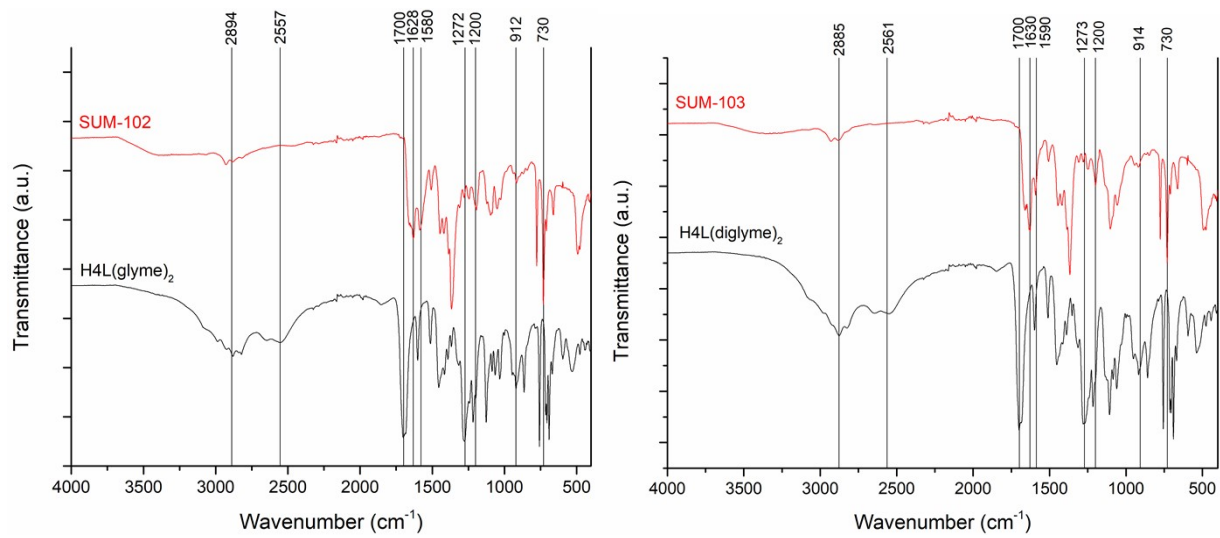


Fig. 5 FT-IR spectra of SUM-102, SUM-103 vs corresponding ligands.

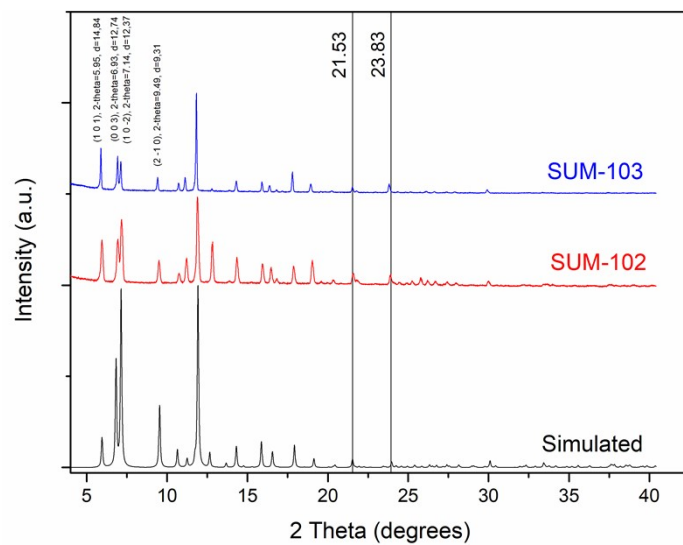


Fig. 6 PXRD diffractograms of SUM-102 and SUM-103. Simulation made from single crystal data of SUM-102 .

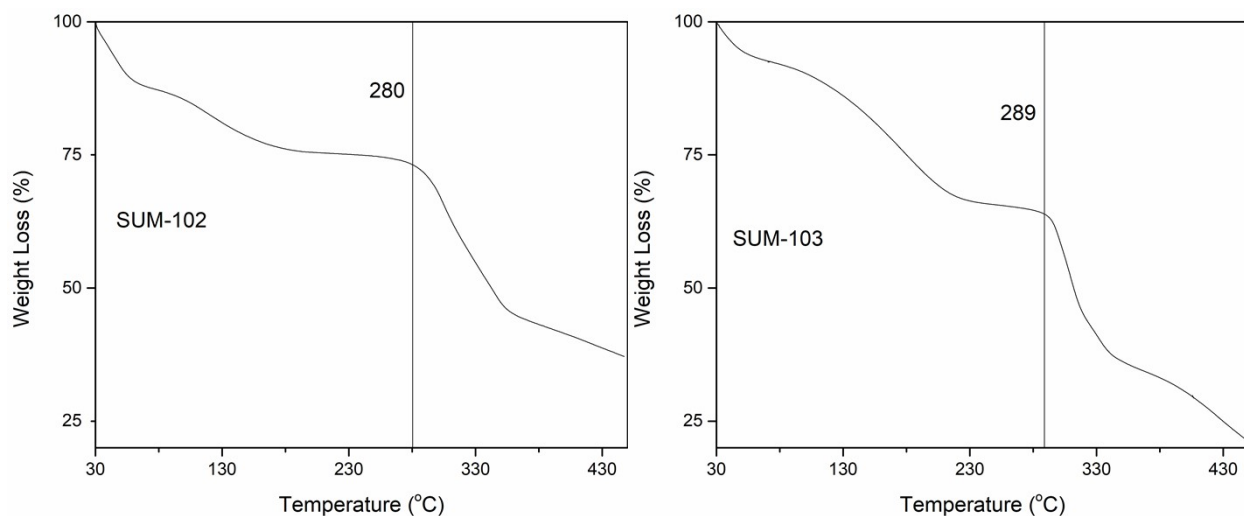


Fig. 7 TGA of SUM-102 and SUM-103.

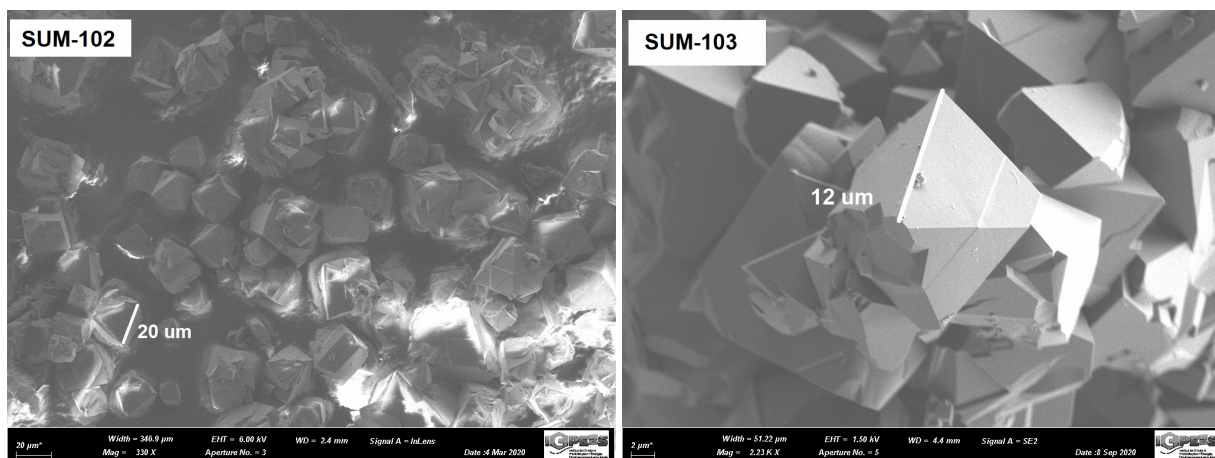


Fig. 8 SEM images of MOF's.

4. Methylene Blue adsorption

The adsorption capacity of MB was calculated based on Equation (1)^{a-c}. The equilibrium adsorption capacity of adsorbent was calculated using Equation (2)^c.

$$Q_t = (C_o - C_t) \cdot V/m \quad (1)$$

$$Q_e = (C_o - C_e) \cdot V/m \quad (2)$$

where Q_t and C_t define the adsorption capacity of the adsorbent (mg/g) and the adsorbate concentration (mg/L), respectively. V represents the volume of adsorbate solution and m the mass of MOF adsorbent. Likewise, Q_e and C_e define the adsorption capacity of adsorbent and adsorbate concentration (mg/L), respectively, at the equilibrium conditions.

The MB isotherms (SI^*) were fitted with Langmuir and Freundlich models in order to calculate the maximal adsorption capacity and get insights about the nature of the adsorption. Linear form of Langmuir equation is expressed as indicated below:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

C_e is the equilibrium concentration, Q_e is equilibrium uptake capacity. K_L and Q_m are obtained from the slope and the intercept of C_e/Q_e vs Q_e plot. R^2 of the linear plot is 0.9992 which shows applicability of this model.

Besides, the separation factor- R_L is calculated with Eq (4).

$$R_L = \frac{1}{1 + C_m K_L} \quad (4)$$

C_m is maximal initial concentration of methylene blue. The R_L shows favorability of adsorption. The value between 0 and 1 shows good adsorption.

To fit the data to Freundlich model the Eq (5) was used:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

To find K_F and $1/n$ (adsorption constants), the plot of $\ln Q_e$ vs $\ln C_e$ were drawn. R^2 is 0.7507 which doesn't show a good agreement of this model. The values of adsorption constants for both isotherms are summarized in Table 1.

Table 2 Parameters of isotherm modelling for SUM-103.

Isotherm model	Constants	
Langmuir	Q_m (mg/g)	194
	K_L (L/mg)	0.0777
	R_L	0.0605
	R^2	0.9992
Freundlich	K_F (mg/g)	39.16
	$1/n$	0.3429
	R^2	0.7507

In order to properly describe the adsorption process, two popular methods for studying the adsorption kinetics were applied: Pseudo-first order (PFO) and pseudo second order (PSO). Linear equation of PFO (6) and PSO (7) could be expressed as below:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \quad (7)$$

Q_e and Q_t are the amounts of methylene blue adsorbed (mg/g) on MOFs at equilibrium and at the time t . k_1 (min^{-1}) and k_2 ($\text{g}/\text{mg}\cdot\text{min}$) are the rate constants of PFO and PSO, respectively.

Table 3 Parameters of kinetics modelling for SUM-103.

Kinetic model	Constants	
Pseudo First Order	K_1 (L/min)	0.0042
	Q_e (mg/g)	2.29
	R^2	0.9959
Pseudo Second Order	K_2 (g/mg·min)	0.0041
	Q_e (mg/g)	15.21
	R^2	0.9997

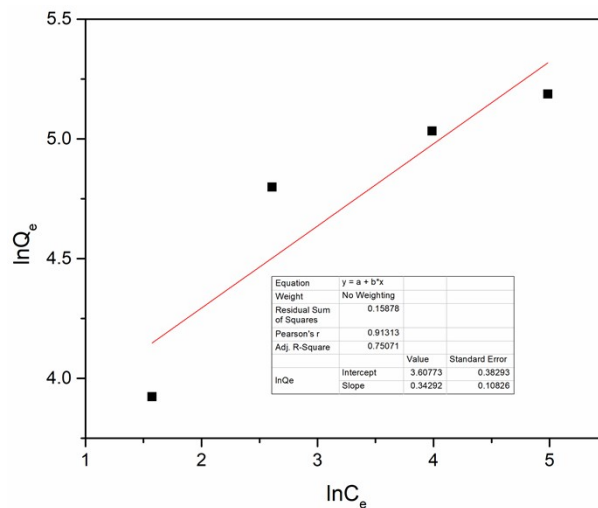
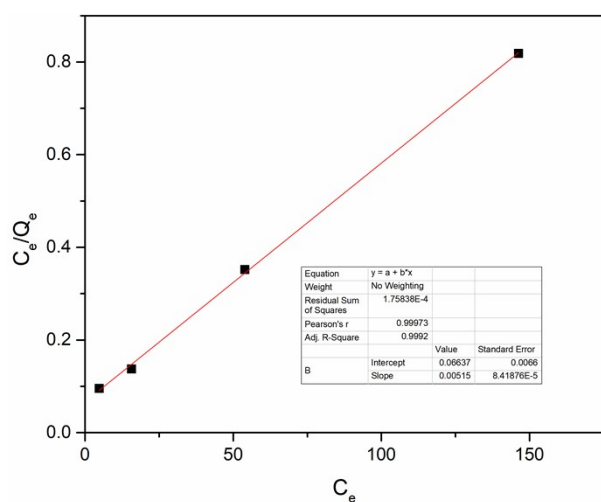


Fig. 9 Langmuir and Freundlich modelling of MB adsorption of SUM-103.

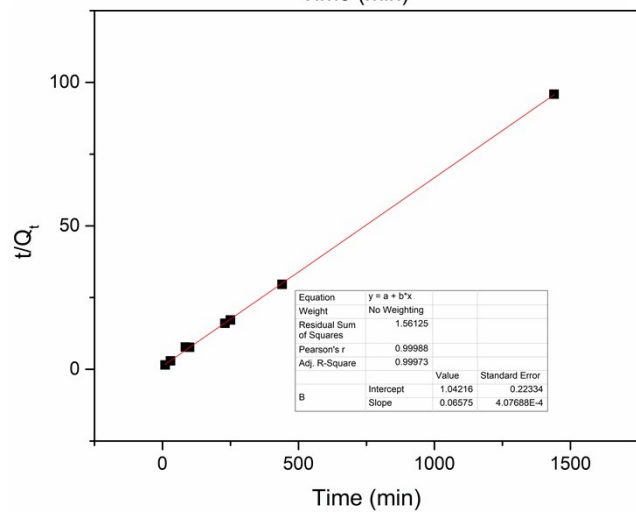
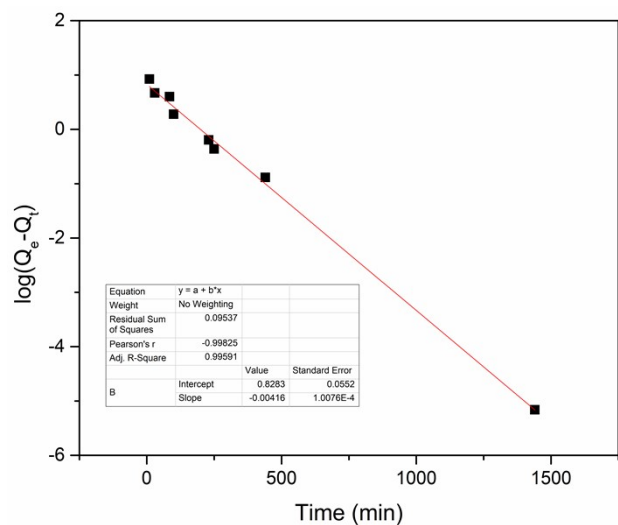


Fig. 10 PFO and PSO modelling of MB adsorption of SUM-103, room temperature.

Time (min)	Concentration (ppm)	Log(Q _e -Q _t)	t/Q _t
0	15.1	1.18	-
10	8.52	0.924	1.52
30	4.79	0.669	2.91
85	4.12	0.602	7.74
100	2.02	0.278	7.65
230	0.762	-0.196	16.0
250	0.560	-0.323	17.2
440	0.255	-0.886	29.6
1440	0.125	-3.92	96.2

Table 4 Kinetic data for SUM-103.

References:

Preparation of Compound 1, 2: D. A. Vazquez-Molina, G. M. Pope, A. A. Ezazi, J. L. Mendoza-Cortes, J. K. Harper, F. J. Uribe-Romo, *Chemical Communications*, 2018, **54**, 6947-6950.

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