Electronic Supplementary Information

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

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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)benzenearonic 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:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 166.38, 150.39, 138.69, 134.88, 130.45, 129.65, 129.40, 116.06, 71.88, 70.79, 69.68, 69.42, 69.02, 52.47.

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

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

Compound 4:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 166.32, 150.28, 138.61, 134.90, 130.47, 129.71, 129.44, 116.28, 71.01, 69.32, 59.23, 52.47.

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

Elemental analysis (%) for C$_{36}$H$_{42}$O$_{14}$ 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:**

\(^1\)H NMR (300 MHz, DMSO) \(\delta\) 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) \(\delta\) 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: C\(_{28}\)H\(_{26}\)O\(_{12}\), 554.14 found: C\(_{28}\)H\(_{25}\)O\(_{12}\), 553.14

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

**Compound 6:**

\(^1\)H NMR (500 MHz, DMSO) \(\delta\) 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) \(\delta\) 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: C\(_{32}\)H\(_{34}\)O\(_{14}\), 642.19 found: C\(_{32}\)H\(_{34}\)O\(_{14}\)K, 681.16 (one K atom plus)

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

**Fig. 2** Proton NMR spectra of substituted terphenyl tetraester (3, 4) and substituted terphenyl tetracarboxylate ligands (5, 6)
Fig. 3 Carbon NMR spectra of substituted terphenyl tetraester (3, 4) and substituted terphenyl tetracarboxylate ligands (5, 6)
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(NO$_3$)$_2$.3H$_2$O 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 2σ(F). The final cell constants of a = 18.5565(7) Å, b = 18.5565(7) Å, c = 38.7407(16) Å, volume = 11552.9(10) Å$^3$, 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-/Å$^3$ and the largest hole was -1.076 e-/Å$^3$ with an RMS deviation of 0.326 e-/Å$^3$. On the basis of the final model, the calculated density was 0.103 g/cm$^3$ and F(000), 368 e-.
Table 1. Crystal data for SUM-102.

| Description                              | Value                                      |
|------------------------------------------|--------------------------------------------|
| 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                     | $a = 18.5565(7) \text{ Å}$, $\alpha = 90^\circ$ |
|                                          | $b = 18.5565(7) \text{ Å}$, $\beta = 90^\circ$ |
|                                          | $c = 38.7407(16) \text{ Å}$, $\gamma = 120^\circ$ |
| Volume                                   | 11552.9(10) Å³                            |
| $Z$                                      | 2                                          |
| Density (calculated)                     | 0.103 g/cm³                                |
| Absorption coefficient                   | 0.097 mm⁻¹                                 |
| $F(000)$                                 | 368                                        |
| Theta range for data collection          | 1.37 to 27.48°                             |
| Index ranges                             | $-23 \leq h \leq 24$, $-22 \leq k \leq 23$, $-50 \leq l \leq 50$ |
| 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                       | $\Sigma w(F_o^2 - F_c^2)^2$                |
| Data / restraints / parameters           | 3224 / 2 / 107                             |
| Goodness-of-fit on $F^2$                 | 0.882                                      |
| $\Delta/\sigma_{max}$                    | 0.004                                      |
| Final R indices                          | 2575 data; $I > 2\sigma(I)$: $R1 = 0.0865$, $wR2 = 0.2479$ |
|                                          | all data: $R1 = 0.1040$, $wR2 = 0.2680$    |
| Weighting scheme                         | $w=1/[\sigma^2(F_o^2)+(0.1962P)^2+111.3399P]$ |
| 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.
4. Methylene Blue adsorption

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

\[
Q_t = (C_0 - C_t) \cdot V/m \quad (1)
\]

\[
Q_e = (C_0 - C_e) \cdot V/m \quad (2)
\]

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:
\[
\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)
\]

Ce is the equilibrium concentration, Qe is equilibrium uptake capacity. Kᵢ and Qᵢ are obtained from the slope and the intercept of Ce/Qₑ vs Qₑ plot. R² of the linear plot is 0.9992 which shows applicability of this model.

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

\[
Rₑ = \frac{1}{1 + C_m K_L} \quad (4)
\]

Cₑ is maximal initial concentration of methylene blue. The Rₑ 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 Kᵢ and 1/n (adsorption constants), the plot of lnQₑ vs lnCe were drawn. R² 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       | Qₑ (mg/g)  | 194        |
|                | Kᵢ (L/mg)  | 0.0777     |
|                | Rₑ         | 0.0605     |
|                | R²         | 0.9992     |
| Freundlich     | Kᵢ (mg/g)  | 39.16      |
|                | 1/n        | 0.3429     |
|                | R²         | 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:

\[
\ln \left( \frac{Q_e - Q_t}{Q_e - Q_t} \right) = \ln Q_e - k_1 t \quad (6)
\]

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

Qₑ and Qₜ are the amounts of methylene blue adsorbed (mg/g) on MOFs at equilibrium and at the time t. k₁(min⁻¹) and k₂ (g/mg·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 | K₁ (L/min) | 0.0042 |
|                    | Qₑ (mg/g)  | 2.29   |
|                    | R²         | 0.9959 |
| Pseudo Second Order| K₂ (g/mg·min) | 0.0041 |
|                    | Qₑ (mg/g)  | 15.21  |
|                    | R²         | 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(Qe-Qt) | t/Qe |
|------------|---------------------|------------|------|
| 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:

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