Free-Standing Metal-Organic Framework (MOF) Monolayers by Self-Assembly of Polymer-Grafted Nanoparticles

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SUPPORTING INFORMATION

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Materials

All starting materials and reagents were purchased from commercial suppliers (Sigma-Aldrich, Fisher Scientific, Acros Organics, and others) and used without further purification.

Synthesis of cat-CTA (3).



Scheme S1. Synthesis of 2-cyano-5-((3,4-dihydroxyphenethyl)amino)-5-oxopentan-2-yl dodecyl carbonotrithioate (cat-CTA) **(3)**.

NHS-CTA (2). A 100 mL round bottom flask was charged with **1** (Scheme S1, 1 g, 2.5 mmol, 1 eq., Combi-blocks), *N*-hydroxysuccinimide (428 mg, 3.6 mmol, 1.5 eq.) and 40 mL of dry dichloromethane. The flask was degassed with argon for 5 min and cooled to 0 °C, after which EDC (760 mg, 4.0 mmol, 1.6 eq.) was added and the reaction was left to stir at room temperature under an argon atmosphere overnight. Upon completion, the organic layer was washed with 1 M HCl (1x100 mL), saturated NaHCO₃ (1x100 mL), brine, and dried with Na₂SO₄. Compound **2** was purified using column chromatography (EtOAc/hexane, 0-50%, elutes at 35%) to give a yellow solid. Yield: 1.01 g, 81%. ¹H NMR (300 MHz, CDCl₃): δ 3.38 – 3.27 (m, 2H), 2.93 (t, *J* = 8.4 Hz, 2H), 2.85 (s, 4H), 2.72 – 2.59 (m, 1H), 2.52 (ddd, *J* = 14.4, 9.3, 7.1 Hz, 1H), 1.88 (s, 3H), 1.76 – 1.63 (m, 2H),

1.58 (s, 1H), 1.42 (s, 1H), 1.26 (s, 18H), 0.88 (t, J = 6.7 Hz, 3H). ESI-MS(+) Experimental: m/z 523.13 [M+Na]⁺, Calculated for [C₂₃H₃₆N₂O₄S₃]: 500.14.

cat-CTA (3). A 100 mL round bottom flask was charged with 2 (1 g, 2.0 mmol, 1 eq.), dopamine hydrochloride (417 mg, 2.2 mmol, 1.1 eq.) and 50 mL of dry THF. The flask was degassed with argon for 5 minutes and cooled to 0 °C, after which triethylamine (306 µl, 2.2 mmol, 1.1 eq.) was added dropwise and the reaction was left under an argon atmosphere in the ice bath to warm to room temperature overnight. After 24 h, the reaction was diluted with 100 mL of 1M HCl and extracted with CHCl₃ (3x50 mL). The combined organic layers were washed with brine and dried with Na₂SO₄. Compound **3** was purified by column chromatography (EtOAc/hexane, 0-70%, elutes at 50%) and dried overnight in a vacuum oven to give a resinous, amber oil. Yield: 880 mg, 82%. ¹H NMR (500 MHz, CDCl₃): δ 6.81 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 1.8 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 3.47 (dd, *J* = 5.9, 4.5 Hz, 2H), 3.32 (t, *J* = 7.5 Hz, 2H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.54 – 2.45 (m, 1H), 2.45 – 2.38 (m, 2H), 2.37 – 2.28 (m, 1H), 1.86 (s, 3H), 1.75 – 1.60 (m, 3H), 1.43 – 1.33 (m, 2H), 1.25 (s, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). ESI-MS(+) Experimental: *m*/z 539.21 [M+H]⁺, Calculated for [C₂₇H₄₂N₂O₃S₃]: 538.24.

MOF Syntheses

UiO-66(Zr). A 250 mL flask was charged with terephthalic acid (440 mg, 2.7 mmol, 1 eq.) and $ZrCl_4$ (617 mg, 2.7 mmol, 1 eq.) and dissolved in 150 mL DMF. Acetic acid (4.55 mL, 80 mmol, 30 eq.) was added, and the solution was divided into 15 mL portions in 6 dram vials with Teflon lined caps. The vials were placed in a sand bath in a preheated 120 °C

oven to crystallize for 24 h. The vials were cooled to room temperature, combined into 50 mL centrifuge tubes, and the white solid was collected by centrifugation (7000 rpm, 10 min). The particles were then washed through repeated dispersion/centrifugation cycles with DMF (2x40 mL, 2 h each) and methanol (3x40 mL, 24 h each) and dried in a vacuum oven at 50 °C overnight.

UiO-66(Zr)-NH₂. A 20 mL vial was charged with ZrCl₄ (61 mg, 0.26 mmol, 1 eq.) and 2aminoterephthalic acid (43 mg, 0.26 mmol) and dissolved in 15 mL DMF. Acetic acid (0.45 mL, 7.9 mmol, 30 eq.) was added and the vial was then placed in a 120 °C oven for 24 h. After cooling to ambient temperature, the particles were collected by centrifugation (7000 rpm, 10 min.). The particles were then washed through repeated dispersion/centrifugation cycles with DMF (2x40 mL, 2 h each) and methanol (3x40 mL, 24 h each). Using a modified procedure, the formyl groups were restored to free amine. 200 mg of UiO-66(Zr)-NH₂ was added to 10 mL MeOH:H₂O 1:1 mixture with 50 μ L of conc. HCl and refluxed overnight. The solid was collected by filtration and washed with methanol.

MIL-88B(Fe)-NH₂. A 150 mL flask with a stir bar was charged with 640 mg of Pluronic F127 surfactant dissolved in 60 mL of DI H₂O. Iron(III) chloride hexahydrate (716 mg, 2.6 mmol, 2 eq.) was added and the solution was stirred for 1 h, after which acetic acid (2.4 mL, 42 mmol, 32 eq.) was added. After stirring 1 h, 2-aminoterephthalic acid (240 mg, 1.3 mmol, 1 eq.) was added and the suspension was kept stirring for 2 h. The reaction mixture was transferred to a 100 mL autoclave and placed in a preheated oven at 110 °C oven for 24 h. The solution was cooled to room temperature and the dark purple particles were washed through repeated dispersion/centrifugation cycles with DMF (2x30 mL, 30

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min. each) and ethanol (4x30 mL, 30 min. each) and dried in a vacuum oven at 60 °C overnight.

Characterization

Nuclear Magnetic Resonance. Proton nuclear magnetic resonance spectra (1H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts are reported in parts per million (ppm) referenced to the appropriate solvent peak.

Gel Permeation Chromatography (GPC). Gel permeation chromatography (GPC) was performed in THF at 35 °C with a flow rate of 1.0 mL/min using an Agilent 1260 HPLC with diode array, Wyatt DAWN HELEOS 8+ light scattering detector, Viscostar III viscometer, and Optilab TrEX refractive index.

Powder X-Ray Diffraction (PXRD). ~50 mg of dry MOF powder or 0.5 cm² or SAMM was mounted on a silicon sample holder for analysis by PXRD. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Ka (I = 1.5418 Å), with a scan speed of 2 sec/step, a step size of 0.05° in 20, and a 20 range of 2-50°.

BET Surface Area Analysis. Samples for analysis were evacuated on a vacuum line overnight at room temperature prior to analysis. ~50 mg samples were then transferred to pre-weighed sample tubes and degassed at 105 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. After degassing, the sample tubes were re-weighed to obtain a consistent mass for the

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samples. BET surface area (m^2/g) measurements were collected at 77 K with N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using volumetric techniques.

Scanning Electron Microscopy (SEM). MOF particles or MMM films (~3 mm²) were transferred to conductive carbon tape on a sample holder disk, and coated using an Ir-sputter coating for 8 sec. A FEI Quanta 250 SEM instrument was used for acquiring images using a 5 kV energy source under vacuum at a working distance at 10 mm.

Figures and Tables

Table S1. Surface area results from N_2 gas sorption analysis. Mass loss indicates percent mass loss during TGA heating up to 600 °C normalized with respect to the unfunctionalized MOF.

Material	Surface area (m²/g)	Normalized mass loss (%)	Approximate Corrected Surface Area (m²/g)
UiO-66(Zr)	1039	0	1040
UiO-66(Zr)-CTA	1342	3.5	1389
UiO-66(Zr)-PMMA	846	20	1015
UiO-66(Zr)-NH ₂	1010	0	1010
UiO-66(Zr)-NH ₂ -CTA	1078	0	1078
UiO-66(Zr)-NH ₂ -PMMA	591	17	692



Figure S1. SEM images of the different MOFs before and after functionalization with cat-CTA. a) UiO-66(Zr). b) UiO-66(Zr)-CTA. c) MIL-88B(Fe)-NH₂. d) MIL-88B(Fe)-NH₂-CTA. d) UiO-66(Zr)-NH₂. e) UiO-66(Zr)-NH₂-CTA. All scale bars are 1μm.



Figure S2. PXRD spectra of UiO-66(Zr) (simulated pattern), UiO-66(Zr), UiO-66(Zr)-CTA, and UiO-66(Zr)-PMMA.



Figure S3. PXRD spectra of UiO-66(Zr) (simulated pattern), UiO-66(Zr)-NH₂, UiO-66(Zr)-NH₂-CTA, and UiO-66(Zr)-NH₂-PMMA.



Figure S4. PXRD spectra of MIL-88B(Fe)-NH₂ (simulated pattern), MIL-88B(Fe)-NH₂, MIL-88B(Fe)-NH₂-CTA, and MIL-88B(Fe)-NH₂-PMMA.



Figure S5. ¹H NMR of terephthalic acid (top) and cat-CTA (middle) compared to digestion of UiO-66(Zr)-CTA (bottom).



Figure S6. N_2 sorption isotherm for UiO-66(Zr), UiO-66(Zr)-CTA, and UiO-66(Zr)-PMMA with respective BET surface areas.



Figure S7. N₂ sorption isotherm for UiO-66(Zr)-NH₂, UiO-66(Zr)-NH₂-CTA, and UiO-66(Zr)-NH₂-PMMA with respective BET surface areas.



Figure S8. N_2 sorption isotherm for MIL-88B(Fe)-NH₂ and MIL-88B(Fe)-NH₂-PMMA with respective BET surface areas.



Figure S9. TGA data for UiO-66(Zr), UiO-66(Zr)-CTA, and UiO-66(Zr)-PMMA.



Figure S10. TGA data for UiO-66(Zr)-NH₂, UiO-66(Zr)-NH₂-CTA, and UiO-66(Zr)-NH₂-PMMA.



Figure S11. Image of monolayer film of UiO-66(Zr)-PMMA showing the faint iridescent color.



Figure S12. GPC traces of the polymer recovered from the supernatant from the RAFT polymerization time study with UiO-66(Zr)-CTA.



Figure S13. GPC traces of the polymer brush recovered from the UiO-66(Zr)-PMMA surface after the RAFT polymerization time study.



Figure S14. ¹H NMR of 2-aminoterephthalic acid (top) and cat-CTA (middle) compared to digestion of UiO-66(Zr)-NH₂-CTA (bottom).



Figure S15. Free-standing films of MOFs and SEM images. a) MIL-88B(Fe)-NH₂-PMMA. b) UiO-66(Zr)-NH₂-PMMA. All scale bars are 1 μ m.

Determination of amount of cat-CTA on the surface of UiO-66(Zr)-CTA.

The average facet length of the UiO-66(Zr) particle was determined to be roughly 250 nm based on SEM images. The surface area and volume of each particle was calculated as a cube for simplicity.

MOF surface area =
$$6 \times (2500\text{\AA})^2 = 3.75 \times 10^7 \text{\AA}^2$$

$$MOF \ volume = (2500\text{\AA})^3 = 1.56 \times 10^{10} \text{\AA}^3$$

The dimension of a single edge of the unit cell for UiO-66(Zr) is 2.08 nm according to the literature (*J. Am. Chem. Soc.* 2008, 130, 42, 13850-13851.), so the surface area and volume of the unit cell are

Unit cell surface area = $6 \times (20.8\text{\AA})^2 = 2596\text{\AA}^2$

Unit cell volume =
$$(20.8\text{\AA})^3 = 8999\text{\AA}^3$$

The number of unit cells per crystal are found by dividing the volume of the MOF by the volume of the unit cell

Unit cells per
$$MOF = \frac{1.56 \times 10^{10} \text{\AA}^3}{8999 \text{\AA}^3} = 1.73 \times 10^6$$

Assuming a defect free MOF, there are 24 benzenedicarboxylate (BDC) ligands per unit cell, so the total number of BDC per MOF is

BDC ligand per $MOF = 24 \times (1.73 \times 10^6) = 4.17 \times 10^7$

The molecular formula of a UiO-66(Zr) unit cell is $Zr_{24}O_{120}C_{192}H_{96}$ which corresponds to a formula mass of 6512.12 g/mol. The molecular weight of a single UiO-66(Zr) is equal to the number of unit cells per MOF multiplied by the formula mass

molecular weight of
$$UiO - 66(Zr) = (1.73 \times 10^6) \times 6512.12 = 1.13 \times 10^{10} g/mol$$

With these values, it was calculated that for 10 mg of MOF the mol of BDC

$$mol \ of \ BDC = \frac{0.010g \ UiO - 66}{1.13 \times 10^{10} g / mol} \times 4.17 \times 10^7 = 0.037 mmol$$

The ¹H NMR of digested UiO-66(Zr)-CTA was used to find a ratio of BDC ligand (labeled a in Figure S5) the CTA (labeled b in Figure S5) to the, which was 80. Therefor the moles of cat-CTA per 10mg of UiO-66(Zr) crystal is

 $\frac{0.037 mmol}{80} = 0.46 \mu mol$

And the mass of cat-CTA given a molecular weight of 539.2 g/mol is

$$4.6 \times 10^{-7} mol \times 539.2 \frac{g}{mol} = 0.25 mg$$