

Dysprosium-carboxylate nanomeshes with tunable cavity size and assembly motif through ionic interactions

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1. EXPERIMENTAL METHODS

The experiments were carried out in two distinct custom designed ultra-high vacuum systems, where the base pressure was below 5×10^{-10} mbar. Measurements at cryogenic conditions (~ 4 K) were performed in an ultra-high vacuum system that hosts an Omicron LT-STM. Variable-temperature STM (77 - 393 K) using an Aarhus-150 STM and XPS investigations were carried out in a unique ultrahigh-vacuum system to allow precise control of surface composition. All STM images were taken in constant-current mode with electrochemically etched tungsten tips, applying a bias (V_{bias}) to the sample. The XPS spectra were recorded utilizing Al $K\alpha$ X-rays of 1,486.6 eV, a FOCUS 500 monochromator, and a PHOBIOS 100 hemispherical electron energy analyzer. The Cu(111) substrate was prepared by standard cycles of Ar⁺ sputtering (800 eV) and subsequent annealing to 723 K for 10 minutes. TPA and TDA molecular species were purchased from Sigma-Aldrich, whereas PDA linkers were synthesized (see the SI for the synthetic details and spectroscopic characterization). The metal-organic architectures were fabricated following a two-step protocol. First, a submonolayer molecular coverage was prepared by organic molecular-beam epitaxy (OMBE) from a quartz crucible held at 400 K (TPA), 508 K (PDA), 543 K (TDA), respectively onto a clean Cu(111) crystal at 373 K if not stated otherwise. Subsequently, dysprosium adatoms were sublimated by means of electron beam evaporation from an outgassed Dy rod (99.9%, MaTecK GmbH, 52428 Jülich, Germany).

2. MOLECULAR MODELS OF LINKER SPECIES

The modelling of the linker species was done in the framework of the HyperChem software package using first semi-empirical AM1 method to calculate single point distribution of charges and second MM+ molecular mechanics with atomic charges to optimize the molecular geometry.

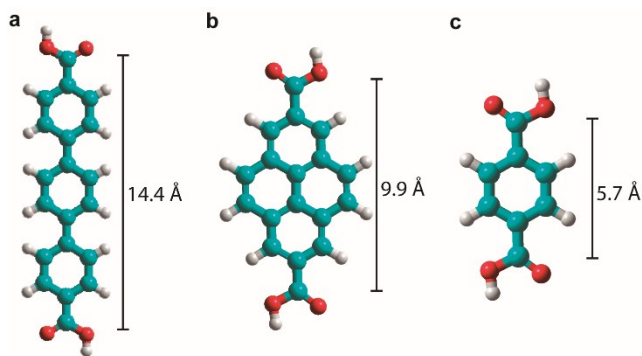


Figure S1. Molecular structure of: a) p-terphenyl-4,4''-dicarboxylic acid (TDA, **1**), b) Pyrene-2,7-dicarboxylic acid (PDA, **2**). (c) Benzene-1,4-dicarboxylic acid (TPA, **3**). Distances are given between terminal carbon atoms. Carbon, oxygen and hydrogen atoms are depicted in green, red and white, respectively.

3. MODELLING OF SUPRAMOLECULAR ARCHITECTURES

In order to model the supramolecular architectures, we superimpose the previous molecular models on perfectly calibrated STM images. Next we measure the projected distances. Importantly, a plausible rotation of the carboxylate moieties due to steric hindrance could modify the bond distances in the range of tenths of angstroms, an effect which is already introduced within the error bars of the measurement.

4. IMAGING OF DYSPROSIUM ADATOMS

Depending on the tip state, the dysprosium adatoms in the reticular architectures could be visualized as voids or dim protrusions (cf. Figure S2), as previously encountered for Gd:TDA directed assemblies on Cu(111).¹

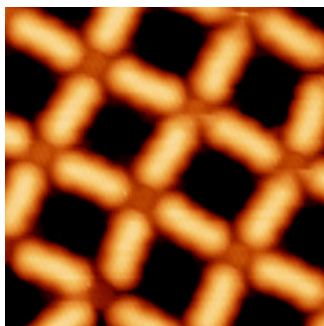


Figure S2. High resolution STM image of Dy:TDA reticular architecture, whereas linkers are identified as bright rods and dysprosium atoms as dim protrusions. Image recorded at 4 K (59 Å x 59 Å, $V_b = 1$ V).

5. LARGE SCALE STM IMAGES OF DY-DIRECTED ASSEMBLIES

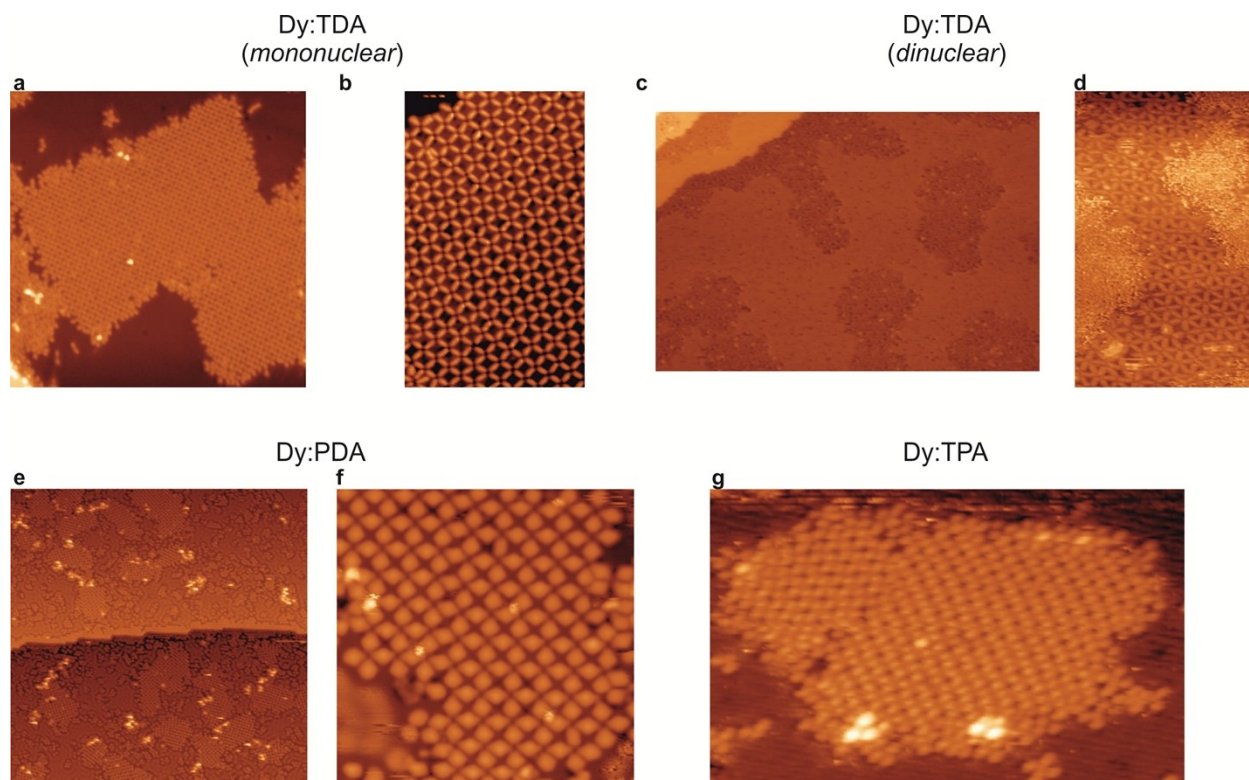


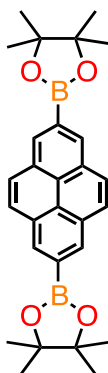
Figure S3. Large scale STM images of Dy-directed architectures on Cu(111). a-b Dy:TDA reticular network. c-d Dy:TDA quasi-hexagonal assembly. e-f Dy:PDA metallo-supramolecular network. g) Dy:TPA reticular architecture. a) $809 \text{ \AA} \times 809 \text{ \AA}$, $V_b = -0.5 \text{ V}$, recorded at 4 K. b) $199 \times 326 \text{ \AA}$, $V_b = -0.2 \text{ V}$, recorded at 4 K. c) $700 \text{ \AA} \times 473 \text{ \AA}$, $V_b = -1 \text{ V}$, recorded at rt. d) $186 \text{ \AA} \times 300 \text{ \AA}$, $V_b = -1 \text{ V}$, recorded at rt. e) $1000 \text{ \AA} \times 1000 \text{ \AA}$, $V_b = -1 \text{ V}$, recorded at 4 K. f) $141 \text{ \AA} \times 141 \text{ \AA}$, $V_b = -1 \text{ V}$, recorded at 4 K. g) $309 \text{ \AA} \times 193 \text{ \AA}$, $V_b = -1 \text{ V}$, recorded at rt.

6. SYNTHESIS OF PDA LINKERS

PDA was synthesized according to a modified literature protocol by Ir-catalyzed C-H borylation of pyrene,² followed by conversion of the boronate group into bromides using CuBr₂.² Finally, halogen-metal exchange reaction followed by addition of solid CO₂ yielded pyrene-2,7-dicarboxylic acid in quantitative yield.³

Thin layer chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm Merck Silica Gel F254. **Column chromatography** was carried out using Merck silica gel 60 Å (particle size 40-63 µm or 60-200 µm). **Melting points** (m.p.) were measured on a SMP-20 in open capillary tubes and have not been corrected. **NMR spectra** were obtained on a JEOL Eclipse 400FT (400 MHz 1H). Chemical shifts are reported in ppm using the solvent residual signal as an internal reference (Chloroform-*d*: δH = 7.26 ppm, Dimethyl Sulfoxide-*d*₆: δH = 2.50 ppm). The resonance multiplicity is described as s (singlet) or bs (broad signal). Mass spectroscopy. **ESI-MS** (5600 eV; CHCl₃/MeOH or DMSO/MeOH mixtures) were performed on a Perkin-Elmer API1. **Chemicals** were purchased from Sigma Aldrich, TCI, Acros, Fluorochem and Alfa Aesar and used as received. **Solvents** were purchased from Sigma Aldrich, VWR and Acros, and deuterated solvents from Sigma Aldrich and Cambridge Isotope Laboratories. Dry THF was obtained by distillation with Na/benzophenone.

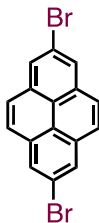
Pyrene-2,7-bis(4,4,5,5-tetramethyl-[1, 3, 2]dioxaborolane)



A Schlenk flask, under Ar, was charged with pyrene (1.00 g, 4.94 mmol) and B₂pin₂ (2.70 g, 10.62 mmol) in dry THF (5.0 mL) and the solution was degassed with a ‘freeze-pump-thaw’ cycle. To this mixture was added a degassed solution of [Ir(μ-OMe)cod]₂ (33 mg, 0.05 mmol), 4,4’-di-*tert*-butyl-2,2’-bipyridine (29 mg, 0.10 mmol) and B₂pin₂ (55 mg, 0.21 mmol) in dry THF (2.5 mL). The tube was sealed, degassed one last time with ‘freeze-pump-thaw’ cycle and the reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was left to cool to r.t. and then passed through a silica plug (CH₂Cl₂) and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO₂, hexane/CH₂Cl₂ 7:3) to obtain product as white solid (1.81 g, 81 % yield).

m.p. > 250 °C. ¹H NMR (400 MHz, Chloroform-*d*): δ 8.62 (s, 4H, Pyr-*H*_{1,3,6,8}), 8.08 (s, 4H, Pyr-*H*_{4,5,9,10}), 1.46 (s, 24H, -BO₂C₂(CH₃)₂). MS (ES +): found 454 (M⁺), C₂₈H₃₂B₂O₄ requires 454.25. Characterization in accordance with literature.²

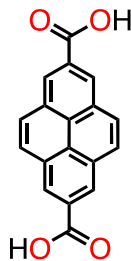
2,7-Dibromopyrene



To a solution of 2,7-bis(pinacolborano)pyrene (0.35 g, 0.75 mmol) in THF/MeOH (10 mL, 1:3) was added a solution of CuBr_2 (1.04 g, 4.64 mmol) in H_2O (7.5 mL). The mixture was heated at 90°C overnight, left to cool down and concentrated under reduced pressure. H_2O was added and the white precipitate collected by filtration and washed with H_2O , Et_2O and hexane. The product was extracted in hot PhCH_3 and the solvent was removed under reduced pressure. Finally, the product was obtained as an off-white solid by crystallization from boiling acetone (0.17 g, 64 % yield).

m.p. $> 250^\circ\text{C}$. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.31 (s, 4H, Pyr- $H_{1,3,6,8}$), 8.01 (s, 4H, Pyr- $H_{4,5,9,10}$). **MS** (ES +): found 360 (M^+), $\text{C}_{16}\text{H}_8\text{Br}_2$ requires 357.90. Characterization in accordance with literature.²

Pyrene-2,7-dicarboxylic acid



To a solution of 2,7-dibromopyrene (0.10 g, 0.28 mmol) in dry THF (25 mL) under Ar and at -78°C an excess of $n\text{BuLi}$ (1.4 mL of a 1.6 M hexane solution, 2.26 mmol) was added dropwise. The mixture was stirred at -78°C for 30 minutes under Ar. At this point, excess CO_2 gas was added (dry ice in a 1 L round-bottom flask was bubbled into the solution by cannula). The mixture was left to warm up to room temperature and left stirring overnight. H_2O was added and the mixture was concentrated under reduced pressure. The residual aqueous phase was treated with 1 M aq. HCl solution to yield a precipitate that was collected by filtration and washed with H_2O , hexane, EtOAc and finally Et_2O . The solid was dried to obtain product as bright yellow solid (74 mg, 91 % yield).

m.p. $> 250^\circ\text{C}$. $^1\text{H NMR}$ (400 MHz, Dimethylsulfoxide-*d*₆): δ 13.39 (bs, 2H, Pyr-COOH), 8.91 (s, 4H, Pyr- $H_{1,3,6,8}$), 8.40 (s, 4H, Pyr- $H_{4,5,9,10}$). **MS** (ES +): found 290 (M^+), $\text{C}_{18}\text{H}_{10}\text{O}_4$ requires 290.06. Characterization in accordance with literature.³

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