

Supporting Information:

High-quality 2D metal-organic coordination network providing giant cavities within mesoscale domains

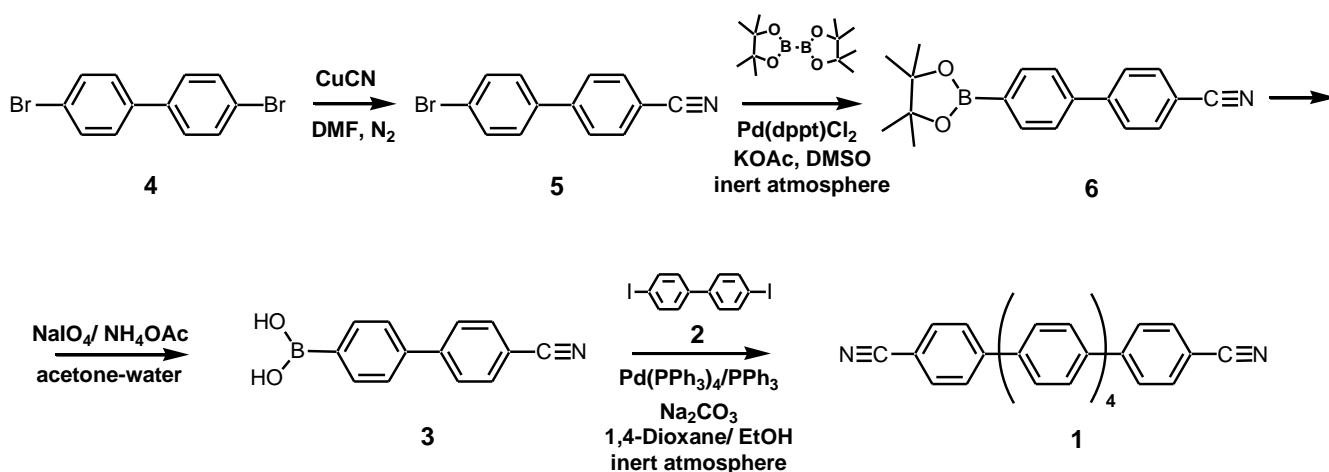
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A. Synthesis of compound 1 (NC-(Ph)₆-CN).



Scheme S1. Synthesis of hexaphenyl-dicarbonitrile 1.

The compound NC-(Ph)₆-CN (**1**) was synthesized according to the divergent approach described in Scheme S1 which involves typical bis-Suzuki coupling reactions¹ of 4,4'-bis-iodo-diphenyl (**2**) with two equivalents of boronic acid (**3**) in presence of catalytic amount of Pd(0). Compound **5** was synthesised by a simple route involving the displacement of halogen with 1 equiv of CuCN per mole of the dihalogenated biphenyl in refluxing dimethylformamide. The reaction mixture was very conveniently separated by preparative thin layer chromatography. In a few runs the main components of the reaction mixture were isolated and were approximately those expected for a statistical reaction. As indicated in Scheme S1, boronic acid **3** was prepared from the corresponding bromide **5** in two-steps procedure in excellent yield.

1. Y. Liu, G.W. Gribble *Tetrahedron Letters*, **2000**, *41*, 8717–8721

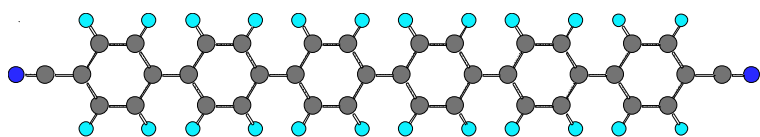
Experimental Section

Materials and Methods

All reagents were purchased from commercial sources and used as received. FT-IR spectra were recorded on a Perkin Elmer Spectrum GX spectrometer in KBr pellets, Maldi-Tof spectra were recorded on Perceptive Biosystems Voyager-DePro, and melting points were measured on Büchi B-545 using open-ended glass capillaries.

4-Bromo-4'-cyanobipheny (**5**)², 4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-biphenyl-4-carbonitrile (**6**)³ and 4'-cyano-4-biphenylboronic acid (**3**)³ were prepared according to the literature procedures.

[1,4';1',1'';4'',1''';4''',1'''';4''''',1''''''']Sexiphenyl-4,4''''-dicarbonitrile (**1**).



Under nitrogen atmosphere in a round bottomed two-neck flask 4'-cyanobiphenyl-boronic acid (**3**) (47.0 mg, 0.21 mmol) and 4,4'-bis-iodo-diphenyl (**2**) (36 mg, 0.09 mmol) were dissolved in 80 mL of a mixture formed by 1,4-dioxane/EtOH (5/1). Slight excess of base, 2 mL of 2M Na₂CO₃, was added to the solution of reactants. The so obtained mixture was initially warmed to 80°C for 20 min, and then the catalysts Pd(PPh₃)₄ (40 mg) and PPh₃(20 mg) were added. The mixture was refluxed for 2 days till absence of **2** (monitored by TLC). The reaction mixture was cooled down to room temperature and the precipitate formed was collected by filtration, washed with H₂O (till pH = 7), MeOH and Et₂O. Recrystallisation from C₂H₂Cl₄ with charcoal followed by filtration of the hot solution (~500 mL) through wad afforded 10.4 mg (yield 23 %) of compound **1** as a white powder, m.p. > 300°C (in open-ended capillary). The solubility of **1** is too little in all available solvents to record NMR-spectra.

MALDI-TOF, *m/z*: found 507.5457 (M⁺, 100%), calculated for C₃₈H₂₄N₂ (M⁺) 508.1934.

FT-IR (KBr, *v*/cm⁻¹): 3038 (*v*_{C-H aromatic}, w), 2228 (*v*_{C≡N}, vs), 1602 (s), 1486 (s), 1398 (m), 1274 (w), 1181 (m), 1002 (w), 812 (vs), 559 (m), 521 (m).

2. J. M. McNamara, W. B. Gleason *J. Org. Chem.*, **1976**, *41* (6), 1071

3. S. Yu, J. Saenz, J. K. Srirangam *J. Org. Chem.* **2002**, *67*, 1699-1702

B. SUPPLEMENTARY STM DATA

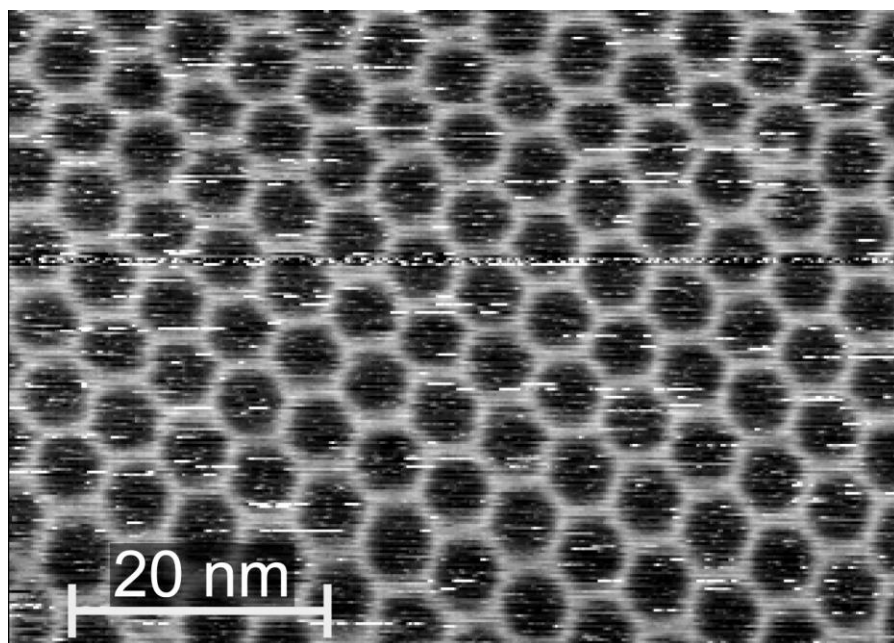


Figure S1. STM image of the metal-organic nanomesh recorded at room temperature demonstrating its thermal stability under such conditions. The white stripes indicate that guest species, trapped at low temperatures, diffuse freely through the nanomesh [Sample bias $V_B = 0.34$ V, tunneling current $I_t = 26$ pA].

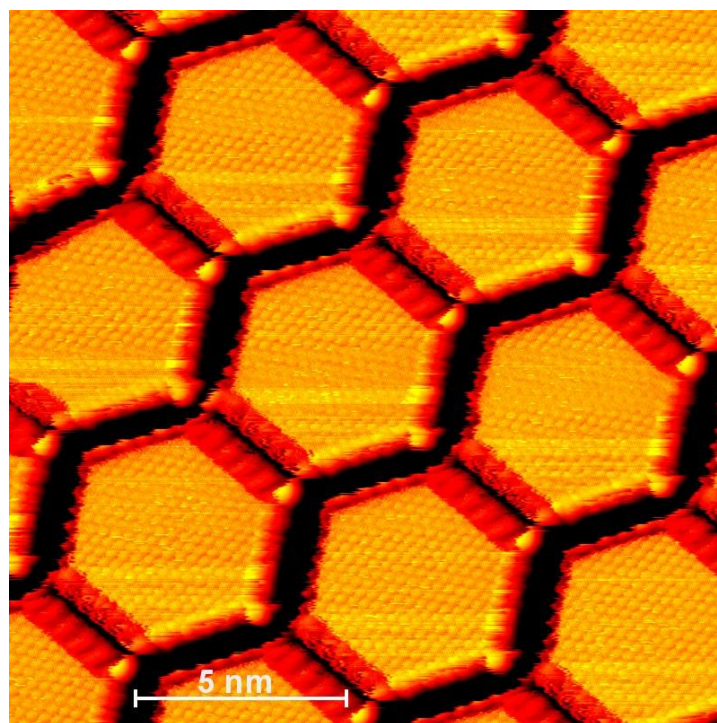


Figure S2. STM image showing simultaneous resolution of the metal-organic nanomesh together with the underlying Ag(111) atomic lattice. The repetition of the atomic pattern within the cavities strongly supports the commensurability of the honeycomb superstructure having a unit cell of the (20x20) substrate lattice unit vectors [$V_B = 0.5$ V, $I_t = 0.1$ nA].

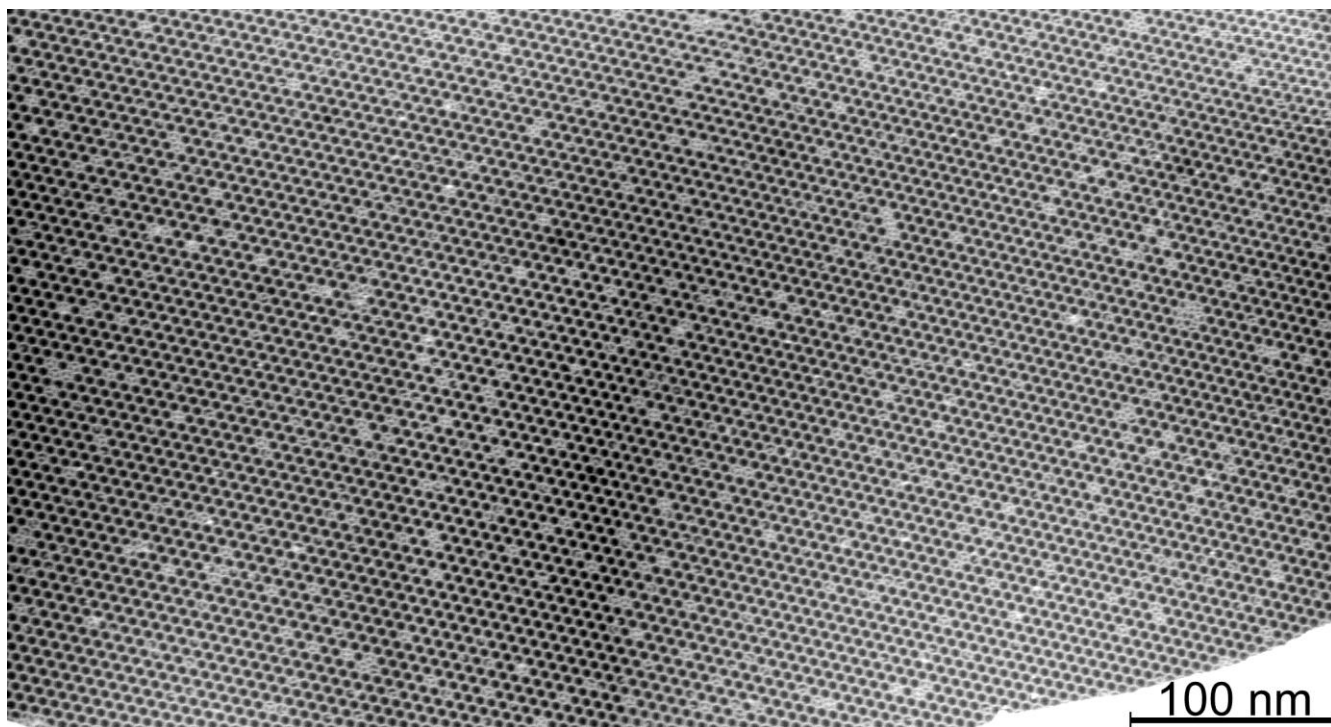


Figure S3. Large-scale STM image of the metal-organic nanomesh showing the regularity of the network throughout the 240000 nm² surface area [$V_B = 1$ V, $I_T = 0.1$ nA]. The percentage of pores with trapped linkers is well below 10 % in the imaged area and can be further reduced by fine-tuning the network formation conditions, mainly determined by the stoichiometric ratio between Co and linkers.

Acknowledgement: We thank W. Krenner for help with the STM measurements of the room-temperature data.