Supporting Information

2D short range disorderd crystalline networks from flexible molecular modules

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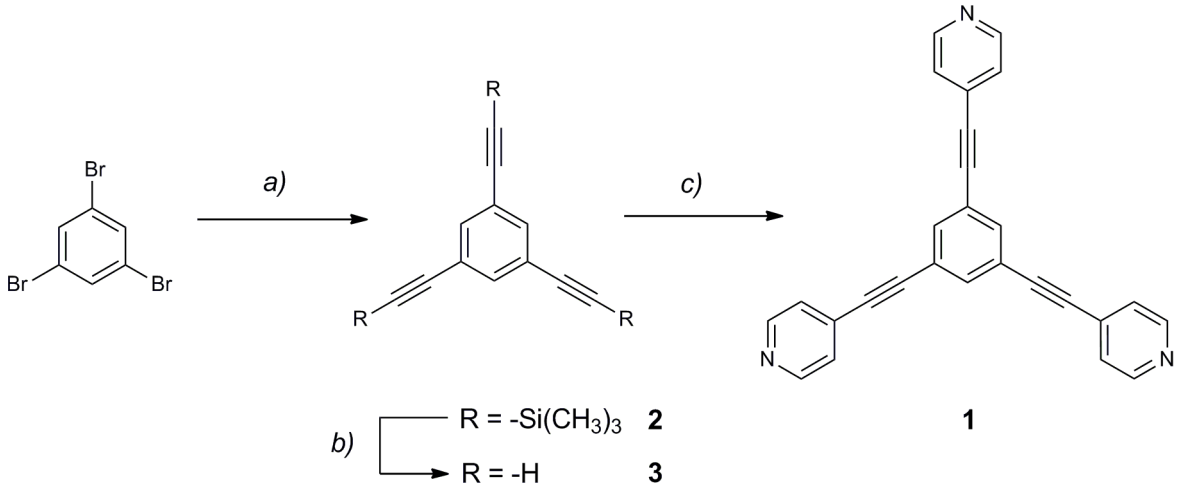
Synthesis

The synthesis of molecule **1** is outlined in Scheme 1. The Pd-catalyzed *Sonogashira* cross-coupling reaction was exploited as general procedure in the synthesis of **1**. Therefore, in the first step of the synthesis 1,3,5-tribromobenzene in Et_3N was reacted with three equivalents of trimethylsilylacetylene (TMSA) in the presence of catalytic amounts of $[PdCl_2(PPh_3)_2]$ and CuI affording the TMS-protected triethynylbenzene **2** in 24% yield (Scheme 1, path *a*). Molecule **2** was subsequently dissolved in a mixture of THF and MeOH and deprotected of the TMS-groups by means of K_2CO_3 producing the free triethynylbenzene derivative **3** with a yield of 88% (Scheme 1, path *b*). By applying again a Pd-catalyzed *Sonogashira*-type reaction,[1] one equivalent of **3** was coupled with 4-iodopyridine affording the targeted compound **1** in 22% yield (Scheme 1, path *c*).



Scheme SI 1. Synthesis of the 1,3,5-tris(pyridin-4-ylethynyl)benzene **1**. *Reagents and Conditions: a)* TMSA, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, rt 16h, 24%; *b)* K_2CO_3, MeOH/MeOH, rt 2h, 88%: *c)* 4-iodopyridine, $[PdCl_2(PPh_3)_2]$, CuI, iPr_2NH, rt 16h, 22%.

General synthetic details

Compounds **2** and **3** were prepared and characterized according to literature data.[2] Solvents and reagents were purchased as reagent-grade and used without further purification. Compound **1** was characterized by Melting Point, ^{1}H-, and ^{13}C-NMR. ^{1}H NMR spectra were recorded at 25 °C in $CDCl_3$ on a 400 MHz

Jeol instrument. Chemical shifts are reported in ppm downfield from Me_4Si using the residual solvent signals as an internal reference. Coupling constants (*J*) are given in Hz.

1,3,5-Tris(pyridin-4-ylethynyl)benzene 1 - To a solution of **3** (85 mg, 0.55 mmol) in dried *i*Pr_2NH (4 ml), 4-iodopyridine (0.37 g, 1.8 mmol), [$PdCl_2(PPh_3)_2$] (19 mg, 0.03 mmol) and CuI (10 mg, 0.05 mmol) were added under Ar. The mixture was degassed by three "freeze-pump-thaw" cycles and stirred for 16h at rt. Upon completion, monitored by TLC (eluents: AcOEt/cyclohexane 7:3), the crude solution was filtered through celite and the filtrate was cleaned with repeated cyclohexane washing. After the removal of the solvent *in vacuo*, the residue was purified by silica gel chromatography (eluents: AcOEt/cyclohexane 7:3) affording pure **1** as a white crystalline solid (0.15 g, 22%). M.p.: 233-235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* 6.0, 6H, Pyridine-*H*); 7.74 (s, 3H, Ph-*H*), 7.38 (d, *J* 6.0, 6H, Pyridine-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.94, 135.18, 130.58, 125.50, 123.37, 91.40, 88.22. Spectral characterization agrees with previously reported data.[3]

References

1 Sonogashira, K., Tohda, Y. & Hagihara, N. A Convenient Synthesis of Acetylenes: Catalytic Substitutions of Acetylenic Hydrogen with Bromoalkenes, Iodoarenes and Bromopyridines. *Tetrahedron Lett.* **16**, 4467-4470 (1975).

2 Takaishi, S., Kuroyama, Y., Sonogashira, K. & Hagihara, N. A Convenient Synthesis of Ethynylarenes and Diethynylarenes. *Synthesis* **08**, 627-630 (1980).

3 Stang, P. J., Oleyuk, B., Muddiman, D. C. & Smith, R. D. Transition-Metal Mediated Rational Design and Self-Assembly of Chiral, Nanoscale Supramolecular Polyhedra with Unique T Symmetry. *Organometallics* **16**, 3094-3096 (1997).

Coexistance of phase α and phase β at intermediate coverage (0.2 ML to 0.5 ML).

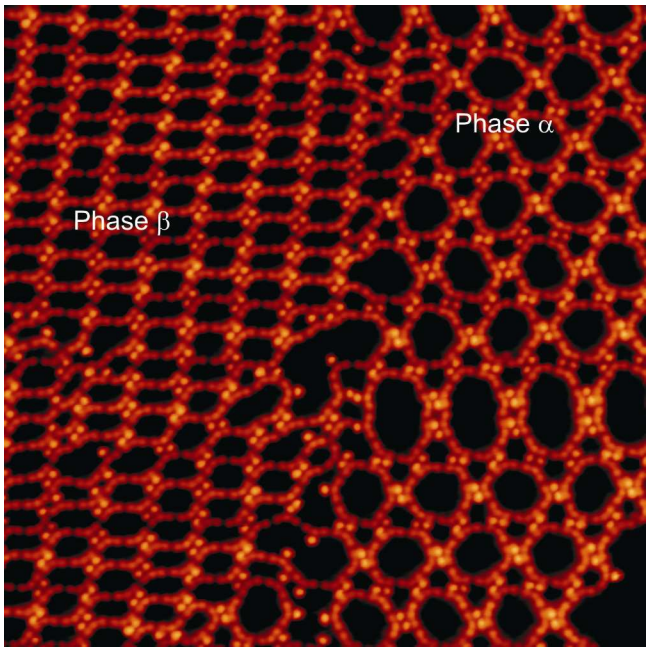


Figure SI 1. Self-assembly of module **1** on Cu (111) for a coverage of 0.2 ML. A high resolution STM (CO terminated tip) image highlights the coexistence of two different 2D short range disordered crystalline networks (phase α and phase β, respectively). Scanning conditions: I = 0.1 nA, V_b = -0.2 V. Size: 395 x 395 $Å^2$.

Crystalline assembly (phase γ) obtained after the deposition of 0.6 ML of compound 1 on Cu(111).

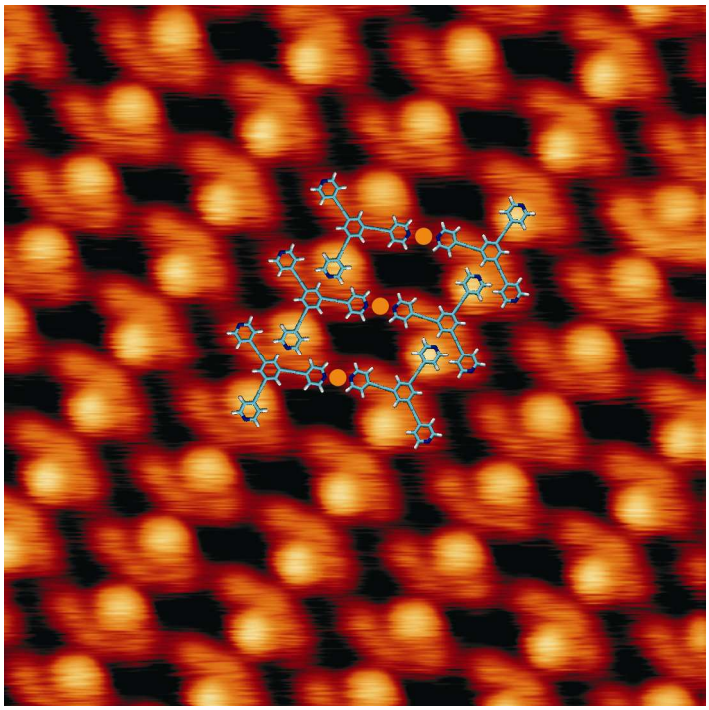


Figure SI 2. Crystalline assembly of compound 1 on Cu(111) at height coverage. STM image and molecular model superposition. The assembly is made by just one scissomer, the same as in phase β, exhibiting two different orientations. The network is stabilized by a simultaneous expression of pyridyl-pyridyl and pyridyl-Cu-pyridyl interactions. Image size: 93 x 93 $Å^2$. Tunneling parameters: a) I = 0.2 nA, V_b = 1.3 V.

Types of pores that constitute the 2D random network.

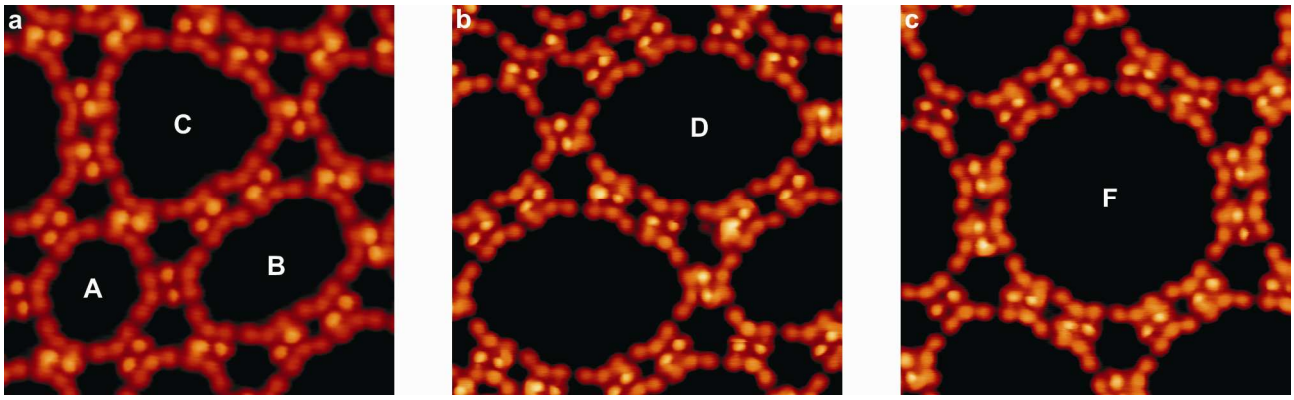


Figure SI 3. High resolution STM images (CO terminated tip) depicting different types of pores that constitute the 2D random network coexisting with phase α after the deposition of compound **1** on Cu(111). All image sizes are 121 x 121 $Å^2$. Tunneling parameters: a) I = 0.1 nA, V_b = -0.2 V; b-c) I = 0.1 nA, V_b = -0.08 V.

Flexibility of building blocks of phase α shown during scanning with an STM tip.

A movie is provided displaying the variation of the shape of the pores A of phase α by a mechanism exploiting the flexibility of the terminal pyridyl legs.

Technically, the movie presents images of 444 x 444 $Å^2$ size, a resolution of 512 x 512 lines, with a scanning speed of 0.328 s/line, which gives a total time of 336 seconds per image. Tunneling parameters for all the images are I = 0.11 nA, V_b = -0.7 A.

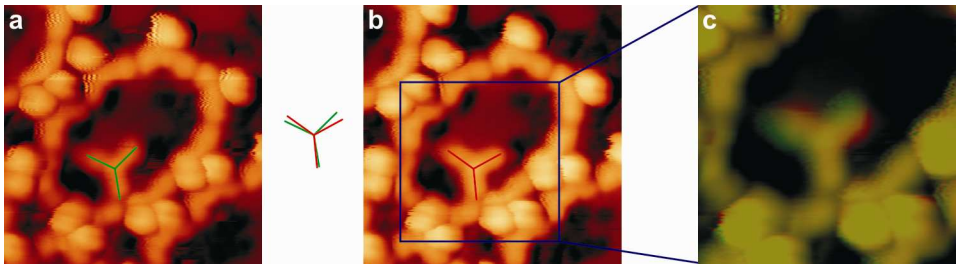


Figure SI 4. STM images depicting the molecular flexibility of compound **1** on Cu(111) induced by scanning with an STM tip. a) Initial and final b) configuration of a molecule trapped in a pore of type B. Images a and b were recorded subsequently. c) Zoom in and color code superposition on image a) of the difference between image a) and a subsequent image (b), after inducing a change in the conformation of the trapped molecule via STM tip scanning. A "stick" representation is used to clarify the flipping of two of the pyridyl functions of the molecular module. Images sizes: a-c) 71 x 71 $Å^2$; c) 45 x 45 $Å^2$. Tunneling parameters: a-c) I = 0.5 nA, V_b = -1.4 V.