ESI to accompany:

Programmed assembly of 4,2':6',4"-terpyridine derivatives into porous, on-surface networks

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Methods section

Samples were prepared and investigated under ultrahigh vacuum (UHV) conditions with a base pressure of 5×10^{-11} mbar. Substrates were prepared by cycles of sputtering the Au(111) crystal (MaTecK GmbH) with Ar⁺ ions at 1 keV and subsequent annealing at 630 K. Molecule deposition onto the sample was done by thermal evaporation from a commercial evaporator (Kentax GbmH) at 480 K. Metal adatoms were supplied by e-beam evaporator (Oxford Applied Research). Coverage was controlled by a quartz crystal microbalance. All preparation steps and the X-ray photoelectron spectroscopy (XPS) measurements were carried out at room temperature. The XPS measurements were performed at the Laboratory for Micro- and Nano-technology at the Paul Scherrer Institute (PSI). A monochromatic Al k α X-ray source was used, resulting in a full width at half maximum (FWHM) of 1 eV. Peak analysis was performed with Unifit software. All STM images were recorded with 1 V and 10 pA, at 5 K in constant current mode (Omicron Nanotechnology GmbH) and processed with WSxM software.¹ The STM tip was made of 90% Pt and 10% Ir wire, mechanically cut and sputtered *in situ* with Ar⁺ ions.



Fig. S1. Arrangement of molecules of ${\bf 1}$ in the close-packed domain which permits $NH_{imidazole} \hdots NH_{tpy}$ hydrogen bond formation.



Fig. S2. Chirality imposed on the 6-fold motif supported by $\rm NH_{imidazole} ^{...} N_{tpy}$ hydrogen bonds (imidazole units in red); one dimeric motif between adjacent hexamers is highlighted in blue.



Fig. S3. Domains with opposite handedness are present on the Au(111) surface.



Fig. S4. Overview image showing the chains of metallomacrocycles which generally follow the Au(111) herringbone reconstruction.



Fig. S5: XPS analysis of multilayers of **1** on Au(111). Total C:N ratio => 3.6:1 (corresponding to 18:5) N 1s deconvolution => -NH- : -N= ratio is 1:4 Detailed N 1s peak positions analysis is presented in Table S1.

Table S1: XPS N 1s peak positions of **1** experimentally obtained, imidazole -NH, pyridine and imidazole -N=, and Cu-coordinated N.

Molecule/Substrate	-NH [eV]	-N= [eV]	N-Cu [eV]
Multilayer 1 /Au(111)	400.3	398.9	-
1 /Au(111)	399.6	398.3	-
1 +Cu/Au(111)	399.6	398.3	399.7

Table S2: Literature comparison of values in Table S1.

-NH [eV]	- N = [eV]	N-Cu [eV]
399.9 ²	398.3 ⁴	400.2^{4}
399.8 ³	398.6 ²	
	398.8 ³	

- 1 I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705.
- 2 X. F. Dai, J. L. Qiao, X. J. Zhou, J. J. Shi, P. Xu, L. Zhang and J. J. Zhang, *Int. J. Electrochem. Sci.*, 2013, **8**, 3160.
- A. Shchyrba, C. Wäckerlin, J. Nowakowski, S. Nowakowska, J. Björk, S.
 Fatayer, J. Girovsky, T. Nijs, S. C. Martens, A. Kleibert, M. Stöhr, N. Ballav, T.
 A. Jung and L. H. Gade, *J. Am. Chem. Soc.*, 2014, **136**, 9355.
- 4 D. Skomski, C. D. Tempas, K. A. Smith and S. L. Tait, *J. Am. Chem. Soc.*, 2014, **136**, 9862.