

ELECTRONIC SUPPLEMENTARY INFORMATION

Convergent and divergent two-dimensional coordination networks through substrate-activated or quenched alkynyl ligation

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CONTENTS:

1. Methods and experimental details
2. Statistical analysis of Ni-1 coordination motifs
3. References

1. Methods and experimental details

All experiments have been carried out in two separate ultrahigh vacuum chambers (base pressure $\sim 2 \times 10^{-8}$ Pa) hosting a home-made variable-temperature scanning tunnelling microscope (STM) and a low-temperature STM (5 K), respectively, and standard tools for preparation of well-defined metal surfaces.

Clean Cu(001), Ag(001) and Au(111) surfaces were prepared by repeated cycles of Ar⁺ sputtering and annealing to 800 K, followed by a slow substrate cooling to room temperature. The metal-organic networks were prepared either by subsequent deposition of molecular species and metal atoms (Ni or Fe) at room or elevated temperature with and without post-annealing up to 450 K or by simultaneous deposition of Fe atoms and 4,4'-di-(1,4-buta-1,3-diyne)-benzoic acid (**1**) on the substrate held at 450 K.^{S1, S2}

The molecules of **1** were deposited by thermal evaporation from a quartz crucible held at the temperature of 560 K and metal atoms using a standard e-beam evaporator (Omicron EFM3) at a flux current of 1 nA. During the deposition (5 – 45 minutes) the pressure was lower than 2×10^{-7} Pa. Subsequently, the samples were transferred to the STM. STM images were acquired either at room temperature or 5 K using electrochemically etched tungsten or gold tips with a sample bias in the range from -1.4 to +1.0 V and tunnelling currents ranging from 0.08 to 1.0 nA. The detailed parameters used for each image presented in the main text are listed in table S1.

The synthesis of the molecules **1** is described in the Supporting Information of ref. S1.

Table S1. Acquisition parameters for images presented in the main text: bias voltage (U_B), tunnelling current (I), and sample temperature (T ; RT = room temperature, *i.e.* 293 – 308 K).

Figure	U_B (V)	I (nA)	T	Figure	U_B (V)	I (nA)	T
1(a)	-0.6	0.3	5 K	3(a)	-1.1	0.2	RT
1(b)	-0.2	0.3	5 K	3(b)	-1.1	0.2	RT
1(c)	-0.9	0.08	RT	4(a)	-1.3	0.2	RT
1(d)	-1.4	0.2	RT	4(b)	-1.2	0.2	RT
2(a)	1.0	0.5	5 K	5(a,b)	-1.2	0.2	RT
2(b)	0.5	1.0	5 K	5(c)	-1.3	0.2	RT

2. Statistical analysis of Ni-1 coordination motifs

The detailed analysis on Ni-induced bending of **1** and Ni-1 binding motifs observed in Fig. S1a (reproduced Fig. 4a from main text) is shown in Fig. S1b-d.

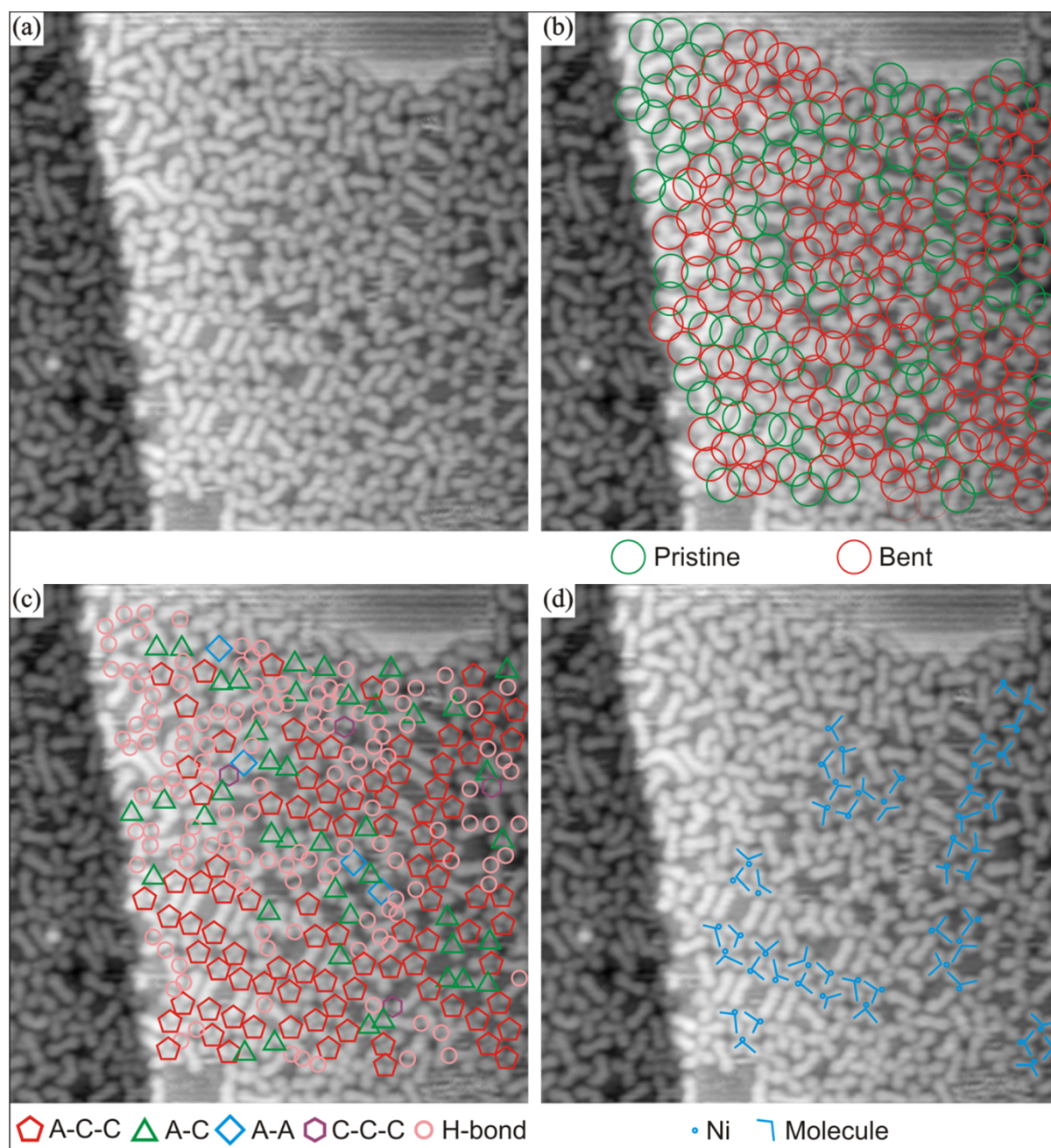


Fig. S1. (a) Non-marked image used for a detailed analysis presented in (b) – (d). (b) Classification according to the molecule shape: the pristine and the bent molecules are marked by green and red circles, respectively. (c) Classification according to different coordination motifs (synthons) featuring Ni and either alkynyl (A) or carboxyl (C) groups of distinct molecules. The residual hydrogen bonding (H-bond) is marked where possible. (d) Basic structural units, in which all molecules display Ni-alkynyl binding, are highlighted by broken lines.

The classification of molecules **1** according to their shape presented in Fig. S1b reveals that there is still a significant number of molecules possessing an unperturbed shape, *i.e.* the one observed in the pure molecular phases. The positions of the pristine molecules and residual patches of the deprotonated molecular phase suggest that the Ni-**1** disordered coordination network is formed by transformation of the deprotonated molecular phase without a significant transport of molecular components.

Upon Ni binding **1** reshapes as a result of re-hybridization of one of its alkynyl bonds. The resulting bending angle is close to 90° but it can vary to accommodate the mutual binding with surrounding molecules. As drawn in Fig. S1c the dominant binding motifs are Alkynyl-Carboxyl-Carboxyl (A-C-C) – 66 % (excluding hydrogen bonding), and Alkynyl-Carboxyl (A-C) – 29 %. The other types – Alkynyl-Alkynyl (A-A), and Carboxyl-Carboxyl-Carboxyl (C-C-C) – constitutes only a minor fraction of the total number of all coordination motifs, *i.e.* 3 % for A-A and 2 % for C-C-C. The ratio of dominant modes determined on different samples and in different images varies depending on the sample preparation: the relative fraction of the A-C-C motif increases from 20 to 66 % at the expense of A-C (75 – 30 %) with increasing Ni:**1** ratio and increased post-annealing temperature. Moreover, a relatively large fraction of binding is still mediated by hydrogen bonding. The complexity of the disordered phase is further increased by the fact that Ni atoms are either positioned at the surface or embedded within the first substrate layer.^{S2}

The Ni-**1** basic structural units are highlighted in Figure S1d. Their categorisation reveals three dominant structural units as depicted in Fig. S2a-c.

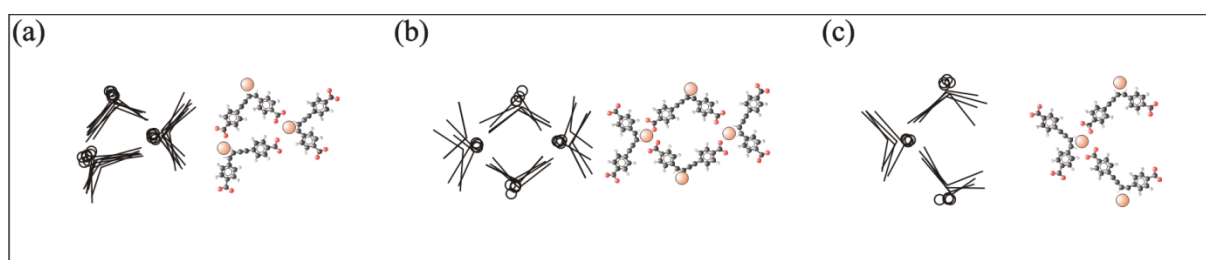


Fig. S2. Tentative models of mutually aligned basic structural units displayed in Fig. S1d. The broken line/ball sketches show the observed spread in the position of metal atoms and the shape/position of the molecules.

6. References

(S1) C. S. Kley, J. Cechal, T. Kumagai, F. Schramm, M. Ruben, S. Stepanow, and K. Kern, *J. Am. Chem. Soc.*, 2012, **134**, 6072.

(S2) J. Cechal, C. S. Kley, T. Kumagai, F. Schramm, M. Ruben, S. Stepanow, and K. Kern, *J. Phys. Chem. C*, 2013, **117**, 8871.