

Competing Interactions in Surface Retention with a Prochiral Dicarbonitrile Linker

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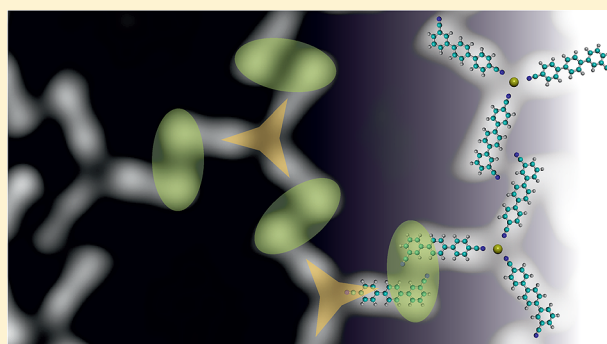
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S Supporting Information

ABSTRACT: The organic and metal-directed assembly of a prochiral carbonitrile (CN) oligophenyl molecule on a smooth noble metal substrate was investigated by combined scanning tunneling microscopy and computational modeling. The molecule is functionalized with two CN groups in *meta* and *para* positions of the terminating phenyl rings of the *p*-terphenyl backbone. Upon deposition on a Ag(111) surface, we observe two different organic supramolecular networks, one of them reflecting a chiroselective assembly. After coevaporating small amounts of Co, a hybrid network comprising both CN–phenyl and metal coordination bond motifs could be observed. Intriguingly, the CN group in the *para* position is favored for the metal coordination, whereas the *meta* group remains in a CN–phenyl motif. Computational modeling suggest that the high stability of the *meta* CN–phenyl motif is causing this selective interaction. An increase of the metal adatom ratio eventually induces divergent assembly of a room-temperature stable 2D random metal–organic network.



INTRODUCTION

The principles of supramolecular chemistry¹ offer promising routes to design specific molecular assemblies fulfilling the needs of functional surfaces for gas sensing,² surface protection,³ and molecular electronic⁴ applications. A detailed understanding of the organization of low-dimensional self-assembled structures on interfaces is essential to develop strategies for further applications.^{5–7} A series of synthesis protocols have already been tested employing van der Waals forces or dipolar interactions,^{8,9} hydrogen bonding,^{10–12} and metal–ligand coordination.^{13–16} In particular, metal–organic coordination compounds comprise robust bonds with a typical strength of $\approx 100 \text{ kJ mol}^{-1}$, resulting in room-temperature (RT) stable structures¹⁷ that are moreover of special interest for the exploration of interfacial metal–organic frameworks (so-called SurMOFs).¹⁸ However, only rarely has the simultaneous action of metal coordination bonding and other noncovalent interactions been explored for the fabrication of nano-architectures.^{19–21}

Chainlike oligophenyl molecules are of interest due to their promising light-emitting properties^{22,23} and have been successfully employed to create self-assembled metal coordination networks on metal surfaces when functionalized with carbonitrile groups.²⁴ The prefixes *para* and *meta* describe the position of the CN substituents at the terminating phenyl ring

in relation to the position of the adjacent phenyl ring. A linear species with two CN groups on both ends in *para* positions^{13,25–31} and a nonlinear species with its functional groups in *meta* positions of the terminating phenyl rings^{16,32} were studied until now, and this class of molecules will be referred to as linkers in the following. The supramolecular structures exhibit striking differences depending on the length of the molecular backbone and the position of the functional CN groups. *para* dicarbonitrile polyphenyl species (backbone length of three to six phenyl entities) form highly regular Co-directed nanomeshes that are templated by the surface.^{13,27,29,30} By changing the CN groups' position from the *para* to the *meta* site, a 2D random network evolves with a multitude of motifs.¹⁶ The molecule presented here is an intermediate between both linker types and was designed to shed light on the formation mechanism of regular and disordered structures.

We report here on the self-assembly of [1.1';4',1'']-terphenyl-3,4''-dicarbonitrile (*pNC-pPh₃-mCN*) molecules on Ag(111) studied by scanning tunneling microscopy (STM) at 6 K and at RT in the absence and presence of Co adatom coordination centers.

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METHODS

The compound $[1.1';4',1'']$ -terphenyl-3,4''-dicarbonitrile is known in the literature³³ but has been synthesized in a different way. To avoid the formation of an isomeric mixture, the synthesis has been performed stepwise by coupling 1-bromo-4-iodo-benzene with 1 equiv of 3-phenylboronic acid first and with 1 equiv of 4-phenylboronic acid on the second step under typical Suzuki conditions with 10 mol % Pd(0). A detailed description of the synthesis can be found in the Supporting Information. The geometry of the free molecule was calculated in the semiempirical AM1 framework. STM images have been processed using the WSxM software.³⁴ The experiments were performed using an Aarhus variable-temperature (cf. www.specs.de) and a Createc low-temperature STM (cf. www.createc.de and ref 35). The employed Ag(111) substrate was prepared by standard procedures (cycles of Ar⁺ sputtering and annealing) to obtain extended, flat terraces separated by monatomic steps. The molecules were deposited from a quartz crucible in an organic molecular-beam epitaxial source at 450 K, with the substrate kept at 300 K. Subsequently, the submonolayers of the molecular films were exposed to a beam of cobalt atoms. After the preparation, the sample was transferred in situ to the STM, where the topography was recorded at $T = 300$ or 6 K. The images presented in Figure 5a,b were measured at room temperature. Figures 2a–c and 3a,b comprise micrographs recorded at 6 K. To simplify the calculations and their interpretation, the substrate was not considered in the first principle calculations, and only the intermolecular binding was studied. It was assessed using the projector augmented-wave (PAW) approach as implemented in the ABINIT code,^{36,37} within the local density approximation (LDA) for the exchange-correlation energy. The cutoff energy used is 30 Ry. Periodic boundary conditions were applied, and a minimal void spacing of 8 Å is present between image molecules, ensuring an error lower than 10 meV/molecule as drawn from convergence checks. All atoms are in the same plane, and full relaxation is allowed within the plane.

RESULTS AND DISCUSSION

The molecule *p*NC-*p*Ph₃-*m*CN consists of three phenyl rings forming the molecular backbone connected by two rotatable σ -bonds (see Figure 1). Two reactive CN groups at the outer phenyl rings in *meta* and *para* positions enable the molecule to form 2D supramolecular networks.^{13,28,29} Upon adsorption, the prochiral molecule isomerizes into a *laevus* (L) and a *dexter* (D) enantiomer. To distinguish between these two isomers, we marked the L-species with red and the D-species with blue

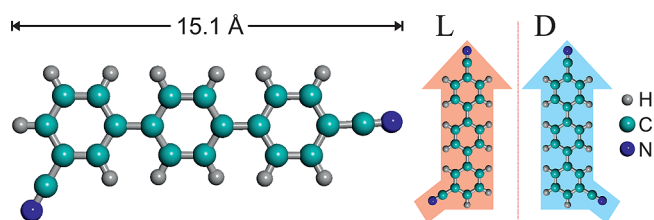


Figure 1. Atomistic model of $[1.1';4',1'']$ -terphenyl-3,4''-dicarbonitrile (*p*NC-*p*Ph₃-*m*CN) with an approximate length of 15.1 Å. Adsorbed on the surface, the molecule deconvolutes into two enantiomers: L and D marked with the red and blue arrow, respectively. In the atomistic molecular model, blue indicates nitrogen, cyan carbon, and white hydrogen.

arrows. The arrowhead points to the direction of the *para*-oriented CN group, whereas the direction of the *meta* CN group is labeled by the short tail pointing either left or right. After deposition, a natural ratio of 50% L- and 50% D-enantiomers can be assumed to be present on the surface.³⁸ On the surface, the molecule is imaged as a rodlike protrusion with a length of ~ 13 Å and an apparent height of 1 Å. Polyphenyl molecules are well-known to adsorb preferentially with their extended π -system nearly parallel to the substrate on noble metal surfaces, such as Ag(111).^{13,25,39} At low coverage, the molecules decorate preferentially the bottom side of the step edges, suggesting a high mobility of the molecules at RT. With increasing coverage, the molecules assemble in islands.

Organic Supramolecular Assembly. Figure 2a shows an STM topography overview at 6 K of the structures formed by

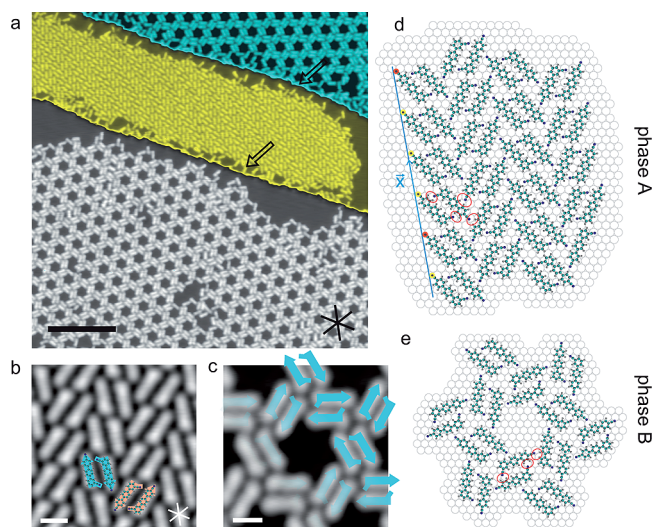


Figure 2. Molecular self-assembly of nonlinear dicarbonitrile linkers on Ag(111) at 6 K visualized by STM. (a) Two phases are visible on different terraces ($U_t = -0.6$ V, $I_t = 0.21$ nA, scale bar = 11 nm). The high symmetry directions of the surface are marked by the black star. (b) The dense-packed structure can be found in three orientations and its mirror symmetric equivalents ($U_t = -0.06$ V, $I_t = 0.41$ nA, scale bar = 1 nm; high symmetry directions of the surface marked by white star). (c) A hexagonal chiral phase comprising exclusively one enantiomer (D) of the molecule ($U_t = -0.05$ V, $I_t = 0.1$ nA, scale bar = 1 nm). (d) Atomistic model of the dense-packed structure apparent in (a) and (b). (e) Atomistic model of the porous phase visible in (a) and (c).

the nonlinear ditopic linker after deposition of ~ 0.5 ML on a Ag(111) surface at 300 K. Three terraces with two different molecular patterns are resolved. A dense-packed layer (phase A) in yellow and a honeycomb pattern (phase B) marked in gray and blue are identified. Phase A has a density of 0.98 molecules/nm², which is significantly higher than the one of phase B (0.64 molecules/nm²). In either phase, the regular pattern is distorted close to the step edges (marked with an arrow). The islands are extended over wide areas in a highly regular manner, just limited by the terrace size. RT experiments show that phase A is RT-stable but phase B is not. A 2D surface gas of highly mobile molecules is present between the dense-packed islands at RT. Phase B is thus presumably evolving from the surface gas phase while cooling down the sample.

For a detailed structural analysis, high-resolution low-temperature STM images from the chevron-like formation in

phase A (Figure 2b) and the porous hexagonal structure in phase B (Figure 2c) were recorded. Phase A exhibits one basic intermolecular bond motive (blue and red arrows in Figure 2b) comprising two molecules with the same chirality aligned antiparallel and stabilized by CN–phenyl attractions between the *meta* positioned CN group and the neighboring molecule organic ring system. The underlying driving force is the recently described attractive interaction between proton acceptors and organic ring systems.⁴⁰ This most reasonable interaction between two molecules forming a dimer results in the slight offset between the two molecules within the dimers and allows us to assign a certain chirality to the molecules. The atomistic model depicted in Figure 2d is based on careful measurements of orientations in the networks combined with the assumptions that the phenyl backbone follows the high symmetry substrate directions and the preferred CN adsorption site is the hollow position.²⁵ Vector $\vec{x}$ is pointing in the direction of identical dimer rows and is tilted about 20° away from the substrate high symmetry direction. Every fourth molecule along this direction is placed on a hollow position (red dot in Figure 2d), and the three molecules in between are at intermediate position (marked yellow). The intermolecular bonds stabilizing the organic network are marked with red circles in the atomistic model. The bond distances are consistent with *ab initio* calculations of adsorbed porphyrins with CN terminated substituents⁴¹ and comparable to previous experiments on similar dicyanitrile polyphenyl species.^{25,28,29,32} Phase A contains both surface enantiomers in the same ratio, and three orientations with respect to the Ag(111) high symmetry axes plus their mirror symmetric counterparts were found, reflecting the substrate three-fold symmetry.

Phase B exhibits organizational chirality and comprises the dimer motif as well. Figure 2c shows a high-resolution image of the blue area in the overview (Figure 2a) superimposed with arrow symbols indicating the orientation and the chirality of the molecules. The formation consists exclusively of D-type enantiomers, implying enantioselectivity during the self-assembly process. On the other hand, the fact that only one type of enantiomer can be found on each terrace might reflect chirality switching during network formation. Such a process requires a rotation of the phenyl ring with the CN group in the *meta* position parallel to the σ -bond connection of two adjacent phenyl rings. The feasibility of this rotary motion is supported by recent findings where complex adsorbed molecules undergo similar conformational changes.⁴² The weak interaction of the phenyl ring with the substrate supports a rotary motion as well.^{43,44} The gray area in Figure 2a is the same structure composed of dimer motifs assembled by L-enantiomers. Both hexagonal structures are oriented $\pm 15^\circ$ away from the $\langle 1\bar{1}0 \rangle$ substrate direction. However, both orientations are commensurate with the substrate (atomistic model depicted in Figure 2e). The pore size of the hexagons is $\sim 10 \text{ nm}^2$. Some pores host guest molecules, but the overall network organization remains unaffected by the additional molecules. Defects have generally been found due to dislocations in the substrate or near step edges. The coexistence of phases A and B hints to very similar energetics within the two phases being both based on the same inherent dimer building blocks. Although, a coexistence of both phases on the same terrace could not be observed.

Selective Metal–Ligand Interactions in a Molecular Network. The homogeneity and long-range order in the organic layer vanishes after adding Co adatoms to a surface with $\sim 0.4 \text{ ML}$ of molecules, and the open porous random

network depicted in Figure 3a evolves, showing the situation for a Co/linker ratio of $\sim 1.3:3$. Herewith, the cobalt adatom

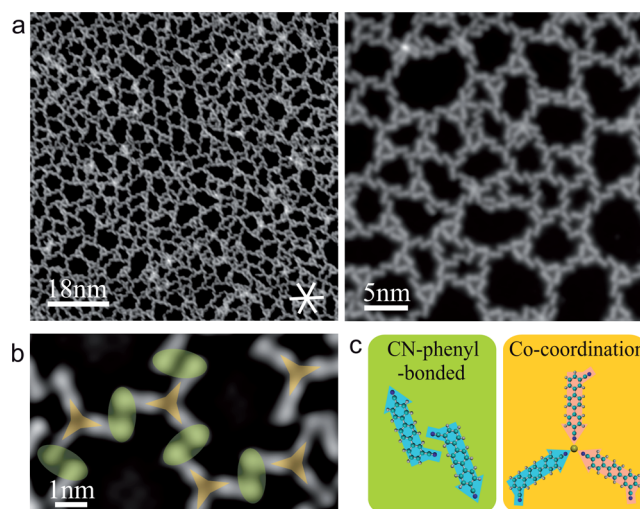


Figure 3. Hybrid Co-coordinated and CN–phenyl random porous network visualized with STM at 6 K. (a) STM overview image on the structure after coevaporation of only a small amount of Co adatoms ($U_t = -0.6 \text{ V}$, $I_t = 0.11 \text{ nA}$). (b) High-resolution topographic image of the hybrid structure combined with a superimposed color scheme marking the bond nature. Green marks the CN–phenyl motive and yellow the Co-coordination ($U_t = -1.0 \text{ V}$, $I_t = 0.2 \text{ nA}$). (c) Atomistic models of the dominant bond motifs (highlighted with the same color code).

amount is too low to coordinate all CN groups. The network comprises a combination of Co centers with preferential three-fold carbonitrile coordination (marked in yellow in Figure 3b) and CN–phenyl bonding motifs (marked in green in Figure 3b), showing irregular pores with a size ranging from 5 to 50 nm^2 . It is highly remarkable that the *para* positioned CN group seems to be favored to coordinate to the Co metal centers compared to the *meta* positioned CN group in this substoichiometric assembly. Every CN group in the *para* position is coordinated to the Co adatom, whereas the *meta* positioned CN group is only metal coordinated if the molecule is connecting two metal centers. For the given ratio between linkers and Co adatoms, $\sim 60\%$ of the molecules form a *para*-coordinated starlike trimer motive that interacts with adjacent trimers via the residual uncoordinated CN groups in the *meta* position. Figure 3c depicts an atomistic model of the two dominant supramolecular motifs (CN–phenyl interaction in green and the coordination node in yellow). The metal coordination motif is already known from hexagonal networks employing molecules with two *para* positioned CN groups and variable chain length.^{25,30} The starlike formation of the Co-coordinated structure exists with all combinations of surface enantiomers, and its composition seems to be dictated by the interaction with the neighboring trimers. The structure as a whole is not RT-stable, and the outer phenyl rings with the *meta* positioned CN groups assumably adapt by rotation of the terminal phenyl ring to neighboring trimers during cool down. The flexibility of three-terminal molecular modules has been reported to promote disorder in 2D confined molecular networks²¹ and is the most likely reason for preventing the network presented here from stabilizing into a regular structure. An influence of the surface atomic lattice on the random network formation could not be observed.

There are two possible reasons why the *para*-oriented CN group is favored to coordinate to the metal centers. One might be a different chemical reactivity of the two CN groups of the molecule. Similar to organic chemistry of electrophilic aromatic substitution reaction,⁴⁵ the electronic structure of the *para* positioned CN group might differ from the *meta* positioned CN group, resulting in a diverging chemical reactivity. The other reason might be that the network is optimizing its energy by favoring the *meta* CN–phenyl bond type depicted in Figure 3c. To illuminate the origin of the different affinity of *para* and *meta* groups toward the metal center, we performed density functional theory calculations for the CN–phenyl interaction. The respective binding energy (E_B) per molecule was evaluated for the most prominent CN–phenyl bond configurations shown in Figure 4. The pertaining energies are specified in

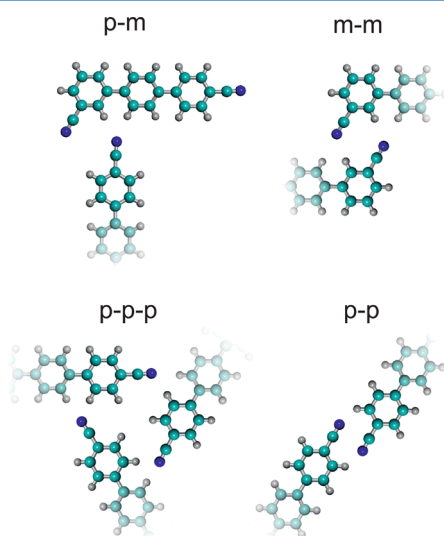


Figure 4. Atomistic model of the four most evident CN–phenyl bond motifs used in the DFT calculations of the binding energies.

Table 1. Evaluation of the Binding Energy per Molecule (E_B), Calculated by DFT for the Molecular Motifs Shown in Figure 4

	<i>p-m</i>	<i>m-m</i>	<i>p-p</i>	<i>p-p-p</i>
E_B [meV]	~300	600	436	310

Table 1 and are comparable to the bond energies found in similar CN–phenyl stabilized networks.⁴⁶ The *m-m* motif features the highest binding energy since it offers a geometrical stabilization by two noncovalent bonds supporting each other similar to a chelate complexation.⁴⁷ Though the influence of a divergent chemical reactivity of the molecules CN groups cannot be excluded from affecting the structure of the network, it is clear that there is an appreciable energy gain of the entire network when the *meta* positioned CN groups are involved in *m-m* bond motifs.

Fully Reticulated Metal–Organic Network. By increasing the amount of Co in the molecular pattern, a completely reticulated metal–organic network evolves. The assembly depicted in Figure 5a is characterized by an oversupply of Co, resulting in a fully saturated metal–organic network (bright spots on the surface represent Co clusters and indicate an

excess of Co), and the Co-coordination is now the exclusive binding motive stabilizing the network even at RT. The whole random metal–organic network is built by only a small selection of possible coordination motifs (for a list of all possible three- and four-fold metal–organic coordination motifs, see the Supporting Information), and it is noteworthy that it strikingly resembles the one found for the similar asymmetric linker that has both CN groups in the *meta* position¹⁶ (*mNC-pPh₃-mNC*), though the number of adsorption-induced conformations is reduced from three to two in the present network. On the other hand, the number of potential coordination node motifs remains unchanged compared to the *mNC-pPh₃-mNC* assembly since a directionality of the molecule in the nodal motifs, not present before, has been introduced as an additional degree of freedom. Typical arrangements of three- and four-fold coordinated chain motifs are illustrated in Figure 5b. Besides the chain motifs, bifurcation motifs of the pattern exhibit three- and four-fold coordination as well. A low molecular coverage leads to an enhanced number of chain motifs, and with increasing coverage, the bifurcation motifs become more prominent. In contrast to the hybrid network described above, the fraction of the three-fold coordination motifs dropped from almost 100% to 56%. A statistic of the node distribution is shown in Figure 5d. DFT calculations for a phenyl ring tailored with two CN groups on opposite sides indicate an energy preference for the three-fold coordination of about 90 meV per coordination node.²⁹ A frequently found motif in the pattern is a metal–organic dimer (MOD) that consists of two homochiral molecules aligned antiparallel with their backbones and connected by a Co adatom between the CN groups. Two of these MODs can only be joined by a four-fold coordinated Co adatom.

The atomistic models in Figure 5c display two characteristic node formations predominant in the network including the MOD formation (red circle). The formerly expressed starlike formation is not a decisive structural motive anymore. For *mNC-pPh₃-mNC*, a similar dimer formation was found³² where the *meta*-oriented CN groups point toward each other and are coordinated by a Co adatom. Within the MOD, the *meta* positioned CN groups coordinate with the Co metal adatom as well as the *para* CN group of the neighboring molecule. A single dimer only comprises one enantiomer; nevertheless, the natural ratio between the two surface-induced enantiomers is preserved in the overall structure. In contrast to the organic network, the chiral selectivity is confined to the interaction of two molecules constructing a MOD. The coordination of *meta* positioned functional groups presumably hinders the backbone rotation and the commutation of the surface enantiomers during cool down, and the entire character of the adsorbate–adsorbate interaction is changed toward predominantly lateral metal coordination.

CONCLUSION

We studied the organic and metal-directed assembly of the asymmetric ditopic *pNC-pPh₃-mCN* linker molecule on Ag(111) with STM at 6 K and room temperature. Our results reveal two surface-induced isomers of the molecule forming two different supramolecular networks, whereby phase A features the molecular isomers in an equal ratio and phase B is enantiopure. The coevaporation of small amounts of transition-metal adatoms (Co) generates structures with competing interactions between metal–organic and organic binding. At small Co concentrations, the functional moieties of

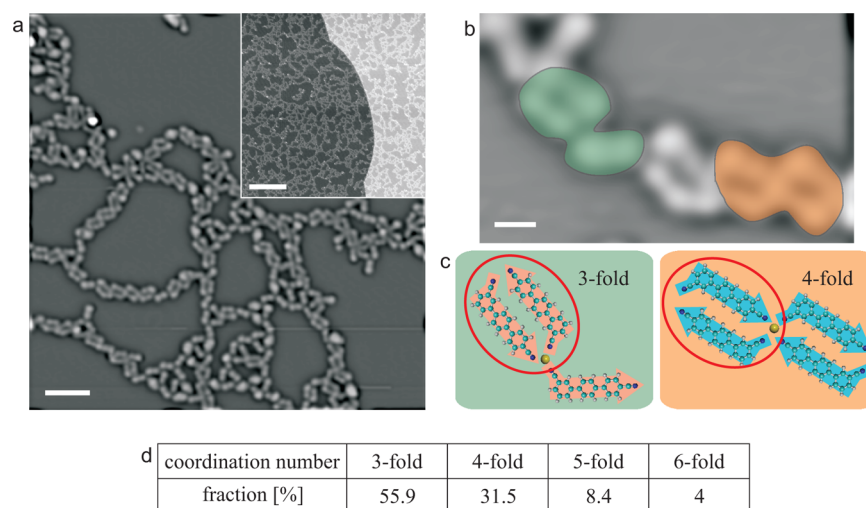


Figure 5. STM images of a Co mediated reticulated random metal–organic network. (a) Topography of the open porous Co-coordinated network built up by repeated metal coordination motifs. The inset shows an overview of the metal–coordination network ($U_t = -0.66$ V, $I_t = 0.1$ nA, scale bar = 5 and 140 nm for the inset, $T = 6$ K). (b) High-resolution image of the main bond motifs ($U_t = -1.0$ V, $I_t = 0.2$ nA, scale bar = 1 nm, $T = 6$ K). (c) Atomistic model of typical three- and four-fold coordination motifs. The red circle marks the metal–organic dimer motif. (d) Evaluation of the node distribution in (a).

the molecule at the *para* position favor three-fold metal–ligand interactions and the functional moieties in the *meta* position CN–phenyl interactions. DFT calculations on different CN–phenyl motifs indicate that there is an energy gain of the entire network when the *meta* positioned CN groups are involved in CN–phenyl bond motifs rather than the *para* positioned CN groups. Additional Co evaporation creates a fully reticulated thermally robust (RT stable) metal–organic network constructed of distinct three- and four-fold nodal motifs. The divergent assembly network exhibits a central metal–organic dimer motif, but no long-range order, similar to recent observations of a 2D random metal–organic network obtained with a related asymmetric linker.¹⁶

■ ASSOCIATED CONTENT

Supporting Information

Survey of possible coordination motifs and synthesis procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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