

Orthogonal Insertion of Lanthanide and Transition-Metal Atoms in Metal–Organic Networks on Surfaces**

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Abstract: The orthogonal coordinative properties of tetrapyrrole macrocycles and nitrile ligands have been used in a multi-step procedure towards interfacial d-f hetero-bimetallic nanoarchitectures based on a free-base porphyrin derivative functionalized with meso-cyanobiphenylene substituents. Molecular-level scanning tunneling microscopy studies reveal that the porphyrin module alone self-assembles on Ag(111) in a close-packed layer with a square unit cell. Upon co-deposition of Gd atoms, a square-planar motif is formed that reflects the fourfold coordination of CN ligands to the rare-earth centers. The resulting nanoporous network morphology is retained following exposure to a beam of Co atoms, which induces selective porphyrin metalation and ultimately yields a gridlike 2D metallosupramolecular architecture.

The design of functional coordination architectures has attracted increasing interest over the last few decades as, depending on the chemical nature of the metal ion center and the organic ligand, these materials may find different applications in gas storage, light-emitting devices, sensing, and electronic devices.^[1] In this respect, the combination of

a supramolecular chemistry approach with advanced scanning probe microscopy and interface analysis techniques has emerged as a powerful strategy to explore surface-confined metal-organic coordination networks (MOCNs) of distinct dimensionality, with ultimate spatial resolution.^[2] A large number of examples describing the coordination aptitudes of different organic ligands with transition metals on surfaces that give rise to discrete^[3] or extended one-^[4] and two-dimensional^[5–7] coordination architectures have been reported. In particular, free-base and metalated porphyrins^[8] were shown to be exceptional scaffolds^[9] that could be deposited on surfaces.^[6,10] Notably metallotetrapyrroles with a flat adsorption geometry present coordinatively unsaturated sites that, depending on their affinity towards axial ligands, provide potential for sensing,^[11,12] catalysis,^[13] and magnetochemistry.^[12]

Surprisingly, molecular-level investigations that focus on assembly procedures relying on orthogonal coordination interactions have been rarely reported to date. Although this approach has been recognized as a versatile conceptual basis to engineer novel materials and nanoarchitectures with multimodal functionalities, it is mostly limited to space-averaging studies that make use of surface-tethered self-assembled monolayers as platforms.^[14] Orthogonal interactions are particularly promising to explore pathways for the controlled organization of different units, including metal centers, in a programmed fashion. Figure 1 illustrates potential routes to handle specific metal centers by combining orthogonal metal-organic interactions on surfaces, by either exploiting peripheral ligand groups (Figure 1a shows a hypothetical case) or by making use of both peripheral moieties and macrocycles (Figure 1b depicts the scenario that has been successfully realized). In this respect, surface-confined hybrid systems containing both lanthanides and transition-metal centers are attractive as they could afford new functional materials with properties that cannot be obtained from the single elements.^[15,16] Potential applications include magneto-responsive devices and molecular spintronics, where unique features can be obtained by magnetic exchange interactions between the 3d and 4f elements.^[16,17]

Considering the low activation barrier for the metalation of tetradentate free-base tetrapyrroles with small metal atoms such as Co or Fe,^[18–20] one could in principle orthogonally coordinate^[14,21] peripheral ligands with larger atoms such as lanthanides. Given this premise, herein we introduce the combination of orthogonal coordination interactions on surfaces to develop exemplary d-f nanoarchitectures.^[14,21] The assembly procedure was directly investigated at the molecular level by using low-temperature scanning tunneling

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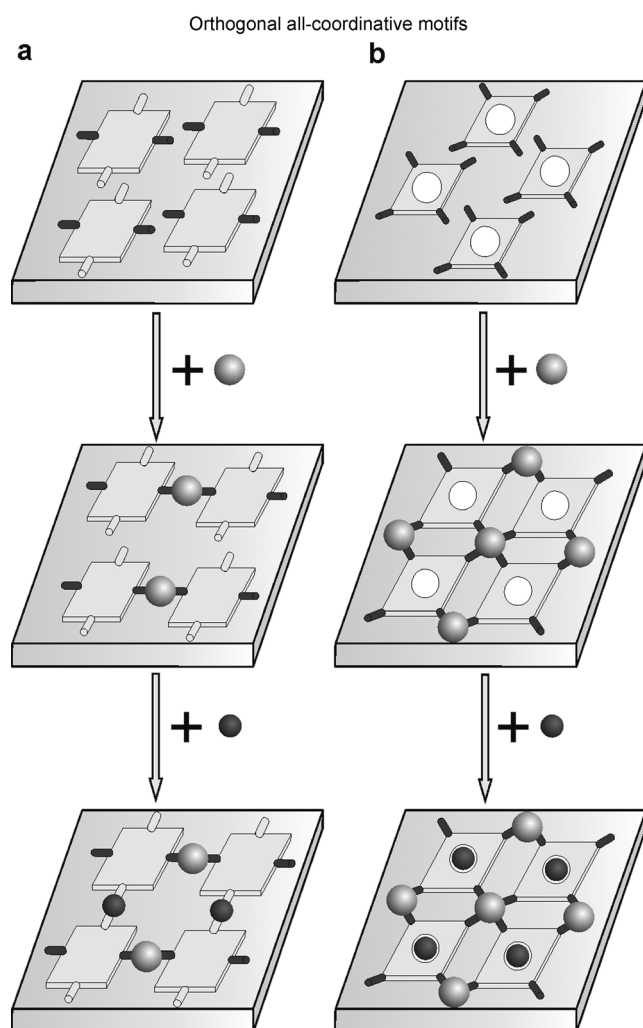


Figure 1. Schematic illustration of envisaged approaches to bimetallic interfacial networks by exploiting coordinative interactions. The combination of two orthogonal motifs that a) make use of peripheral ligands and b) combine them with reactive macrocycles. Metal atoms are depicted by light and dark gray spheres.

microscopy (STM), which reveals subtle details of the resulting arrangements. As an example, we engineered hybrid lanthanide/transition-metal-organic coordination networks on an atomistically clean Ag(111) metal support (see the Supporting Information for the experimental procedures). The employed free-base tetra[(4-cyanophenyl)phen-4-yl]porphyrin (2H-TPCN, Figure 2a and see the Supporting Information for the molecular synthesis) is equipped with four meso-4-cyanobiphenylene ligands. The deposition of Gd atoms onto a preassembled 2H-TPCN array gives rise to a nanoporous metal-organic layer with the cyano groups engaged in fourfold Gd $\cdots$ NC coordination nodes. Subsequent exposure to a beam of Co atoms^[19,20,22] under appropriate conditions results in selective metalation of the tetrapyrrolic macrocycles, while preserving the reticulating Gd $\cdots$ NC motifs, ultimately leading to a hybrid array with the topology of an alternating bimetallic square grid. Importantly, the sequence of metal exposure is a decisive parameter for the successful

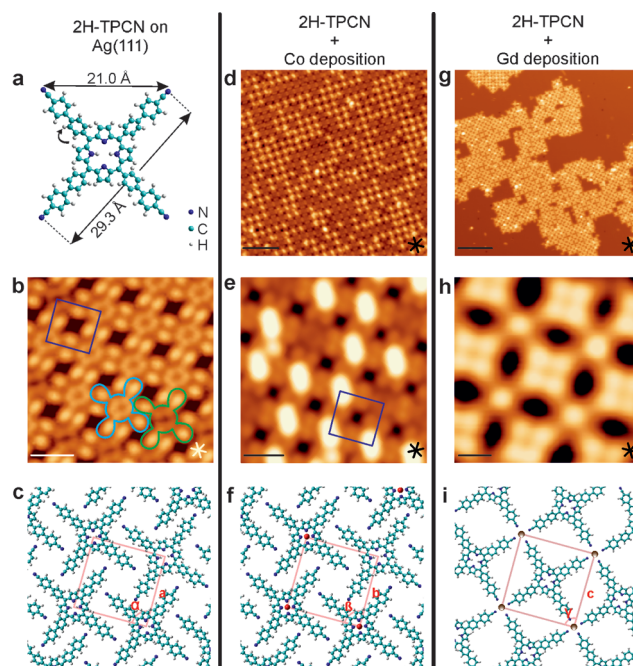


Figure 2. a–c) Tetragonal network formed upon self-assembly of 2H-TPCN on Ag(111). a) Top-view: ball-and-stick model of 2H-TPCN from semiempirical AM1 calculations in HyperChem. b) High-resolution STM image revealing submolecular features. The colored contours (green and blue) indicate the two tautomers ($V_b = -0.5$ V and $I_t = 70$ pA). Scale bar: 2 nm. c) Molecular model of the assembly presented in (b). d–f) Metalation of 2H-TPCN networks on Ag(111) by deposition of Co atoms. d) Overview STM image ($V_b = -1$ V and $I_t = 200$ pA). Scale bar: 10 nm. e) High-resolution image ($V_b = -1$ V and $I_t = 90$ pA). Scale bar: 2 nm. f) Atomistic model of (e) which facilitates the identification of the metalated and nonmetalated macrocycles. g–i) Fourfold Gd-nitrile mononuclear coordination as a result of Gd-directed assembly of 2H-TPCN. g) Overview STM image ($V_b = 0.5$ V and $I_t = 53$ pA). Scale bar: 20 nm. h) High-resolution data of the assembly revealing a 1:1 (2H-TPCN/Gd) stoichiometry ($V_b = 1$ V and $I_t = 67$ pA). Scale bar: 1 nm. i) Atomistic model of (h). For (c, f, i), C, N, H, Gd, and Co atoms are depicted in green, blue, white, brown, and red, respectively. The square unit cells are shown in pink, where a , b , and c represent the side length (see text) and α , β , and γ the enclosed angles.

expression of a bimetallic network capitalizing on orthogonal coordinative interactions.

The deposition of 2H-TPCN on Ag(111) held at 300 K results in the formation of a 2D close-packed assembly. High-resolution STM data (Figure 2b) reveal submolecular features and the layer organization. The porphyrin units appear to be twofold symmetric, with the meso substituents observed as four bright protrusions and the central tetrapyrrolic macrocycles as rings with a bright or a dim appearance (blue or green contour plot in Figure 2b) associated with the tautomers (see Figure S4 in the Supporting Information).^[23] The supramolecular network presents a square unit cell with side length $a = 20.4 \pm 0.5$ Å (enclosed angle $\alpha = 90 \pm 1^\circ$) and is stabilized by lateral noncovalent interactions between neighboring 4-cyanobiphenylene groups (Figure 2b,c, N $\cdots$ H distance: 3.1 ± 0.5 Å).

Based on previous investigations describing the selective metalation of free-base porphyrins by using an atomic beam of Co or Fe at 300 K,^[19,20] in situ Co metalation of a submonolayer of 2H-TPCN was achieved on Ag(111). Consistent with these earlier findings, Figure 2d,e evidences the appearance of a new species with a central rodlike protrusion that we identify as a Co-TPCN derivative. Importantly, the layer organization is preserved in this step, despite the known affinity of CN groups to Co atoms favoring the formation of metal-organic networks at room temperature with related linkers.^[7,24] We attribute this behavior to the increased stability of the preorganized supramolecular network structure stabilized by multiple noncovalent interactions.^[25]

Next we explored the coordination aptitude of 2H-TPCN towards Gd atoms, which were also evaporated onto a submonolayer of 2H-TPCN held at 300 K. In marked contrast to the fivefold coordination nodes formed by dicyano-oligophenylene ligands and Ce or Gd on Ag(111),^[26] an extended porous gridlike array is formed with a mononuclear square-planar motif (Figure 2g,h). No porphyrin metalation interferes, and the Gd centers appear as bright round protrusions regardless of the bias polarity. A statistical analysis of the Gd...NC distances gives a projected average bond length of 2.7 ± 0.5 Å, in agreement with recent STM observations on Gd-dicyano-oligophenylene units.^[27] The Gd nodes span a square network with a unit cell vector $c = 24.5 \pm 0.5$ Å. The TPCN orientation with respect to the atomic lattice of the close-packed substrate is identical in the noncoordinated and coordinated cases. The absence of macrocycle metalation by Gd is tentatively assigned to a higher activation energy barrier (as also observed in the liquid phase),^[28] the larger geometric footprint and adsorption energy of 2H-TPCN. Interestingly, structural analogues exist in the solid state, where lanthanide centers can steer the expression of two-dimensional fourfold-reticulated sheets in *ab* planes.^[29] The propensity of 2H-TPCN linkers towards lateral coordination also prevails with increased substrate temperatures up to 500 K during Gd deposition, and the same two-dimensional superstructure is found without any evidence of metalation.

Taking advantage of the affinity of the tetrapyrrolic macrocycle for Co atoms and the selective formation of fourfold Gd...NC interactions, we thus probed the fabrication of heterometallic networks containing both Gd and Co atoms. To this end, Co atoms were evaporated onto a 1:1 2H-TPCN/Gd network with the substrate held at 300 K. The STM data depicted in Figure 3a,b clearly reveal that the reticulated network and the fourfold Gd...NC complexes are preserved following Co deposition. Inspecting the architectures at negative bias (see Figure S5a,b in the Supporting Information for an overview and Figure 2c,d for high-resolution data) emphasizes the presence of metalated species, namely the appearance of coexisting ring-shaped and rodlike macrocycles that are assigned to the free-base and Co porphyrins, respectively. Importantly, all the Co porphyrins are in perfect registry with the lanthanide-directed coordination network, with no structural deviations of the gridlike assembly. We also tried to realize more perfect architectures, however this could not be achieved with the present system. This limitation is presumably related to the symmetry and lattice mismatch

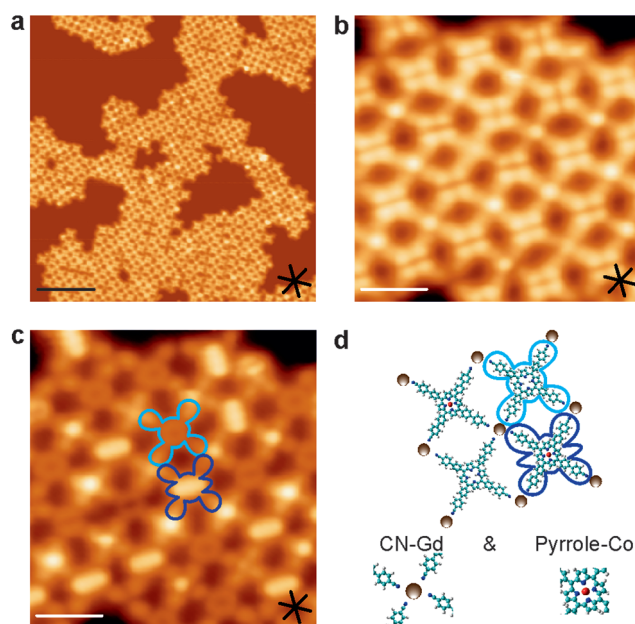


Figure 3. Lanthanide-directed assembly and orthogonal interactions yield domains of a heterobimetallic porphyrin network comprising Gd and Co centers in specific coordination environments. a) Overview STM image of the d-f assembly ($V_b = 1$ V and $I_f = 100$ pA). Scale bar: 10 nm. b) Data recorded at $V_b = 1$ V with similar appearance of the metalated and free-base porphyrins, each showing bright lobes localized at the four meso positions ($I_f = 75$ pA). c) At negative bias voltage ($V_b = -1$ V and $I_f = 75$ pA) free-base and Co-metalated macrocycles appear as ring-shaped cores and elongated protrusions along two different orientations, respectively (highlighted by light blue and dark blue contours, respectively). Gd atoms are visualized as round dots irrespective of the applied bias voltage. b,c) Scale bar: 2 nm. d) Atomistic model of (c). C, N, H, Gd, and Co atoms are depicted in green, blue, white, brown, and red, respectively.

between the 2D coordination superlattice and the hexagonal substrate.

We discard the possibility of Co atoms being attached to the lanthanide vertexes for the following reasons: 1) the aspect and size of the rare-earth centers is equivalent, within the heterogeneity, before and after Co deposition, 2) no clustering is observed at the vertexes,^[30] thus keeping the structure of the coordination network intact, and 3) within the experimental error, the node to node distance after Co-metalation (35.1 ± 0.7 Å, see Figure S6c in the Supporting Information) is identical to the Gd-Gd distance in the nonmetalated architecture (34.5 ± 0.6 Å, see Figure S6b in the Supporting Information). This value is significantly larger than the Co-Co distance (32.4 ± 0.9 Å) in Co-directed TPCN networks observed after annealing the sample at 348 K to promote metal-organic coordination in the absence of Gd (see Figures S6a and S7 in the Supporting Information), thus reflecting the larger size of the lanthanide atoms.

Importantly, the order of metal deposition is a decisive parameter in the assembly procedure. Upon exposure of previously Co-metalated arrays to Gd atoms there is a strict preservation of the close-packed Co-TPCN network, with less than 1 % of the termini coordinated to rare-earth atoms. We tentatively attribute this behavior to a change in the surface

mobility and the coordinative properties of Co-TPCN compared to those of 2H-TPCN.^[31] Thus, our procedure based on a two-step consecutive exposure of 2H-TPCN arrays to Gd and Co provides an example of the fabrication of d-f bimetallic networks with distinct metal centers embedded in specific environments, provided that metalation of the porphyrin macrocycle is accomplished at the appropriate temperature (300 K). In addition, this procedure has the further advantage of using a single molecular module (2H-TPCN) to create such bimetallic arrays, without the necessity of synthesizing ex situ metalated compounds.

In summary, we have successfully engineered d-f bimetallic networks on a well-defined Ag(111) surface by exploiting orthogonal coordination interactions. Systematic molecular-level STM observations allowed the decisive parameters for the assembly procedure to be identified and the resulting nanoarchitectures to be characterized in exquisite detail. First, the deposition on Ag(111) of the pure free-base porphyrins equipped with nitrile termini to favor coordination interactions results in a tetragonal close-packed supramolecular assembly. Subsequent exposure to Gd atoms selectively gives rise to a nanoporous gridlike network stabilized by fourfold Gd···NC coordination. Finally, the co-deposition of Co atoms induces the selective metalation of the central tetrapyrrolic macrocycle, with preservation of the lanthanide coordination network to form a distinct d-f array. To the best of our knowledge, this is the first in situ realization of a 2D lanthanide/transition-metal heterostructure that exploits orthogonal coordination interactions. We envisage that more perfect layers or extended domains could be achieved by optimizing the assembly procedures and material combinations. Our study discloses new avenues to metal-losupramolecular design on surfaces, thereby advancing the development of interfacial d-f nanosystems, where unique features can be obtained by the combined presence of 3d and 4f elements in specific coordination environments and with nanoscale embedding. Such systems bear prospects for engineering magneto-responsive, molecular spintronics or light-emitting devices and single-site heterogeneous catalysis.

Keywords: d-f metal–organic networks · lanthanides · orthogonal interactions · porphyrinoids · scanning tunneling microscopy · transition metals

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