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Controlling the dimensionality of on-surface coordination polymers via endo- or exo-ligation

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ABSTRACT: The formation of on-surface coordination polymers is controlled by the interplay of chemical reactivity and structure of the building blocks, as well as by the orientating role of the substrate registry. Beyond the pre-determined patterns of structural assembly, the chemical reactivity of the reactants involved may provide alternative pathways in their aggregation. Organic molecules, which are transformed in a surface reaction, may be subsequently trapped via coordination of homo- or heterometal adatoms, which may also play a role in the molecular transformation itself. The amino-functionalized perylene derivative, 4,9-diaminoperylene-quinone-3,10-diimine (DPDI), undergoes specific levels of dehydrogenation (-1 H_2 or -3 H_2) depending on the nature of the present adatoms (Fe, Co, Ni or Cu, respectively). In this way, the molecule is converted to an endo- or an exo-ligand, possessing a concave or convex arrangement of ligating atoms, which is decisive for the formation of either 1D or 2D coordination polymers.

INTRODUCTION

Organic and metal-organic networks^{1–18} generated on metal surfaces have been shown to alter the electronic properties of the substrate and to serve as templates for the formation of host-guest complexes,^{19–26} giving rise to complex forms of aggregation.

The mechanisms of on-surface reactions may differ significantly from those in solution,²⁷ thereby creating the opportunity to explore new ‘on-surface phenomena’.²⁸ Coordination between organic molecular ligands and metal adatoms,^{12,29–38} on one hand, and on-surface coupling and breaking of covalent bonds,^{18,28,39–58} on the other, have both been found to give rise to stable, well-ordered structures. There are thus several levels of chemical transformations and bonding interactions determining the assembly of molecular on-surface structures. Through reaction with surface adatoms, the building block or synthon can be modified prior to coordinative polymerization, as exemplified by the deprotonation of COOH to the ligating COO⁻ in carboxylate-based surface coordination polymers.^{35,59–61} In previous work, the nature of the metal adatom exhibited only a minor influence on the topology of the 2D layer,^{62–64} which is commonly predicted on the basis of the organic ligand only.

In this work, we demonstrate how two nitrogen-containing functional groups in a polycyclic aromatic architecture undergo modification depending on the specific reactivity of the available metal adatoms. Previously, we reported the formation of a highly stable porous network upon deposition of 4,9-diaminoperylene-quinone-3,10-diimine (**DPDI**) onto a Cu(111) surface and subsequent annealing.⁶⁵ A closer inspection of the transformation of this planar organic molecule has revealed that it undergoes thermal dehydrogenation generating **deh-DPDI** ($- \text{H}_2$) and, potentially, subsequent ring closure and further dehydrogenation to the poly-azocyclic compound **3deh-DPDI** (-3 H_2) (Figure 1).

Whereas **deh-DPDI** may act as a chelating *endo*-ligand on a metal surface, coordinating single metal atoms or forming 1D chain structures, the diazo units at both ends in **3deh-DPDI** may bridge metal centers, rendering the latter a bridging *exo*-ligand capable of forming 2D-coordination networks. We will show that the observed reactivity and thus the degree of dehydrogenative conversion is specifically determined by the co-deposited or substrate-supplied transition metal adatoms. The geometry of the resulting coordination polymer depends also on the type (Au or Cu) and crystal-index ((111), (100)) of the substrate.

In this report we focus on the assembly of on-surface coordination polymers by a two-stage reactive

dehydrogenation of the amine and imine functional groups in **DPDI**. To investigate the impact of transition metal adatoms on the transformation of the building block and on the formed coordination architecture, we employ a broad portfolio of surface analytical techniques: Scanning Tunneling Microscopy (STM), X-Ray Photoelectron Spectroscopy (XPS), Near Edge X-ray Absorption Fine Structure (NEXAFS) measurements in combination with Density Functional Theory (DFT) computational modeling.

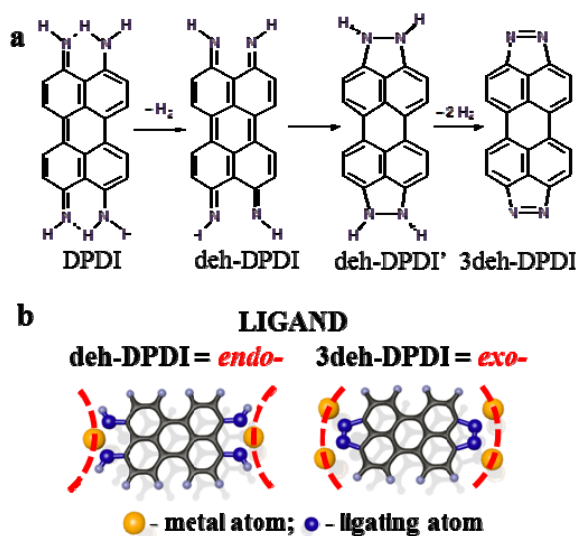


Figure 1. Dehydrogenation of DPDI to a quinoidal bisimino form deh-DPDI, which may act as an *endo*-ligand on a metal surface, and further cyclization and dehydrogenation resulting in triply dehydrogenated DPDI (3deh-DPDI) (Scheme a). In the latter, the diazo units may act as bridging ligands between metal centers, rendering 3deh-DPDI an *exo*-ligand capable of forming 2D-coordination networks (b).

EXPERIMENTAL SECTION

All samples were prepared and investigated under Ultra-High Vacuum (UHV) conditions with a base pressure of $\sim 10^{-10}$ mbar. The crystal substrates were cleaned by cycles of sputtering with Ar^+ ions and subsequent annealing to $\sim 450^\circ C$. The molecules were deposited on the surface by means of thermal evaporation at $\sim 240^\circ C$ from a commercial evaporator (Kentax GmbH, Germany) and metal adatoms by e-beam evaporator, respectively. The amount of the sublimed compound was controlled by a quartz crystal microbalance.

STM images were obtained at 5 K, 77 K or at RT in a constant current mode (typical tunneling current 20-50 pA), the sample bias was selected in the range of 5 mV - 3 V, such that the molecules appear in high contrast. Scanning probe tips were made from Pt-Ir wire (90% Pt, 10% Ir) and cleaned by sputtering with Ar^+ ions.

XPS was used to estimate the coverage of **DPDI** and to verify the stoichiometry after deposition. Also by XPS the element-specific chemical environment (analysis of C1s and N1s signatures), in particular the coordination of **DPDI** with different metal ligands, was tracked. A monochromatized Al-

K_{α} X-ray source was used. The instrumental setup gives a full width at half maximum (FWHM) of 1.0 eV. The energy calibration was performed using a Au(111) reference. All XPS data were obtained at room temperature and the spectra were recorded in normal emission unless stated otherwise.

The NEXAFS measurements were performed on samples held at room temperature at the Surface/Interface: Microscopy (SIM) beam-line of the Swiss Light Source (SLS) using total electron yield acquisition mode.⁶⁶ The spectra were divided by the background obtained on the clean substrate and normalized to pre-edge. The fitting analysis of the spectra was performed by asymmetric Gaussian functions with linearly increasing FWHM for higher photon energies⁶⁷. The onset of the ionization potential was fitted by a broadened step-function.

Periodic DFT modeling was performed with the VASP code⁶⁸ using the projector-augmented wave method⁶⁹ for describing ion-core interactions. Van der Waals interactions were included using the van der Waals density functional,⁷⁰ while local correlation was described by Local-Density Approximations (LDA). The semi-local exchange was described in the Generalized Gradient Approximation (GGA) using an optimized form of the Becke 86 functional.⁷¹

The Cu(111) surface was modeled by a four-layered slab separated by 15 Å of vacuum, with a $p(10 \times 10)$ surface unit cell for the **3deh-DPDI** honeycomb network, as previously determined.⁶⁵ For the **deh-DPDI** chains we used the unit cell illustrated in Figure S7, which gave the most stable structure (see SI for calculations with other unit cells). The calculated lattice constant, obtained with the methods described here, of 3.598 Å was used. In all calculations the plane waves were expanded to a kinetic energy cutoff of 500 eV. For the honeycomb network the 1st Brillouin zone was sampled by the Γ -point only, while for the Co-coordinated deh-DPDI chains a 3×2 k -point sampling was used. All structures were structurally optimized until the residual forces of all atoms, except for the bottom two layers of the slab, kept fixed, were smaller than 0.01 eV/Å.

Simulated core-level shifts were obtained by comparing total energy differences between core-ionized and ground state systems. The total energies of core-ionized systems were computed by using a core-ionized PAW potential for the core-ionized atom as described by Köhler and Kresse⁷².

RESULTS AND DISCUSSION

Dehydrogenation of DPDI and *endo*-/*exo*-ligand formation, controlled by the type of adatoms present on the surface.

First, we investigated the dehydrogenation of adsorbed **DPDI** on Cu surfaces. The changes in the chemical environment of N upon reaction of **DPDI** with adatoms were monitored by XPS (N1s peak) and are represented in Figure 2. Unreacted **DPDI**, after deposition on Cu(111) and Cu(100) substrates, gives rise to two peaks in the N1s spectrum corresponding to the coexisting amino- (~ 399.4 eV) and imino-group (~ 397.5 eV) (Figure 2a; cf. Figure S1 in Supporting Information (SI)). The observed XPS peak positions correspond well to the values reported in the literature (see XPS values in Table S1, S2 of the SI).^{73,74} In spite of the 1:1 stoichiometry between amino and imino nitrogen, we observe unequal intensities of the amine-

and imine-peak even in the native multilayer (cf. Fig S3). We tentatively attribute this to intramolecular hydrogen-bonding ($-\text{NH}_2\dots\text{N}=\text{}$, cf. Fig. 1a) which has been found to yield significant peak shifts^{75,76} and potentially photoelectron scattering effects.⁷⁷ The position of the observed N1s peaks of the **DPDI** monolayer on Cu(111) corresponds well to the XPS data of the **DPDI** multilayer, indicating that neither dehydrogenation nor Cu coordination does occur at room temperature (Figure S3). Even after deposition of Cu adatoms onto the monolayer of **DPDI** on Cu(111), there is no significant modification of the chemical environment of N as monitored by the N1s peaks (cf. Figure S4 in SI). Thus, **DPDI** remains unreacted irrespective of whether it is adsorbed on Cu at room temperature or whether higher thermal energy adatoms from a sublimation source are provided.

Annealing to 300 °C promotes a chemical transformation of **DPDI** on the Cu(111) and Cu(100) substrates, and leads to characteristic changes in the N1s XPS signature. The modified spectrum is characterized by a *single* N1s peak at ~ 399.4 eV reflecting an identical chemical environment of the N atoms contained in **3deh-DPDI** (Figure 2c, Figure S1). The N1s binding energy of Cu-coordinated **3deh-DPDI** corresponds well to the energies reported for related azo-functionalized species.⁷⁸ Moreover, we calculated the average N1s core level shift between imine N contained in isolated **DPDI** on the surface and the azo-N contained in Cu-coordinated **3deh-DPDI**. The resulting shift of +1.56 eV is within the experimental error margin. This reaction is exothermic with a reaction energy of -0.55 eV per molecule. The transformation of **DPDI** into **3deh-DPDI**, containing azo N at both ends, is also supported by the NEXAFS data (*vide infra*).

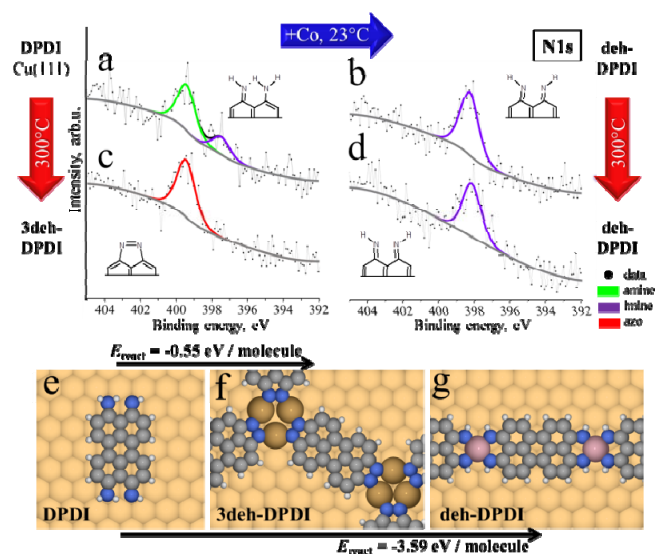


Figure 2. Identification of the various N species in the N1s XP spectra of DPDI on Cu(111): (a) Native DPDI is characterized by two peaks corresponding to amino- (green) and imino- (violet) groups. (b) Upon addition of Co adatoms to native DPDI on Cu(111) at RT, the dehydrogenation occurs readily as recognized by the dominant NH- peak (violet). (c) Annealing of native DPDI on Cu(111) to 300 °C leads to a different reaction product: One peak is visible in the N1s XPS data at the higher binding energy

(BE), which is attributed to azo nitrogen ($\text{N}=\text{N}$). (d) Annealing of the DPDI / Cu(111) in the presence of Co adatoms to 300 °C does not modify a deh-DPDI product. Chemical schemes: Note that the arrangement of the free electron pairs of the $=\text{NH}$ (imine) and $\text{N}=\text{N}$ (azo) ligands determines the role of deh-DPDI as an endo ligand and of 3deh-DPDI as an exo-ligand, respectively. The DFT models with calculated reaction energies (e) the isolated DPDI, (f) the Cu-coordinated 3deh-DPDI and (g) the Co-coordinated deh-DPDI cases. The average N1s core-level shifts with respect to the imine-N atoms of native DPDI are: +1.56 eV for 3deh-DPDI, +0.69 eV for deh-DPDI.

Notably, deposition of Cu adatoms onto **DPDI** on the more inert Au(111) substrate, triggers the same chemical reaction leading to **3deh-DPDI-Cu** complexes, upon annealing to $\sim 300^\circ\text{C}$ (however, the reaction proceeds only for a part of the compound, cf. S5 and discussion in the SI).

The reaction products after annealing **DPDI** at 300 °C on both Cu(111) and Cu(100) substrates were visualized by room temperature STM. These experiments reveal the formation of a highly ordered 2D hexagonal porous network on Cu(111)⁶⁵ and a moderately ordered 2D rectangular network on Cu(100), respectively (Figure 3). The XPS data confirm that both networks consist of **3deh-DPDI** in the role of an exo-ligand (cf. Fig. 2 and SI). The symmetry of the surface is directly reflected by the symmetry of the network (Figure 3a,b,e and 3c,d,f respectively). Due to the reduced commensurability of the rectangular coordination network with the Cu(100) surface lattice and the co-existence of square and rectangular pores (Figure 3h, i), the amount of defects is greater and long-range order is accordingly reduced compared to the corresponding structure on Cu(111).

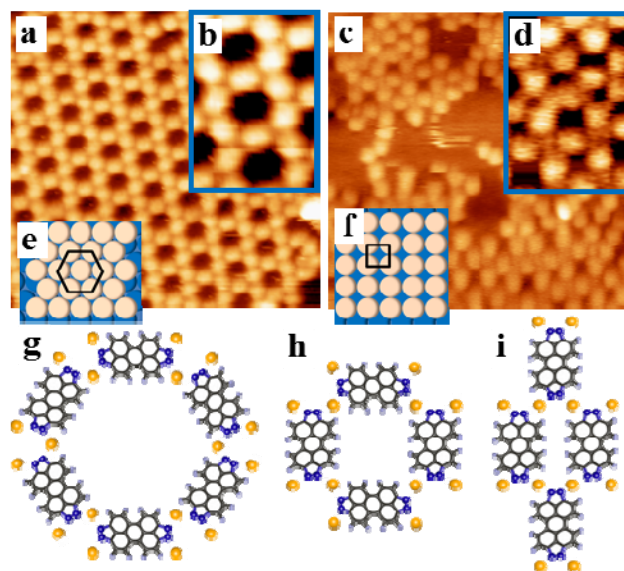


Figure 3. Annealing native DPDI at 300 °C on Cu substrates leads to the formation of exo-ligating 3deh-DPDI. The resulting Cu-coordinated 2D-polymer reflects the symmetry of the underlying substrate: (a,b) hexagonal pores are formed on the Cu(111) surface and (d,e) rectangular pores on the Cu(100) surface, as depicted in the STM images (19×19 nm² and 4×6 nm²). The hexagonal and rectangular symmetry for Cu(111) and

Cu(100) surfaces are depicted in the insets (e) and (f), respectively. Schematic models: (g) hexagonal 3deh-DPDI pore; (h, i) rectangular pores in two configurations: with parallel or perpendicular orientation and corresponding rectangular or square symmetry of the coordination polymer, respectively.

The role of the open d-shell metals, like Co, Fe and Ni, in the on-surface reaction of **DPDI** on Cu(111), was studied in a dedicated series of experiments: After deposition of **DPDI** and subsequent deposition of cobalt atoms at room temperature, the N1s XPS spectrum, presented in Figure 2b, shows significant changes from native **DPDI**. The amino-peak, which is characteristic for the unreacted compound, disappears (Fig. 2b) and only single N1s peak is observed at ~ 398.3 eV. The energy position differs significantly (1.1 eV lower), from the one observed after Cu coordination of **3deh-DPDI** on Cu(111), and is assigned to imino-nitrogen atoms.^{79,80} Upon annealing at ~ 300 °C the N1s peak remains virtually unchanged (~ 398.1 eV) (Figure 2d). The core level shift between this Co-coordinated imine and the uncoordinated imine N has been calculated to be 0.69 eV, which compares well to the experimental data. (Fig. 2e, g). Based on DFT modeling, the calculated reaction energy is -3.59 eV for transforming **DPDI** into Co-coordinated **deh-DPDI**.

The same type of transformation occurs for **DPDI** on a Au(111) substrate (Figure 4a) in the presence of Co adatoms (Figure 4c,f). Moreover, other open 3d-shell transition metal adatoms, such as Fe and Ni, initiate an identical transformation of **DPDI** on Au(111) as recognized in the XPS data showing the dominant imino-peak at low binding energy ~ 398 eV (Ni: Figure 4d and Fe: Figure b,e).

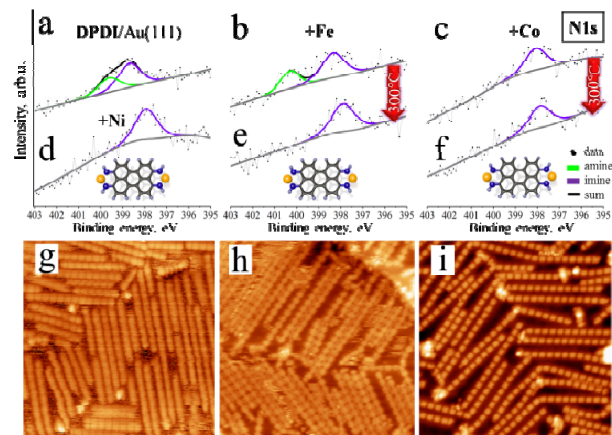


Figure 4. Transformation of DPDI into deh-DPDI (an endo-ligand) in the presence of Ni, Fe and Co on Au(111). This transformation occurs at RT in an on-surface reaction between DPDI and transition metal adatoms as recognized by the change of (a) initial two peaks in N1s spectrum of DPDI on Au(111) into (b)-(f) dominant N1s XPS peak of imine-character. (b) The shoulder of the amine corresponds to small amounts of the unreacted DPDI, which disappears after annealing. The resulting chelating ligand coordinates with adatoms and arranges into a chain architecture. (g-i) STM micrographs of the polymers, created by co-deposition of DPDI with (g) Ni, (h) Fe and (i) Co adatoms on Au(111) at RT ((g) 30×30 nm² at RT; (h),(i) 30×30

nm² at 5 K). Note, the polymers observed in STM are not modified upon annealing.

Annealing of the samples to 300°C only completes a conversion of the unreacted compound (e.g. Figure 4e), however, does not change the final reaction product. The dominant XPS signature is assigned to **deh-DPDI** (see Fig. 1), which is reminiscent of the ubiquitous *acac* (acetylacetonato) ligands in coordination chemistry. This ligand is able to act as a ditopic chelating endo-ligand for the co-deposited transition metals. Therefore, the formation of metal complexes, with two of these bis(imine) units in a square-planar coordination geometry on the different substrates, gives rise to 1D coordination polymers as depicted by STM in Figure 4g-i.

The analysis of the XPS data reveals two types of reaction products for closed vs. open d-shell adatoms coordinating with **DPDI**. Cu adatoms transform **DPDI** into **3deh-DPDI** that may act as a bridging exo-ligand with its convex arrangement of donor atoms. On the other hand, in the presence of Co, Fe, Ni adatoms the less dehydrogenated species **deh-DPDI**, that acts as a ditopic bis(chelating) endo-ligand, are trapped by coordination to the heterometal atoms, forming the chain-like 1D coordination polymers. The adatom-dependent transformations of **DPDI** to **deh-DPDI** or **3deh-DPDI** and coordination to the respective transition metals represent complex multistep processes. Only detailed computational modeling of all possible reaction pathways/sequences on the metal surface(s) would provide insight into the factors governing the final product(s) observed in the transformations described above.

NEXAFS study of the surface-transformed DPDI: Identification of amino-, imino- and azo-nitrogen.

To confirm the assignment of the **deh-DPDI** and **3deh-DPDI** dehydrogenation product in the on-surface coordination polymers, we have employed NEXAFS. The method provides a characteristically different probing mechanism from XPS in that transitions from occupied N1s to unoccupied N2p orbitals are examined. The method is sensitive to both the chemical environment and the orientation of the molecule. Figure 5 displays the NEXAFS data obtained for three samples, (a) unreacted **DPDI**/Cu(100) (not annealed), (b) **DPDI** + Co/Cu(111) and (c) **DPDI**/Cu(111) (annealed to liberate Cu-adatoms and to activate the on-surface reaction). The data is summarized in Table 1, along with the corresponding assignments of the peaks.

The relative orientation of the unoccupied states with respect to the incident X-ray beam as determined in angle-dependent NEXAFS experiments modifies the magnitude of the spectral features. In the present case, electronic states with their nodal plane in out-of-plane orientation were probed in grazing incidence (70° off the surface-normal) with the linear polarization perpendicular to the surface-plane (blue curves in Figure 5). In comparison, the signature of electronic states with their nodal plane oriented in-plane were probed in normal incidence with the polarization of the incident X-ray light oriented parallel to the surface-plane (red curves in Figure 5). The signature of the transitions states derived from C-N and N-N bonds (*vide infra*) clearly establishes that the molecules are oriented in the surface plane.

Table 1. Energies of the NEXAFS N1s peaks, obtained from the fit of data, correspond to amino, imino and azo groups.

| Molecule/NEXAFS | π_1^* , eV | π_2^* , eV | σ_1^* , eV | σ_2^* , eV |
|-----------------|----------------|----------------|-------------------|-------------------|
| (a) DPDI | 399.1 | 403.2 | 408.6 | 414.4 |

| | | | | |
|----------------------|-------|-------|-------|-------|
| (b) deh-DPDI | 398.7 | - | 409.8 | - |
| (c) 3deh-DPDI | 399.6 | 401.2 | 407.0 | 410.7 |

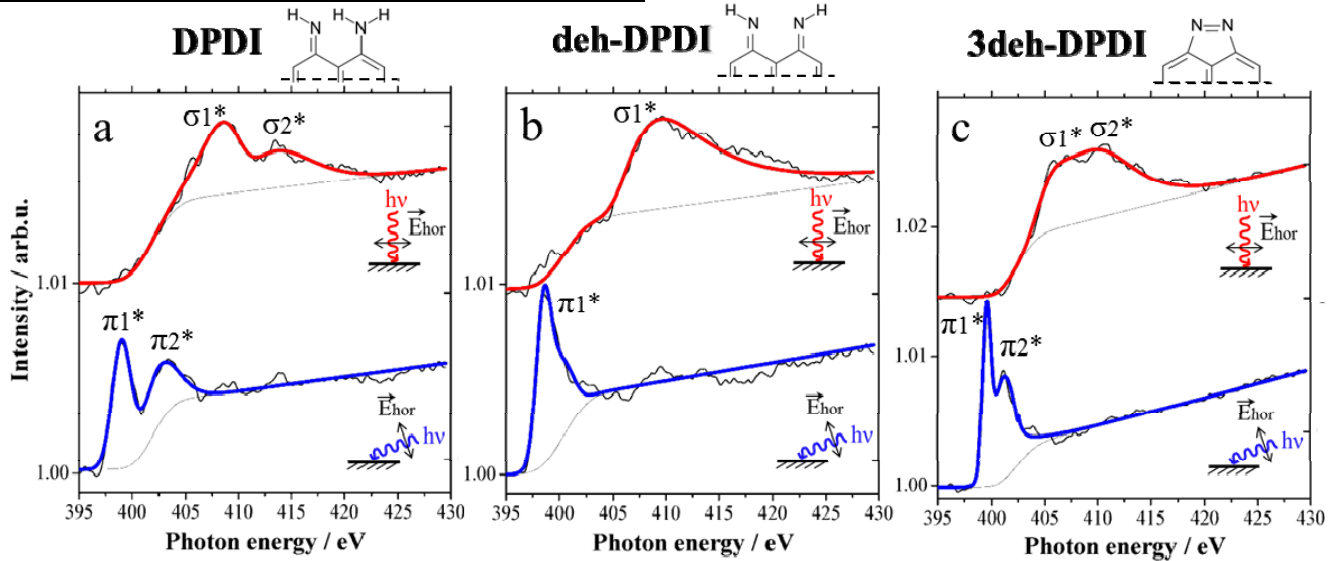


Figure 5. NEXAFS data revealing different DPDI species. In-plane σ^* and π^* resonances are reflected by red and blue curves, respectively. (a) Spectra of unreacted DPDI on Cu(100) contains both amino- and imino-peaks; (b) spectra of deh-DPDI coordinated to Co via imino-nitrogen; (c) spectra of 3deh-DPDI coordinated to Cu via azo-nitrogen.

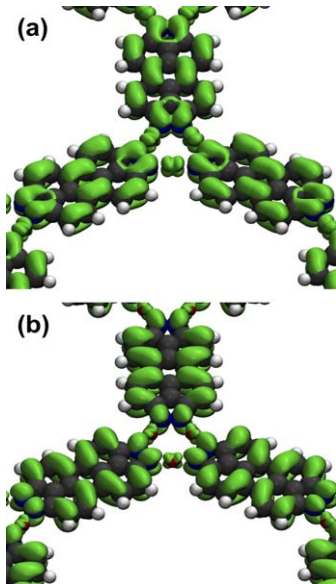


Figure 6. Numerical simulation of Cu coordinated 3deh-DPDI: Absolute contour plots of the (a) HOMO and (b) LUMO of the freestanding 3deh-DPDI network, represented by the band-decomposed density of states closest to the Fermi level below and

above the Fermi level, respectively. The value of the contours is $0.005 e/\text{\AA}^3$.

For the identification of the different N species, we analyze the nitrogen K-edge NEXAFS signature of native **DPDI** on Cu(100) as presented in Figure 5a. We observe two N species via their π^* states (403.2 eV and 399.1 eV) as well as by their σ^* states (414.4 eV and 408.6 eV). The transition energies correspond well with the literature values reported for N atoms of amine and imine character^{81,82} (Supporting Info: Table S3). Note that XPS of unreacted **DPDI** deposited on Cu(100) samples also revealed two different N1s signals, corresponding to the amine and imine nitrogen atoms (Supporting Info: Figure S1a). In case of co-deposited **DPDI** and Co on Cu(111), the observed N K-edge NEXAFS signal differs significantly (Figure 5b).

The spectrum corresponding to **DPDI** with Co adatoms revealed only a single π^* peak (398.7 eV) and a single σ^* peak (409.6 eV), which is consistent with only one type of (imine) nitrogen⁸⁰. This confirms the structural assignment provided above on the basis of the XPS data: The 1D coordination polymer is assigned to **Co-deh-DPDI**. The 2D coordination polymer formed by **DPDI**/Cu(111) after annealing has been assigned to a porous **3deh-DPDI**-Cu network. In this case, the N K-edge NEXAFS signature reveals again very different features compared to the previous cases. Split peaks corresponding to the transitions between the π^* (401.2 eV and 399.6 eV) and σ^* states (410.7 eV and 407.0 eV) (Figure 5c)

are observed. Their energies correspond well to the proposed azo-bridges^{78,83–85} formed upon threefold dehydrogenation of the **DPDI** molecules, as identified already on the basis of XPS. The assignment of unreacted **DPDI** and of **deh-DPDI** in the NEXAFS data is unambiguous. The NEXAFS signals attributed to the azo-N atoms in **3deh-DPDI**, in contrast, requires additional analysis. The observation of the split π^* N peak in case of copper-coordinated **3deh-DPDI** on Cu(111) is unexpected on the grounds of the N species alone. We relate this to ‘donation/back-donation’ effects coming from the coordination of **3deh-DPDI** with the copper atoms.⁷⁸ Specifically, the occupied/unoccupied metal centered orbitals mix with the lowest unoccupied molecular orbital (LUMO) / highest occupied molecular orbital (HOMO) of the molecule, respectively. In the case at hand, this would primarily involve the azo-bridge of **3deh-DPDI** and the Cu adatoms. In order to support the proposed donation/back-donation model as a reason for the split π^* N peak, a DFT modeling study was carried out.

The extended degeneracy of the molecular orbitals across the Cu coordinated **3deh-DPDI** on Cu(111) can be recognized in the numerical simulations as well. In Figure 6 the electron density of the frontier orbitals of the freestanding **3deh-DPDI** network is illustrated which reflects the bonding in the network: the p_z states of the molecule mix with the d states of the Cu atoms. Notably, both the HOMO and the LUMO consist of three electronic states (one per molecule in the unit cell) with their degeneracy lifted due to the molecule-adatom interactions as represented in Figure 7a-b.

The partial density of states (PDOS) of the molecule’s N atoms is significantly altered due to the interaction with the coordinating Cu-adatoms. The calculations of the **3deh-DPDI** reveal a splitting of the peaks in the p_z component of the PDOS localized on the N atoms in vacuum (Figure 7a) after Cu coordination (Figure 7b). This splitting pertains when including the Cu(111) surface in the simulations (Figure 7c). Notably, Co-coordinated **deh-DPDI** chains on Cu(111) give rise to a single (not split) peak in the p_z component of the PDOS of nitrogen (see Fig. S9 of SI).

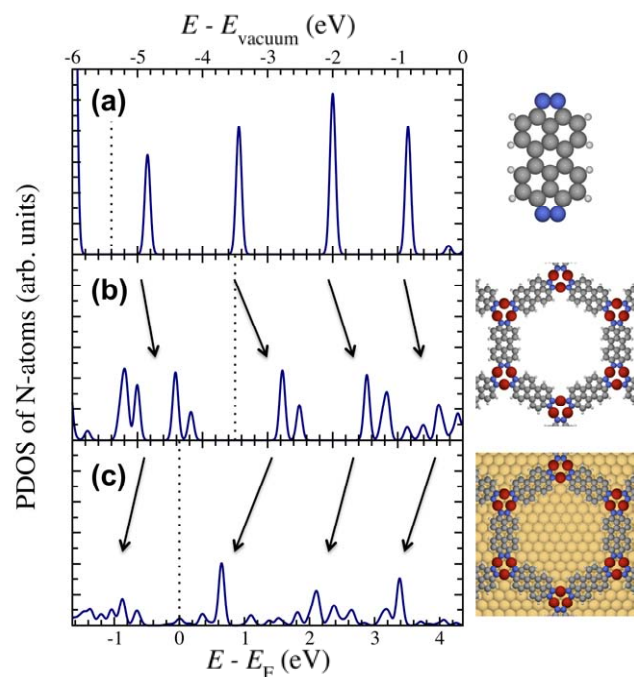


Figure 7. The π -donation/back donation effect upon Cu-coordination of **3deh-DPDI** causes a split in the π^* state, which appears as a double peak in the N K-edge NEXAFS. The partial density of states (PDOS) (a) of the p_z component on the N atoms of the **3deh-DPDI** becomes modified by coordination to Cu-adatoms, both for the (b) freestanding and (c) the surface-supported coordination polymer.

Endo/exo- **DPDI** coordination defines the dimensionality of the on-surface polymer

In the case at hand, the surface deposited **DPDI** molecule acts as a ligand precursor, which is transformed to a ligating structural building block by adatom-specific dehydrogenation (-1 H_2 or -3 H_2). Please note, the hydrogen may be lost as atomic (presumably forming metal-hydrides) or as molecular hydrogen (H_2 gas). The control of polymer topology via endo/exo ligation provides an example of site-specific chemistry in an oligomerization reaction (Figure 8). The linear polymeric structures formed by **deh-DPDI** are imposed by the ditopic nature of the chelating *endo*-ligand, which connects metal centers via the two inward pointing free electron pairs belonging to the N atoms at either end of the **DPDI** molecule (Figure 8, left). The **3deh-DPDI**, which is generated in the presence of Cu adatoms, exhibits a characteristically different arrangement of the free N electron pairs while acting as *exo*-ligand in the coordination. The construction of the network node also depends on the symmetry of the substrate: On Cu(111) three adatoms connect three **3deh-DPDI** molecules in the form of a hexagonal network (Figure 8f and Figure 3a,b,g). On Cu(100) four adatoms interconnect four **3deh-DPDI** molecules in each node thereby forming a tetragonal network (Figure 8d and Figure 3c,d,h,i). At low coverage of **3deh-DPDI** on Cu(100) substrates, however, oligomers nucleate in a bridge-to-bridge fashion, initiating a 1D arrangement (Figure 8e and Figure S2 in SI). The N1s peak in the XPS data is not

modified with increasing sub-monolayer coverage indicating that the chemical environment of the nitrogen atoms remains the same irrespective of whether a 1D or a 2D coordination polymer is present. This supports the notion that the **3deh-DPDI** ligands are fully Cu-decorated at all coverages. We note that initiating the reaction with Cu adatoms requires the highest temperature (300 °C). This is consistent with the position of Cu on the scale of the second ionization energies of the different atoms studied here. The oxidation state of the coordinating atom in the ‘on-surface’ configuration is not trivial to define, as the intermixing between the electronic states of the reacted molecules and the surface has to be taken into account.^{86,87}

The interconnection of the exo-coordinated ligands via Cu adatoms depends critically on the chemical nature of the substrate. In spite of the Cu coordination of **3deh-DPDI**, as seen by XPS, no RT-stable arrangements were observed on Au(111) by STM. However, after cooling the sample to 5 K, single coordinated molecules as well as their vdW condensed islands (Fig. 8g, Fig. S3c-e) have been visualized. The fact that **3deh-DPDI** molecules do not form a coordination polymer on this substrate may be related to one or more of the following factors: (1) a mismatch between the surface registry and the length of the coordination bond (2) an interaction between an electronic state of the substrate and the coordinated ligand or (3) the modified interaction between Cu adatoms and the Au substrate in comparison to the Cu substrate.

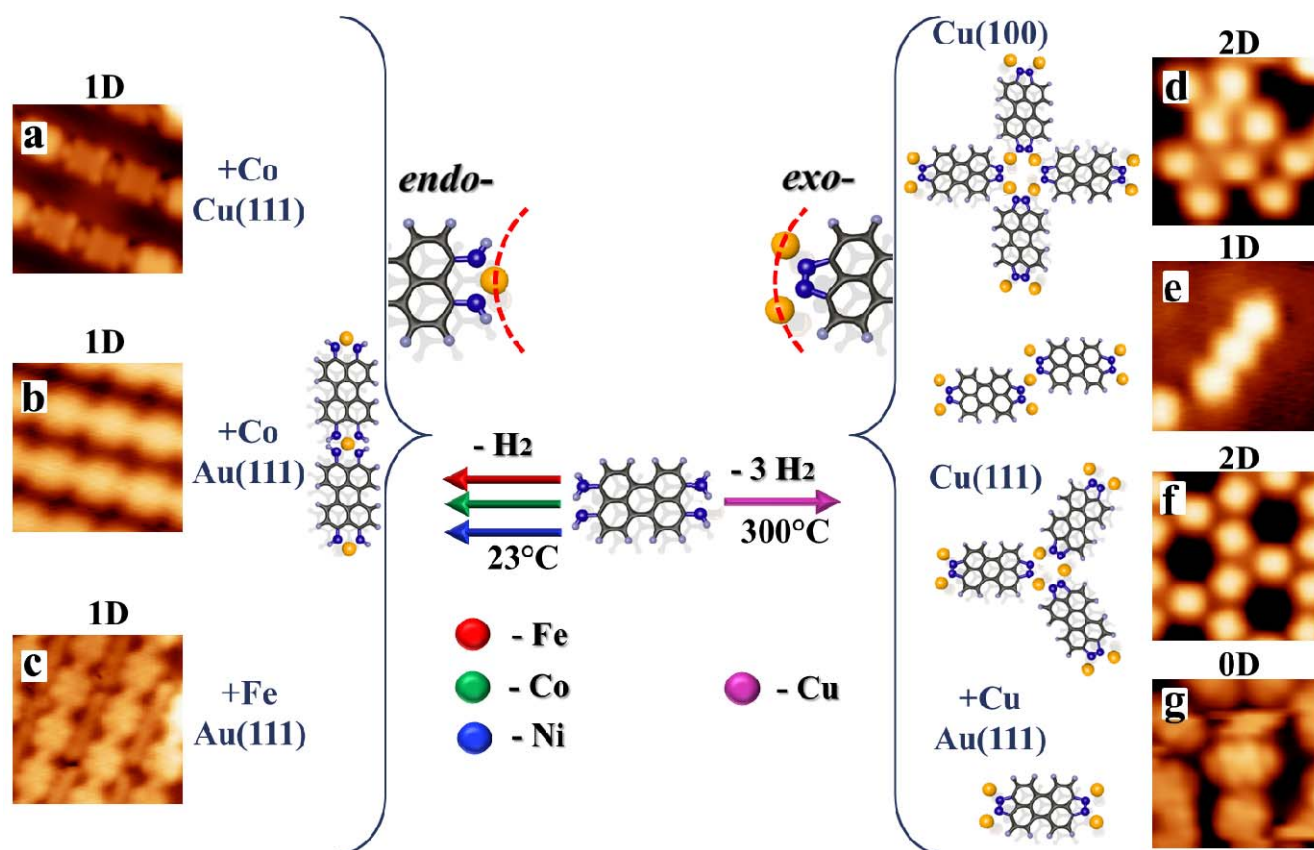


Figure 8. Depending on their reaction partner dehydrogenated DPDI molecules can act as either endo- or exo-ligands in the formation of on-surface coordination polymers. (Top center) The two possible polymerization reactions depend on the involved adatoms (Fe, Co, Ni, Cu) as indicated by the schematic representation and the arrows. Colors indicate the chemical species of adatoms as depicted in the legend; (left) deh-DPDI, an endo-ligand, forms a 1D coordination polymers, while 3deh-DPDI (right), an exo-ligand, forms a 2D-coordination polymers. STM images ((a)-(d), (f),(g) $4 \times 4 \text{ nm}^2$, (e) $5 \times 5 \text{ nm}^2$ taken at 5 K) reveal the chain vs. network character of the formed polymers. (a) – (c) Co or Fe adatoms transform DPDI into deh-DPDI already at RT. In all these cases, the endo-type ligation leads to the formation of straight chains on Cu(111) and Au(111). (d) Annealing of DPDI on Cu(100) promotes a formation of an exo-ligated poly-Cu-3deh-DPDI network with rectangular symmetry. (e) At low coverage the bridge-to-bridge 1D arrangement are observed. (f) Annealing of DPDI on Cu(111) promotes a formation of an exo-ligated poly-Cu-3deh-DPDI network with hexagonal symmetry. (g) Sublimation of DPDI and Cu adatoms on Au(111) and subsequent annealing to 300 °C promotes the formation of isolated, but fully Cu-coordinated 3deh-DPDI. The tunneling parameters for the STM-imaging were optimized for visualization of the coordinating metal adatoms, which appear as protrusions. Notably for poly-Cu-3deh-DPDI no adatoms have been visualized by STM.³⁶

CONCLUSIONS

The on-surface *reactivity* of **DPDI** molecules, and thus the degree of dehydrogenative conversion into either an *endo*- or *exo*-ligand depends neither on the nature (Au or Cu) nor on the crystal-index (111, 100) of the substrate, but is exclusively determined by the metal adatoms. In the presence of Fe, Co and Ni adatoms the reaction proceeds to **deh-DPDI** as a ditopic chelating endo-ligand. This ligand is “trapped” by coordination with the metal adatoms in the formation of 1D coordination polymers. Only in presence of Cu adatoms *and* at elevated temperatures, the dehydrogenation proceeds to **3deh-DPDI** containing two N₂ azo units. Here the two ligating N atoms are linked to two Cu atoms in a convex arrangement at either end of the **3deh-DPDI**. Therefore, two types of molecular building blocks are generated, which differ in the encoded structural information: Due to the characteristic difference in the orientation of the ligating functional groups, the endo-ligand **deh-DPDI** forms 1D coordination polymers, whilst the exo-ligating **3deh-DPDI** acts as bridging building block in 2D surface networks. In the latter case, the resulting *architecture* also depends critically on the chosen substrate: While the reaction itself progresses in the same way, irrespective of whether Cu adatoms are available on Cu(111), Cu(100) and Au(111), the porous network is observed only on the Cu substrates.

In conclusion, **DPDI** provides an instructive example of on-surface reactivity which crucially depends on the adatom chemistry. The combined interplay of all critical factors leads to a remarkable structural variety and the possibility to control the dimensionality and architecture of the surface aggregates. Future research will focus *inter alia* on the reaction mechanisms leading to such new architectures, including detailed theoretical modeling of the reaction sequences involved, and on the exploration the structure-property relationships. This is geared towards designing novel surface materials with tunable, characteristic properties occurring from the interaction of the coordination polymers with the surface.

ASSOCIATED CONTENT

Supporting Information. The following content supplied as Supporting Information: Additional XPS and STM data, Tables of XPS values and references; NEXAFS Table of references; DFT models; PDOS graphs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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