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1D Coordination π -d Conjugated Polymers with Distinct Structures Defined by the Choice of the Transition Metal: Towards a New Class of Antiaromatic Macrocycles

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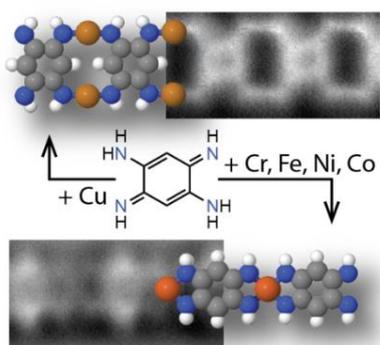
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Abstract: Recently π -d conjugated coordination polymers have received a lot of attention due to their unique material properties, although synthesis of long and defect free polymers remains challenging. Here we introduce a novel on-surface synthesis of coordination polymers with quinoidal ligand under ultra-high vacuum conditions, which enables formation of flexible coordination polymers with lengths up to hundreds of nanometers. Moreover, this procedure allows the incorporation of different transition metal atoms tuning their coordination between four and two-fold. Remarkably, the two-fold coordination mode revealed the formation of wires constituted by (electronically) independent 12-membered antiaromatic macrocycles linked together through two C-C single bonds.

Introduction

One-dimensional (1D) covalent polymers are of considerable interest in many different technological sectors due to their unique electronic properties.^[1-6] The solvent-free synthesis of such nanomaterials at the surface has been emerging as a promising approach to obtain tailored low dimensional materials with atomic precision. Pure organic 1D materials can be obtained through catalyzed C-C coupling reactions on surface from halogenated precursors.^[7-8] Alternatively, 1D coordination-polymers (CPs) can be isolated through coordination chemistry, the covalent bond formation resulting from on-surface reactions between metal atoms and suitable linker groups.^[9-14] One major advantage of this approach is the possibility to tune the properties of the wires by changing the nature of the metal and/or the ligand. In this strategy, the ligand design is crucial since maximizing the conjugation through coordination requires keeping the π -d systems as coplanar as possible. Previous studies reported that low-lying π^* orbitals of quinoidal ligands can mix extensively with the valence d -orbitals of a metal center, yielding complexes in which the electrons could be delocalized over both the metal and the ligand.^[15-17] In this context, 2,5-diamino-1,4-benzoquinonediimines (**2HQDI**) are particularly appealing because of their fascinating optical properties,^[18-19] and remarkable ability to serve as ligand in coordination chemistry. Unlike the N-substituted systems (N-alkyl or N-aryl),^[20-34] the coordination chemistry of the parent (i.e. unsubstituted) molecule **2HQDI** in solution has been poorly investigated probably due to its low solubility and specific reactivity that induced unwanted side-reactions.^[35] Some of us showed that the absence of N-substituents (no steric hindrance) allows a unique behavior resulting from the stepwise formation of coplanar polynuclear complexes **NiQDI** with up to 3 repeat units ($n \leq 3$) (Figure 1a).^[17] The oligomerization reaction proceeds in solution by successive deprotonation/metalation steps from **2HQDI**, affording complexes in which each quinoid ligand is linked to two metal centers through two covalent and two coordinative bonds. As a result, the oxidation state of the metal centers is always +II and the π -system of the bridging unit is fully delocalized, forming π -d delocalized systems.^[36-41] Importantly, the size of the oligomers depends on the nature of the solvent since the oligomerization process stops when the limit of solubility is attained.^[42-43]

Herein, we explore the reaction between transition metal (TM) atoms (Cr, Fe, Co, Ni and Cu) and **2HQDI** directly at the solvent-free solid surface under ultra-high vacuum conditions. We anticipated that this approach^[44] would overcome the limitations observed in solution and could lead to formation of extended flexible covalent coordination polymers with lengths of hundreds of nanometers. In the course of this study, we also observed a different coordination mode of the metal center to the ligand depending on the metal precursors and/or the nature of the substrate, see Figure 1b. More specifically, a new and remarkable coordination mode of the ligand **2HQDI** was observed in the case of reaction with copper, resulting in the formation of wires based on unique (poly) macrocycles, see Figure 1b (**Cu₂QDI**). A combined experimental and theoretical study allowed us to resolve its chemical structure consisting of a 12-membered ring incorporating two copper centers. These macrocycles can be considered as a new class of antiaromatic compounds.^[45-46]

Results and Discussion

The metals Cr, Fe, Co and Ni are introduced as neutral metal atoms from an electron-beam evaporator while Cu is provided directly by the Cu substrate (as detailed in the Supplementary Information). The ligand precursor **2HQDI** is deposited simultaneously by sublimation, and is let to react on Cu(111) and Au(111) surfaces with the metal atoms. With all metals, isolated 1D metal-organic coordination polymers are obtained. As we show, the {Cr, Fe, Co, Ni} containing CPs are based on four-fold square-planar coordination where the metal atom is coordinated head-to-head between two ligands (**MQDI** in Figure 1b). Figure 1c(top, middle) shows a representative high-resolution nc-AFM image **FeQDI/Au(111)**, recorded with CO functionalized tip^[47,48] revealing a characteristic “x-like” contrast feature in between the molecular units. On the contrary, Cu-CPs are based on two-fold linear coordination motifs where each Cu atom is linked to the nitrogen atoms of the ligand arranged side-by-side (**Cu₂QDI** in Figure 1b), as demonstrated by high-resolution nc-AFM image of **Cu₂QDI** wire on Cu(111) (shown in Figure 1d top, middle) exhibiting a distinct structural contrast. Due to the different arrangement of the molecular building blocks, the periodicity of **Cu₂QDI** ($6.8 \pm 0.1 \text{ \AA}$, Figure S1) along the wire is also noticeably shorter compared to $7.7 \pm 0.1 \text{ \AA}$ for **FeQDI**. Notably, **FeQDI/Cu(111)** exhibits a similar AFM contrast as **FeQDI/Au(111)** (Figure S1), featuring the characteristic “x-like” appearance on the Fe.

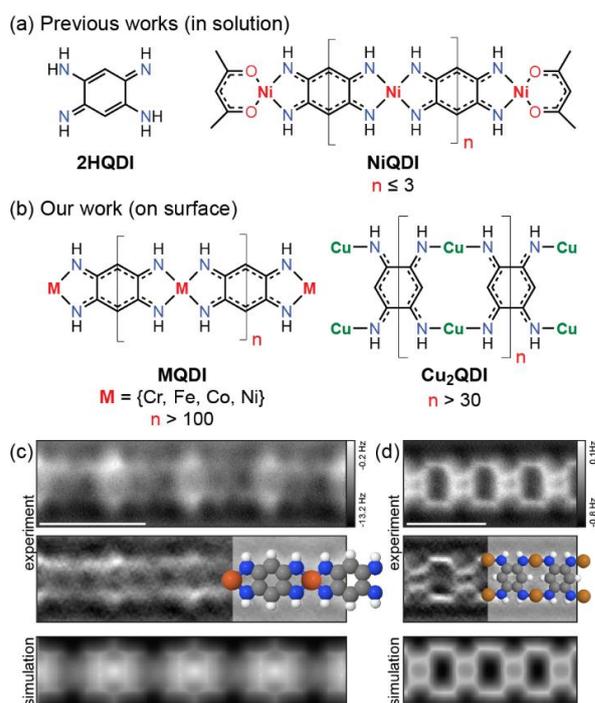


Figure 1: (a) Formation of coplanar polynuclear complexes **NiQDI** in solution (b) On surface formation of structurally distinct four-fold coordinated **MQDI** (M= Cr, Fe, Co, Ni) wires and two-fold coordinated **Cu₂QDI** wires by dehydrogenative metalation. (c, d) Top: High resolution constant height nc-AFM images (scalebar 1 nm) recorded with CO modified tip of **FeQDI** wire on Au(111) [$V_{\text{bias}} = 1 \text{ mV}$, $A_{\text{osc}} = 50 \text{ pm}$] and **Cu₂QDI** wire on Cu(111) [$V_{\text{bias}} = 1 \text{ mV}$, $A_{\text{osc}} = 50 \text{ pm}$]. Middle: High pass filtered version of the high-resolution images for better clarity superimposed with space filling models (C, H, N, Fe and Cu atoms correspond to grey, white, blue, orange and brown colors respectively.). Bottom: Simulated AFM images of **FeQDI/Au(111)** and **Cu₂QDI/Cu(111)** coordination polymers.

To confirm the structures, we carried out total energy DFT-B3LYP^[50-51] calculations of **FeQDI**/Au(111), **FeQDI**/Cu(111) and **Cu₂QDI**/Cu(111) 1D coordination polymers. The lattice vectors of the optimized DFT structures (Figure S2) are in very good agreement with the experimentally acquired values. Furthermore, AFM simulations using the probe-particle model^[52] fully reproduce the experimental AFM contrast, see Figure 1c and 1d (bottom). N-N covalent bonding between the ligands can be firmly ruled out, as it would result in a shorter molecule-to-molecule periodicity (5.7 Å from DFT).

The dehydrogenation reaction on the surface and simultaneous formation of metal coordinated wires is further supported by XPS measurements (Figure S3) of **{Fe,Ni}QDI** wires on Au(111) surface and **Cu₂QDI** wires on Cu(111) surface. N1s XP spectra of native 2HQDI on both Au(111) and Cu(111) reveal two components, corresponding to -NH₂ and -NH groups. In contrast, for the synthesized **{Fe, Ni, Cu₂}QDI wires**, only one N1s component is observed, showing that all four nitrogen atoms of the ligand have identical chemical environments, consistent with the structures shown in Figure 1b. This also excludes the possibility of hydrogen-bonded wire growth.

For **Cu₂QDI**, we could identify 12-membered macrocycles involving twelve π electrons of the ligand. The bridging **QDI** ligand can be indeed described as two nearly-independent six π electrons subunits chemically connected through two C-C single bonds (the so-called “coupling principle”^[49]). As a consequence, the **Cu₂QDI** wires are constituted of electronically independent

macrocycles linked together through two C-C single bonds, preventing a full delocalization over the wire.

Overview STM images of **{Cr, Fe, Co, Ni}QDI** on Au(111), **Cu₂QDI** on Cu(111) and **FeQDI** on Cu(111) are displayed in Figure 2. For **{Cr, Fe, Co, Ni}QDI** on Au(111), very long regular wires easily exceeding lengths of 100 nm can be observed. On Au(111), the wires loosely follow the herringbone reconstruction of the substrate and can be easily manipulated by the STM tip and bent into manifold shapes (Figure S4). This points to their relatively weak interaction with the Au(111) substrate. In the zoom-in STM images (Figure 2), the **Cu₂QDI** wires appear significantly wider compared to the **{Cr, Fe, Co and Ni}QDI** ones and their periodicity along the wire is visibly smaller (in agreement with the nc-AFM observation). In combination with the known coordination geometry of **FeQDI** and **Cu₂QDI** determined by nc-AFM (Figure 1c, d, Figure S1), these two properties show that **{Cr, Fe, Co, Ni}QDI** on Au(111) and **FeQDI** on Cu(111) are essentially isostructural with square-planar bonding scheme. Most of the individual **MQDI** wires on Au(111) are truly one dimensional, although branching between two wires occasionally occurs. Compared to all **MQDI** wires on Au(111), both types of wires (**FeQDI** and the **Cu₂QDI**) branch more frequently on Cu(111) and they follow specific directions of the substrate. By analogy with the growth of organic and inorganic 2D materials at surfaces,^[53-54] the higher frequency of branching suggests that the growth on Cu(111) is more kinetically controlled. This can be attributed to higher diffusion barriers on Cu(111) as compared to Au(111).

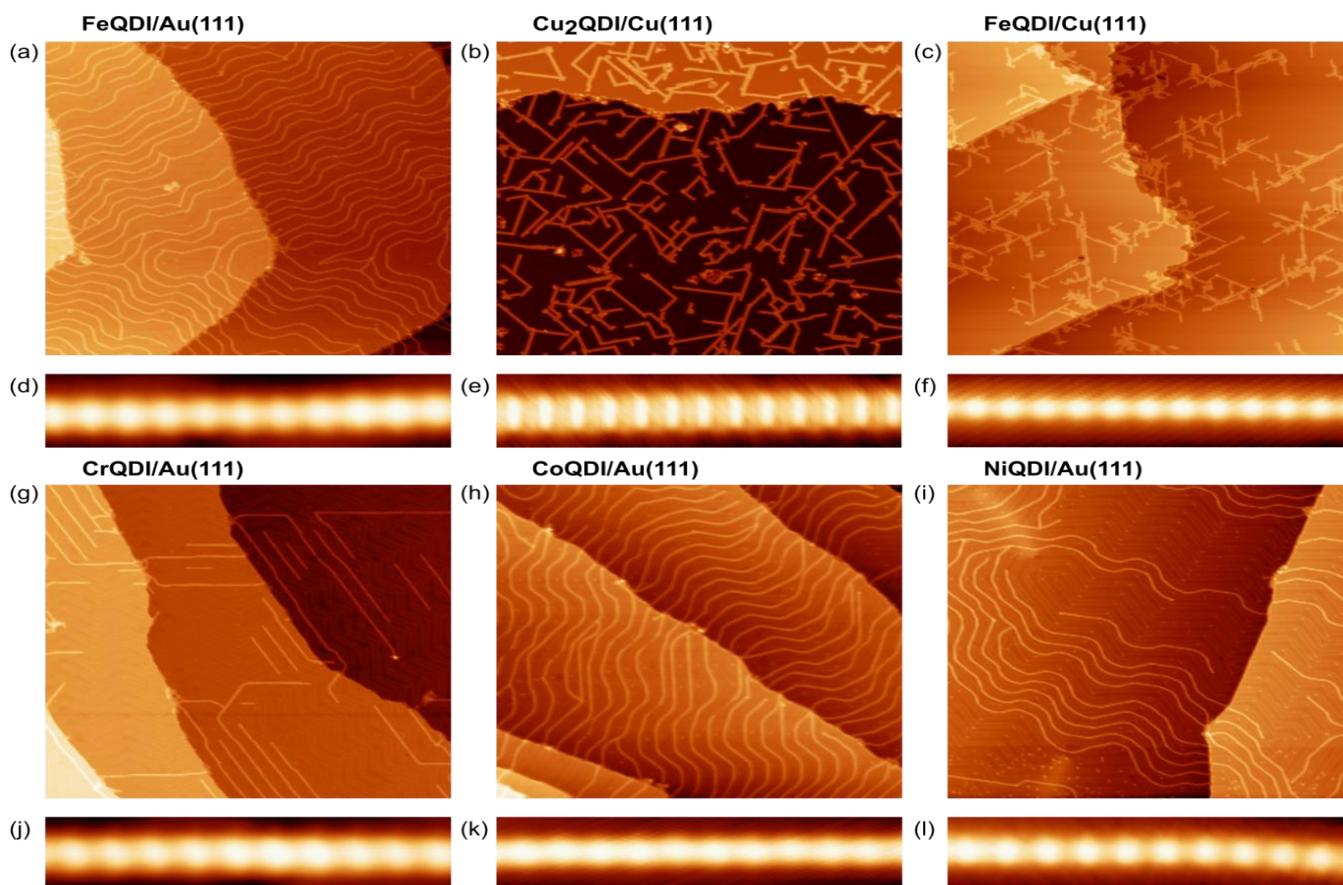


Figure 2: STM images of **{Cr, Fe, Co, Ni}QDI** wires on Au(111) and of **Cu₂QDI** and **FeQDI** wires on Cu(111). The overview images are 200 × 200 nm² and the zoom-in images are 8 × 2 nm². Imaging parameters (bias voltage, tunnel current set point): (a) (500 mV, 10 pA); (b) (1.2 V, 10 pA); (c) (500 mV, 20 pA); (d) (-200 mV, 23 pA); (e) (300 mV, 30 pA); (f) (-200 mV, 50 pA); (g) (100 mV, 30 pA); (h) (350 mV, 10 pA); (i) (100 mV, 42 pA); (j) (30 mV, 10 pA); (k) (-400mV, 32 pA); (l) (100 mV, 42 pA).

Interestingly, while **FeQDI** can be prepared on either Au(111) or Cu(111), we have been unable to prepare **Cu₂QDI** wires on Au(111) by electron-beam evaporation of Cu. We ascribe it to the preferential diffusion of Cu adatoms into the bulk of the Au single crystal.

To understand the origin of the different coordination mechanism of Cu, we analyzed theoretically the formation energies using DFT calculations of free-standing polymers (for details see Figure S5). The **FeQDI** coordination polymer prefers energetically the 4-fold coordination, while the 2-fold coordination is favorable for **Cu₂QDI** wire, in good agreement with the experimental observation. To get more insight into this trend, we also analyzed the electronic structure of the wires. Note, that our DFT B3LYP calculations reveal a closed-shell ground state of **Cu₂QDI** chain, while in the case of **FeQDI**, the chain is open-shell with spin $S = 1$. A detailed experimental and theoretical analysis of magnetic properties of **MQDI** chains is under investigation and it will be published as a separate scientific paper.

Figures S6 and S7 show calculated projected density of states (PDOS) of free standing **FeQDI** and **Cu₂QDI** chains respectively. In the case of the **FeQDI** wire with its four-fold coordination, more d -orbitals are involved in the rehybridization with the p_z -orbitals of the ligand. Also, in the case of other TM atoms (Cr, Co, Ni), partial filling of their d -orbitals promotes strong hybridization with the ligand field adopting the 4-fold coordination.^[17,35] In the case of the two-fold coordinated **Cu₂QDI** chain, only s and d_{yz} orbitals hybridize with p_z -orbitals of nitrogen atoms of the ligand. Since the fully occupied d -orbitals of Cu(I) are reluctant to be involved in the chemical bonding with ligands, the two-fold coordination and thus **Cu₂QDI** structure is preferred. Cu atoms can easily form complexes in +I oxidation state because they are then stabilized by their $3d^{10}$ electronic configuration, unlike Cr, Fe, Co and Ni which prefer oxidation states of +II or higher. The Ni $2p_{3/2}$ XP spectrum of **NiQDI**/Au(111) (binding energy 854.5 eV) firmly supports a +II oxidation state (Figure S3).^[55] In contrast, the Fe $2p_{3/2}$ binding energy of **FeQDI**/Au(111) (707.3 eV) is surprisingly low for a Fe(II) ion. The same effect, *i.e.* high Ni and low Fe binding energy, has been reported for {Fe,Ni}porphyrins, phthalocyanines and related compounds^[56] and is interpreted as a partial shift of electron density from the substrate to the metal ion, in line with the original explanation of this effect.^[57-59] Unfortunately, because of the overwhelming substrate signals we cannot study Cu XP spectra of **Cu₂QDI**/Cu(111).

Indeed, the analysis of the electrostatic potential maps of **FeQDI** (Figure S8a) and **Cu₂QDI** (Figure S8b) (revealing the charge transfer from TMs to the QDI ligand) clearly show that the charge transfer is larger in the case of **FeQDI**, where Fe in four-fold coordination is typically found in +II oxidation state. Consequently, we conclude that Cu in the **Cu₂QDI** polymer is found in +I state. This observation is consistent with the coordination of the copper center through one covalent and one dative bond with the ligand enabling two isomeric electronic structures as shown on Figure 3a. This allows the delocalization of the π - d electrons over the macrocycle, in contrast to the coordination exclusively through dative bonds as observed in supramolecular complexes.^[60]

This picture is also supported by DFT calculations. Namely, the calculated band structure shows relatively strong dispersion of both valence and conduction bands resulting in the band width of ~ 0.5 - 1 eV, see Figure S9a and S9b. Also, real space images of electron

density of both the valence and conduction bands (Figure S9c and S9d) reveal a strong hybridization of d -orbitals with p_z -orbitals of nitrogen atoms on the ligand and delocalization of the electronic states over both TM and ligand. Moreover, the analysis of the bond lengths suggests that in both **FeQDI** (Figure S10a) and **Cu₂QDI** (Figure S10b) wires, the π -system of the quinoidal ligand is strongly delocalized, as shown schematically in Figure 1b. All these findings strongly suggest that the presented 1D coordination polymers exhibit π - d conjugation.

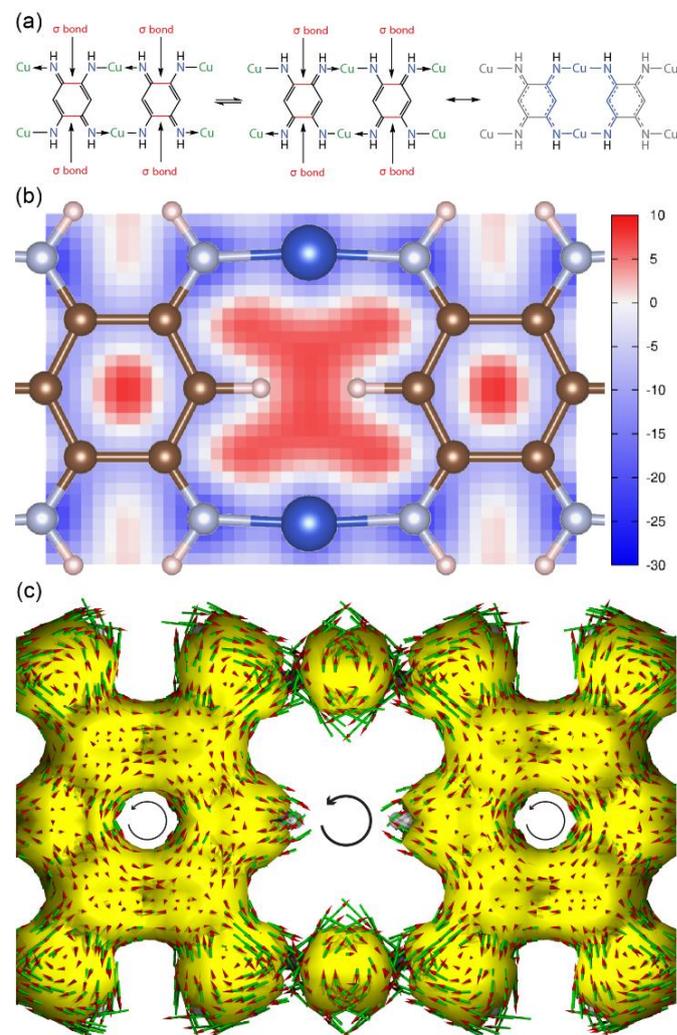


Figure 3: (a) Scheme depicting the bonds and resonating structures of the 12 membered macrocycle in **Cu₂QDI** wires on Cu(111). (b) NICS grid of **Cu₂QDI**/Cu(111). (c) ACID plot of **Cu₂QDI**/Cu(111), black arrow indicating the anticlockwise direction of current density vectors for better clarity. The molecular planes are placed perpendicular to the magnetic field vector. Small green arrows are computed current density vectors.

Next, we provide an analysis of the aromatic character of the macrocycle in the 1D chain **Cu₂QDI**. Figure 3 shows the bond scheme, calculated maps of the nucleus-independent chemical shift (NICS)^[61] and the anisotropy of the current induced density (ACID)^[62] for free-standing **Cu₂QDI** chain. In the case of **Cu₂QDI** chain, the positive NICS values (Figure 3b) with maxima over the C₆ ring of the ligand and the 12-membered macrocycle of +8.6 ppm and +6.6 ppm respectively, indicate that both are antiaromatic in nature. Also the calculated ACID plot of **Cu₂QDI** chain in Figure 3c reveals anticlockwise current density vectors exhibiting paratropic

current and thus antiaromaticity, in agreement with the NICS data. Interestingly, the current density vectors of both the C₆ ring of the ligand as well as the 12-membered cycle are seen as separate loops, hence substantiating that the backbone of the 1D **Cu₂QDI** chain is formed by individual delocalized macrocycles as depicted schematically in Figure 3a. The antiaromatic character of the quinoidal ligand is also confirmed by a negative harmonic oscillator model of aromaticity (HOMA) value of -0.241 (see Supporting Information for HOMA calculations).

In order to understand the aromaticity of conjugated metallacycles, Mauksch and Tsogoeva have worked out the frontier π -orbital topology rule: "The metallacycle is aromatic (antiaromatic) when the number of π -MOs is even and the π -HOMO is of Möbius (Hückel) topology-and vice versa when the number of π -MOs is odd."^[63] The nature of the aromatic stabilization in metallacycles related to the bonding between the transition metals and the adjacent atoms permits two different topologies of the π -d orbital conjugation: Hückel and Möbius topology, where the latter involves the *d*-orbitals introducing a frustrated phase variation of π -orbitals in the metallacycle.^[64] The 12-membered macrocycle in the **Cu₂QDI** chain consists of two *d_{yz}* metal orbitals which change the phase of adjacent π -orbitals of N atom (see HOMO shown in Figure S9b). The presence of an even (two) number of *d*-orbitals causing the change of the phase in the cycle avoids the frustration of the π -orbital phase in the cycle. Consequently, the π -*d* conjugation of the macrocycle can be considered as Hückel topology. The 12-membered macrocycle in the **Cu₂QDI** chain consists of 8 π -MOs (even) and π -HOMO is of Hückel topology, thus the macrocycle is antiaromatic in nature following the Mauksch and Tsogoeva rule, in agreement with the ACID and NICS analysis. Noteworthy, this rule is strictly applicable for the macrocycles whose number of π -electrons is equal to the number of members in the ring, as discussed recently.^[65]

In the case of **FeQDI**, the NICS value (see Figure S11a) for the C₆ ring of the ligand as well as the five membered ring containing the metal is negative (with maximal values of -25.7 ppm and -17.5 ppm respectively) exhibiting aromatic character. The negative values of NICS is indicative of a diatropic ring current in presence of a magnetic field, which agrees with the calculated ACID isosurface for the **FeQDI** chain (see Figure S11b). Nevertheless, we should note that despite relatively large NICS numbers, the ACID plot reveals that the current density is not completely circular on the quinoidal ring. Instead, ACID confirms the existence of two decoupled delocalized π -d electronic systems as schematically depicted in Figure 1b for **MQDI**. This decoupling is also confirmed by a relatively large bond length alternation within the C₆ ring of the ligand (Fig S10). Consequently, the harmonic oscillator model of aromaticity (HOMA)^[66] value of the quinoidal ring is about 0.486, predicting a weak aromatic character (for details of HOMA calculations see Supporting Information).

Conclusion

In conclusion, we presented a novel route to the synthesis of long and defect-free 1D coordination π -d conjugated polymers, achieved by co-deposition of the **2HQDI** molecular precursor and various transition metal (Fe, Co, Ni, Cr, Cu) atoms on metal surfaces under UHV conditions. This approach overcomes the problem of solubility limiting traditional wet chemistry synthesis, and enables to grow up

to hundreds of nanometers long defect-free covalent polymers. By high-resolution AFM imaging and theoretical calculations, we demonstrated that all TMs (except Cu) adopt a four-fold coordination motif with nitrogen atoms of the QDI ligand (**MQDI**). In the case of Cu atoms, we found a new coordination mode of the ligand and the formation of the linear two-fold coordinated **Cu₂QDI** polymer. Our analysis indicates that the electronic states of polymers **MQDI** (M = Fe, Co, Ni, Cr) fully delocalize over both metal and ligand forming π -d systems. In the case of Cu, we observe a unique formation of **Cu₂QDI** wires based on antiaromatic 12-membered macrocycles incorporating two metal centers, chemically connected by two C-C single bonds but electronically independent (no conjugation between the macrocycles), preventing a full delocalization over the wire. We anticipate that the electronic delocalization together with the possibility to incorporate different transition metals provides new route to design π -d polymers of desired magnetic and electronic properties. The on-surface synthesis under UHV conditions provides a unique possibility to further investigate magnetic and electronic properties of individual polymers by means of scanning probe microscopy.^[67]

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Keywords: coordination modes • diamino-benzoquinonediimine • macrocycle • π -d conjugation • scanning probe microscopy

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