Abstract: The very stable helices of 8-amino-2-quinolinecarboxylic acid oligoamides are shown to uptake Cu$^{II}$ ions in their cavity through deprotonation of their amide functions with minimal alteration of their shape, unlike most metallo-organic structures which generally differ from their organic precursors. The outcome is the formation of intramolecular linear arrays of a defined number of Cu$^{II}$ centers (up to sixteen in this study) at a 3Å distance, forming a molecular mimic of a metal wire completely surrounded by an organic sheath. The helices pack in the solid state so that the arrays of Cu$^{II}$ extend intermolecularly. Conductive-AFM and cyclic voltammetry suggest that electrons are transported throughout the metal-loaded helices in contrast with hole transport observed for analogous electrons are transported throughout the metal-loaded helices particularly. Conductive-AFM and cyclic voltammetry suggest that electrons are transported throughout the metal-loaded helices in contrast with hole transport observed for analogous foldamers devoid of metal ions.

Metallo-organic structures containing linear arrays of metal ions have attracted considerable interest as potential one-dimensional materials for the transport of charges and spins. Different approaches exist to produce such objects but, in most cases, the final architectures are dominated by the binding properties of the metal ions and do not preexist in the absence of metals. For example, the formation of polymeric platinum wires is driven by Pt–Pt interactions. Oligomeric or polymeric helicates may form from strands that have no prior organization or from smaller organic precursors, the assembly of which is promoted by the metal. Some folded organic molecules may undergo conformational transitions upon binding multiple metal ions, for example, from helix to rod or rod to helix. Somewhat different is the formation of artificial, metal-mediated base-pairs within DNA duplexes. Though artificial base-pairing does not occur in the absence of metal ions, the metal binding sites may still be preorganized in space within a DNA duplex precursor, provided a sufficient number of flanking Watson–Crick A-T/G-C base pairs have been introduced. In contrast with this background, we present the intriguing discovery that the very stable oligoamide helices of 8-amino-2-quinolinecarboxylic acid (Q, Figure 1b) can be loaded with Cu$^{II}$ ions by replacement of amide protons while barely altering their shape, thus achieving the independent organization of an organic sheath and of a linear array of metal ions of controlled length. Using long helices, arrays of up to sixteen metal centers were produced. We also report the charge transport properties of these Cu$^{II}$-loaded aromatic amide helices. From their redox properties, it is proposed that they are selective for the transport of electrons as opposed to the more classical transport of holes observed in most organic 1D materials. Given the high modularity of the aromatic sequences, for example, the possibility to combine quinoline units with a vast array of other hetero-structures which generally differ from their organic precursors.

Figure 1. a) Metal coordination of 8-amino-2-quinolinecarboxylic acid oligoamides via amide deprotonation; b) chemical structures of quinoline oligoamides ($Q_{m+1}$) and copper-loaded oligomers ($Q_{m+1}$-mCu). See text for reaction conditions.
open up multiple opportunities for designing and fine-tuning new metallolofoldamers.\[9\]

Quinoline oligomers combine several desirable properties, including remarkably stable conformations in a variety of solvents\[10\] and rapid synthetic access.\[11\] These organic helices have been shown to be effective multidimensional charge transporters along their axis,\[12\] a property that may find applications in sensing.\[13\] Holes are transported via a hopping mechanism both through covalent bonds along the helix and through space, that is, between aromatic layers stacked within the helix. The coexistence of alternative pathways may mitigate the effect of localized traps or defects. This results in a very small attenuation of charge transport with increasing helix length ($\beta = 0.06 \; \text{Å}^{-1}$) and high calculated hole mobilities of $0.1–1.0 \; \text{cm}^2\text{V}^{-1}\text{S}^{-1}$ along the helix axis.\[12\] In monolayers of Q₅ oligomers on Au, charge transport perpendicular to the helix axis, that is, between helices, was found to be negligible even when helices are tightly packed. This evidences one-dimensional charge transport in contrast to other electroactive self-assembled monolayers.\[14\]

Quinoline has been extensively used as a ligand to form complexes with various transition metal ions.\[4\] We thus devised that metal ions might be coordinated by Q₅ organic strands at the quinoline nitrogen atoms and, possibly, through amide deprotonation. The introduction of metal ions was expected to profoundly affect charge transport. However, it was not known whether metal binding would also alter the helical structure as is the case in related pyridinecarboxamide helices, which bind CuII to form double helicates that are quite distinct from their single helical precursors.\[15\] The inner diameter of Q₅ helices is narrow, so much so that they are used as capping segments in the design of helical capsules.\[8\] Nevertheless, space suitable to fit a small metal ion might be accommodated upon amide deprotonation which would transform each Q unit into a bidentate ligand. Therefore, we endeavored to investigate metal coordination of CuII by nitro- and ester-terminated Q₂₅₋₇ oligomers having an odd number of units, that is, an even number of amides.

Mixing Q₅ with Cu(OAc)₂ in CHCl₃/MeOH (1:1 vol/vol) led to the instant appearance of a dark green color at room temperature. Binding was found to be strong, and curve fitting of the change of UV/Vis absorbance to a 1:1 binding isotherm yielded a lower estimate for the $K_\text{a}$ of $2.8 \times 10^6 \; \text{Lmol}^{-1}$ (Supporting Information, Figures S1–S3). When mixing Q₃ with Cu(OAc)₂ under the same conditions, the UV/Vis spectrum showed that the single helical shape of the quinoline oligoamides was maintained after complexation with CuII (Figure 2), in sharp contrast with the frequently encountered double stranded helicates.\[4\] Overlays of the structures of Q₅ and Q₇·Cu₄ confirm minimal changes (a slight decrease in curvature) upon metal complexation (Figure S18). All CuII coordination spheres are based on the distorted four-coordinate structure shown in Figure 1a. Occasionally, some characteristic changes in the amide I and II regions (Figure S17). Remarkably, the only base present during the reaction is the acetate counterion. We thus infer that the overall neutral complexes that were formed are stable to the small amount of AcOH produced during the reaction. Q₂₅₋₇·mCu oligomers were nevertheless demetalated and recovered intact by aqueous HCl treatment.

Single crystals of Q₅·2Cu, Q₇·3Cu and Q₉·4Cu suitable for X-ray diffraction analysis were obtained by slow evaporation from chloroform/methanol solutions.\[16\] The structures all showed that the single helical shape of the quinoline oligoamides was maintained after complexation with CuII (Figure 2), in sharp contrast with the frequently encountered double stranded helicates.\[4\] Overlays of the structures of Q₅ and Q₇·Cu₄ confirm minimal changes (a slight decrease in curvature) upon metal complexation (Figure S18). All CuII coordination spheres are based on the distorted four-coordinate structure shown in Figure 1a. Occasionally, some...
endocyclic nitrogen atoms seem to bridge two CuII centers, and the N-terminal nitro group is always involved in coordination with the nearest CuII, so that distorted five and six coordination are also observed (Figure 2d–g). The flexible coordination of CuII thus appears to be a favorable parameter. A few tests were performed with other metals that revealed only weak coordination of PdII by Q7 as well as a double stranded (Q7·Zn)2 helicate (Figures S13–S16), suggesting that the formation of the CuII complexes is not general. A thorough screening of other metals was not performed.

Additional experiments shed light on the reaction pathways to form these complexes. Q7·2Cu was found to lose one CuII in presence of AcOH. A crystal structure of the resulting Q7·Cu was obtained and showed that the N-terminal CuII was missing (Figure S20). Furthermore, when Q7 was reacted with only 1 equiv of Cu(OAc)2, a mixture of products was obtained that yielded remarkable co-crystals. The asymmetric unit contained four different complexes: one Q7·3Cu, two Q7·2Cu, and one Q7·Cu (Figure S20). The CuII occupancy factors were not all 100%, highlighting that helices may have identical shapes with and without CuII and take the same position in the lattice. Remarkably, all structures had a fully labile site. Metalation of Q7 and Q33 was incomplete even after prolonged reactions (75 °C for 2 weeks). We reasoned that full metalation may require a quickly reversible process because random metalation would produce orphan amide groups that can no longer uptake a metal center (Figure 3a). Indeed, in the absence of a cooperative, zipper-like mechanism, the number of possible pathways and intermediates towards full CuII loading increases very fast with increasing oligomer length. There are 32 possible intermediates towards Q7·4Cu, of which 14 need no correction. To produce Q33·16Cu, one can count 3524576 intermediates, of which only 65534 (1.86%) need no correction (See supporting information), and 5841 are fully loaded but include orphan amides. We thus tested higher temperatures and short reaction times and cleanly obtained Q17·8Cu by heating Q17 with Cu(BF4)2 in dimethylformamide at 120 °C for 15 min. Q17·16Cu was obtained similarly, in N-methyl-2-pyrrolidone at 150 °C for 20 min. ESI-MS spectra convincingly showed the completion of the reaction (Figure 3b,c). The counterion used was found to degrade to produce HF, which might also play a role.

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The crystal structures shown in Figure 2 revealed the formation of linear arrays of CuII centers within the organic helices. The distances between individual CuII ions inside the helices are ca. 3 Å, suggesting that only weak or no metal-metal interactions may take place. Indeed metal-metal interactions often require shorter distances (less than ≈2.8 Å for CuII)[17] as observed in various Pt and Au complexes.[18] Nevertheless, magnetic susceptibility measurements revealed an unanticipated ferromagnetic exchange between the paramagnetic CuII. The data could be fitted to an isotropic Heisenberg spin Hamiltonian considering spin S = 1/2 CuII centers (Figures S21, S22). The arrangement of the CuII in the helices suggests a sort of wire. Furthermore, the helices stack in the crystals so as to extend the linear arrays of CuII throughout the entire crystal (Figure 2h–k). Within a columnar stack, helices all have the same handedness, and helix-helix contacts are always head-to-tail, resulting in intermolecular Cu-Cu distances in the 4.3–4.5 Å range. This organization along the helix axis prevails even though the in-plane organization of the helices varies: the columns assume a near perfect pseudo-hexagonal close packing and all have the same handedness in the chiral lattice of Q7·4Cu (Figure 2j,k) whereas they are both right- and left-handed and adopt an almost square packing in the crystal lattice of Q3·3Cu (Figure 2h,i).

We surmised that these materials may behave as strongly anisotropic molecular conductors provided that the alignment of the CuII ions is conducive to charge transport. Unfortunately, the crystals’ robustness was insufficient to directly measure their conductivity using vacuum-deposited electrodes.[19] We thus turned to probing the conductivity of self-
assembled monolayers (SAMs) of the metalated foldamers forming a metal-organic-metal junction, as performed previously on Q5 oligomers. For this purpose, AsgQ5, AsgQ9, and AsgQ24 (Figure 4a) were synthesized as analogues of Q5, Q9, and Q24, respectively (see Supporting Information). In these new compounds, the N-terminal 8-nitro group is replaced by an asparagusic amidomethyl group (Asg). AsgQ5,2Cu, AsgQ9,4Cu and AsgQ24,8Cu were generated by carefully optimizing the copper-loading reaction conditions. The absence of degradation of the S–S bond and the identity of each copper-loaded oligomer were confirmed by mass spectrometry (SI for details, Figure S12). SAMs were produced using the asparagusic group as an anchoring site for the gold surface (Figure 4b, see Supporting information). The successful formation of the corresponding monolayers on gold substrates was evidenced by XPS, spectroscopic ellipsometry and polarization-modulated infrared reflection-absorption spectroscopy (PMIRRAS). The thickness of the monolayers obtained for each complex was found to increase with the length of the oligomers as expected for the formation of compact, vertically-aligned helices (Table S2). Likewise, the PMIRRAS spectra displayed the expected absorption bands corresponding to the metalated foldamers (Figure S23, S24). PMIRRAS signal intensity increases with increasing foldamer length (Figure S23). This can only be possible if the foldamers are oriented perpendicular (i.e. standing vertical or with a constant tilt angle) with respect to the substrate. Finally, the formation of metalated foldamer SAMs was also confirmed by XPS, which clearly showed the presence of sulfur and copper atoms in the surface composition of the monolayers (Figure S25).

The SAMs are designed to form part of a metal-insulator-metal device with the gold substrate acting as a bottom electrode. The other electrode is formed using a conductive Pt-Ir atomic force microscopy tip (conductive-AFM) which is used to locally probe the conductivity of the SAM at a set force by measuring the current as a function of applied voltage. To circumvent tip variability and contact area, the measurements comparing the conductance of the SAMs were done with the same tip at an applied force of 5.1 nN. Under these conditions, the SAMs exhibited conductances between 2 × 10⁻⁹ and 50 × 10⁻¹² S (Figure 4d). Under the same conditions, the conductance of a control non-metalated AsgQ9 SAM was below the detection limit of the instrument. From this, we deduce that the mechanism of charge transport may be different between the metalated and non-metalated foldamer architectures in spite of their similar size and shape. Cyclic voltammetry experiments performed using the Au substrates modified with the AsgQ2n+1,mCu foldamers (Figure 4c), as well as the cyclic voltammograms of solutions of Q2n+1,mCu foldamers (Figure S26) showed a reduction peak whose area increases with the number of CuII ions bound inside the foldamers. The peak areas correlate well with the calculated number of electrons necessary for the complete reduction of the copper in the monolayer (Table S3). The molecular surface densities that can be calculated again support an upright orientation of the helices on the surface (Figure S27). Furthermore, no oxidation event was observed over the potential scanned. From this, we deduce that the presence of the CuII ions is conducive to the transport of electrons via a facile initial reduction step to CuI that would produce mixed valence species such as those recently reported for some metallopolymers. Some structural variations due to the change in the coordination geometry between the CuII, which are present in 4-, 5-, or 6-coordinate geometry and CuI, which prefers a tetragonal coordination, may be expected. We note that the separation between the forward and return waves increases with increasing number of CuII ions, and that this is accompanied by a progressive decrease in the reversibility of the redox process. Together, this could be an indication of differences in the rate of the redox process and a reflection of geometrical changes. It remains that, unlike the non-metalated foldamer helices which are hole transporting materials, the CuII metalated foldamers are geared towards electron transport due to the redox properties of the metal ions.

Comparison of the charge transport properties of the AsgQ2n+1,mCu SAMs reveals that the resistance of the monolayer (R) increases with increasing foldamer length (Figure 4). Linear fitting of a plot of lnR vs. molecular length for the series yields a value of 0.22 ± 0.05 Å⁻¹ for the attenuation factor (see Supporting Information). This value is larger than that determined for the analogous non-metalated foldamers (0.06 Å⁻¹), which would be consistent with the larger reorganization energy generally associated with electron vs. hole transport. It is also plausible that, whereas hole transport in the non-metalated foldamers occurs via multiple charge transport pathways, electron transport in...
the metalated foldamers can occur solely through the linear array of CuII ions. The latter is, therefore, more susceptible to disruption due to conformational or localized defects whose probability increases with increasing molecular size.

In conclusion, loading of up to exactly sixteen CuII ions into quinoline-oligoamide foldamers has been achieved while maintaining their single helical structure. The CuII centers inside the helices were aligned akin to molecular wires. One dimensional alignment of CuII also occurred in crystals by stacking of the helices. The effect of copper loading on the conductance through the foldamers was tested by measuring the resistance of self-assembled monolayers using conductive AFM. It was found that copper loading may switch the intrinsic hole transport of the foldamers to electron transport. Switching of the nature of the charge carriers in these foldamers represents a simple way to profoundly alter the electronic structural alterations upon metalation, as demonstrated by the spontaneous co-crystallization of partially metalated foldamers, may further allow for the construction of multiple molecular p-n junctions with relative ease. Progress in this direction is being made and will be reported in due course.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: CuII coordination · electron transport · helix · metallofoldamers · self-assembled monolayers

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