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Covalently Linked Porphyrins as One-Dimensional Conductors

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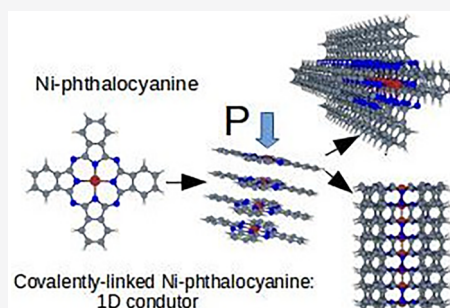


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Supporting Information

ABSTRACT: We apply first-principles calculations to address the problem of the formation and characterization of covalently linked porphyrin-like structures. We show that upon pressure a rehybridization process takes place which leads to one-dimensional compounds resembling nanowires, in which carbon atoms are all 4-fold coordinated. We also show that the resulting nanostructures have metallic character and possess remarkable mechanical properties. Moreover, in the case of porphyrin–metal complexes, we find that the covalently linked structures may be a platform for the stabilization of straight metallic wires.



The chemical versatility of carbon atoms is inextricably linked to the rapid development of nanoscience, especially from the mid-1980s. The discoveries of molecular and solid fullerenes,¹² nanotubes,³ and the characterization of graphene⁴ paved the way for the scrutiny of low-dimensional compounds, leading to the proposal and/or synthesis of a plethora of novel materials. In this context, carbon nanowires, whose synthesis and theoretical characterization⁵ date back to 2014, constitute a typical case. By submitting benzene samples to a 20 GPa high-pressure regime followed by a slowly released to ambient pressure, the authors detected the formation of diamond-like one-dimensional structures, the so-called carbon nanowires, which were characterized by several experimental and theoretical techniques, including X-ray and neutron diffraction, solid-state NMR, Raman spectroscopy, transmission electron microscopy, density functional theory calculations, and molecular dynamics simulations. Soon after the idea was extended to other molecular precursors: pyridine,⁶ aniline,⁷ and thiophene-based⁸ threads were synthesized by slow compression to pressures in the range 23–35 GPa, and theoretical works suggested the possible formation of threads based on several polycyclic aromatic hydrocarbon molecules.^{9,10} Mechanical properties constitute a key aspect of the behavior of these structures. Indeed, predictions^{11–13} of Young's moduli as high as 850 GPa have shown that nanowires may find important applications as ultralight and ultrastrong fibers. In the present work, we focus on porphyrin-like molecules, which play fundamental roles in biological processes and have been extensively investigated as building blocks in nanostructures.^{14–17} We pose the question on whether they may form covalently linked one-dimensional (1D) structures with formation pressures comparable to those measured in nanowire experiments, and we proceed by characterizing its electronic and mechanical properties. We found, indeed, stable porphyrin-like wires held together by

strong carbon–carbon sp^3 bonds, which possess high Young's moduli and metallic characteristics and may be a platform for metallic monatomic wire stabilization.

To address the problem, we employed an *ab initio* formalism based on the density functional theory, pursuing the following scheme. First, we focused on the possible formation of an infinite 1D covalently linked porphyrin, evaluating the pressure required for a complete transformation into a sp^3 -hybridized structure and assessing its stability upon pressure release. Second, we characterized the structural, electronic, and magnetic properties of the porphyrin threads by determining Young's moduli, band structures, and magnetic moments. Finally, we investigated the stability and properties of finite size porphyrin-like threads in structures comprising six molecular units. In our models, we considered two porphyrin-like compounds: porphine molecules, which are extensively employed in theoretical models to investigate porphyrin properties and which may be found in crystalline form,¹⁸ and phthalocyanine molecules, whose crystalline form is commercially available. For both, we considered nonmetal (2H) and metal complexes.

Our geometry optimization calculations were performed within the pseudopotential spin-density functional theory (DFT) formalism,^{19,20} making use of the localized basis set implementation of the SIESTA package.²¹ We employed the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof parametrization (PBE)²² to represent the

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exchange-correlation potential. The Brillouin zone was sampled with a $1 \times 1 \times 18$ grid. The threshold for geometric optimization was set to 0.01 eV/\AA as the maximum force component in any atom. To check the convergence of the electronic structure with respect to the exchange-correlation approximation, we performed calculations within the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional (HSE06)²³ in the all-electron scheme implemented in BAND^{24,25} module of Amsterdam Modeling Suite (AMS) (see the Supporting Information for details). The coordinates and lattice vectors of the main structures investigated in the present work can be found in the Supporting Information.

Our first set of calculations was performed in a unit cell composed of two molecular units separated by a distance d . As initial conditions, we could use either the equilibrium geometries of individual molecules or perturbed configurations, in which small up and down displacements are imposed to the carbon atoms to induce a sp^3 -like corrugation. The covalently linked structures are formed in both schemes; however, we chose the latter approach to avoid metastable conformations (see the Supporting Information for details). We began with 2*H*-porphine and Ni-porphyrin molecules, shown in Figures 1a and 1b, left panels, respectively. The

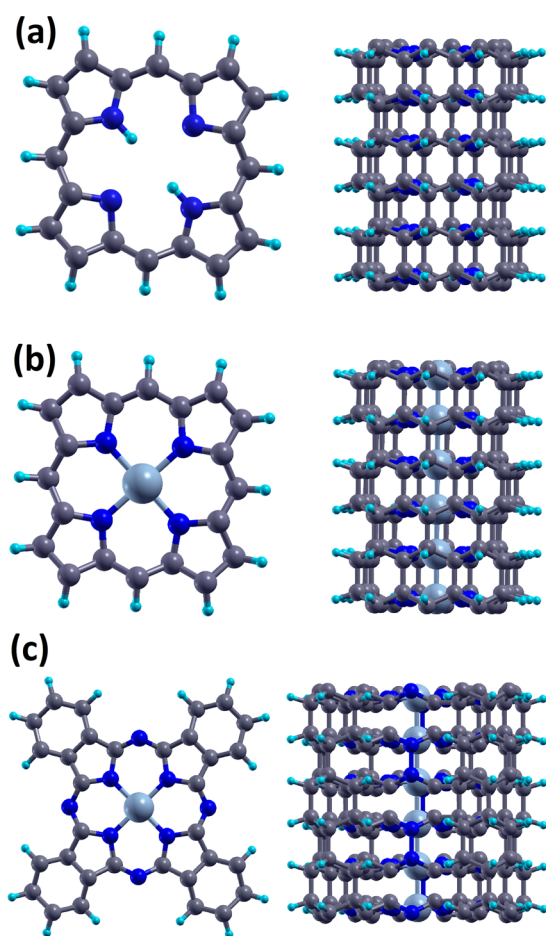


Figure 1. Top and side views (left and right panels, respectively) of the relaxed covalently linked nanostructures: (a) hydrogenated-porphine (b) Ni-porphyrin, and (c) Ni-phthalocyanine. On the right, three periodic images were included for visualization purposes. Gray, blue, cyan, and silver spheres represent carbon, nitrogen, hydrogen, and nickel atoms, respectively.

distance d was varied, starting from the van der Waals distance, $d = 3.35 \text{ \AA}$, and for each value, the lattice vector, set to $2d$, was kept fixed while the geometry was optimized. We searched for the value of d which triggered the sp^2 to sp^3 rehybridization. A slightly larger value of interlayer distance allowed us to pinpoint the maximum compressive pressure, which we defined as the threshold pressure required for a complete restructuring—we found $d = 2.550$ and 2.575 \AA for the porphine and Ni-porphyrin cases, respectively, corresponding to pressures of 35 and 30 GPa, the same order of magnitude which were measured in thiophene nanothread synthesis.⁸ There is an unavoidable ambiguity in the definition of pressure in 1D systems because of the definition of area. Hereafter, we adopt the convention of using the molecular area, defined by the product of the lateral lengths measured as distances between hydrogen atoms in each direction. To allow for comparisons with other conventions, we also express our results as 1D stress,¹³ given in units of nanonewtons. Within this latter choice, the formation thresholds are 32.0 and 27.0 nN for 2*H*-porphine and Ni-porphyrin, respectively.

To investigate stability under pressure release, we performed an unconstrained optimization: starting from the constrained sp^3 -porphine structures, we released the lattice vector and fully reoptimized the systems. The result is shown in Figures 1a and 1b, right panels, with three periodic images included for visualization purposes. For the hydrogenated porphine, we employed two distinct configurations: the first with the N–H bonds align along the vertical direction (two identical units in the primitive cell displaced by d) and the second with the N–H bonds of one porphine rotated by 90° relative to the other. We found that the latter configuration is energetically more stable than the former by 0.1 eV. In both cases, the final geometry is characterized by the binding of the porphine units through carbon–carbon bonds forming a 1D structure with a lattice parameter of 4.38 \AA . The lateral walls are entirely composed of six-membered rings in which the carbon atoms are 4-fold coordinated. The cross section retains the porphine appearance, and the nitrogen atoms, which remain in a planar configuration, keep the same coordination as in the isolated molecules. As for the Ni-porphyrin case, we found essentially the same structural results, as shown in the right panel of Figure 1b. The particularity of this case is the natural formation of a monatomic Ni wire at the center of the structure. As in the isolated molecule, each Ni makes bonds with the four in-plane nitrogen atoms. The choice of Ni was motivated by the expected Ni–Ni bond length in a linear Ni wire compared to the expected distance between porphyrin molecules in an all- sp^3 structure. A systematic study conducted by Ataca et al.²⁶ shows that for linear wires the lattice vector is 2.2 \AA for Ni, and a dimerization is not energetically favored. This value almost perfectly matches the lattice vector of the proposed sp^3 -porphine structures (4.38 \AA and distance between molecules is 2.19 \AA). The choice is not unique. In fact, the results are quite similar for cobalt, which presents a Co–Co bond length²⁶ in linear wire of 2.1 \AA (see the Supporting Information for more details).

We applied the same protocol to another class of porphyrin compounds—the phthalocyanine molecules. In the left panel of Figure 1c, we show the Ni-phthalocyanine complex, featuring its heterocyclic rings linked by nitrogen atoms, and, on the right, the optimized geometry after rehybridization. This system reproduces basically the same geometric aspects of the previous cases, except for a slightly smaller lattice constant

(4.29 Å). The outer nitrogen atoms follow the same corrugation trend of the carbon atoms, typical of a sp^3 hybridization, while the inner ones keep a planar configuration, as in the porphine case. The results for hydrogenated phthalocyanine are analogous.

To assess the electronic properties of the covalently linked porphyrin-like molecules, we performed spin-DFT band structure calculations. We found a metallic behavior for all structures previously described. Three selected cases are shown in Figures 2a–c, corresponding to the 2*H*-porphine, Ni-

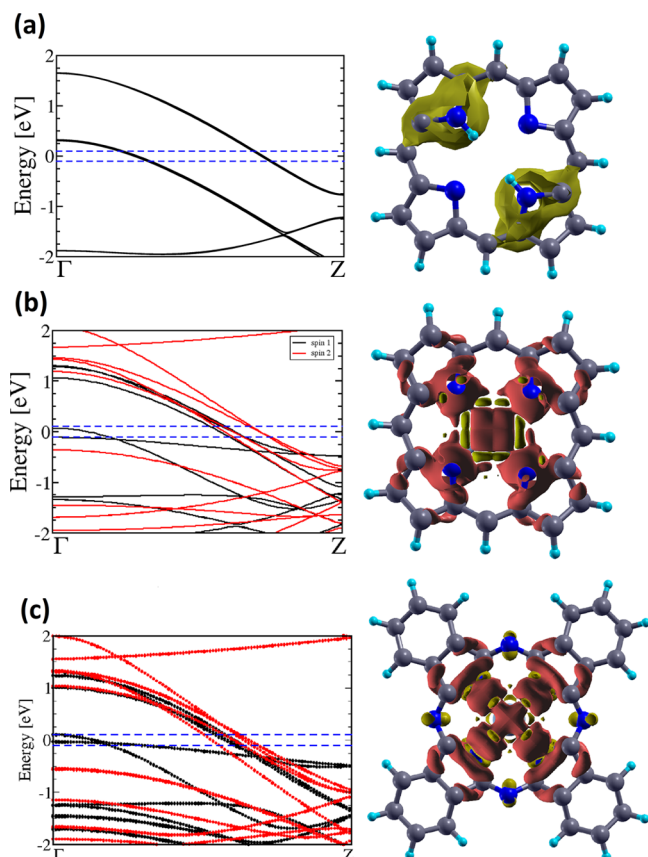


Figure 2. Band structures (left) and charge density isosurface plots (right) for selected cases: (a) hydrogenated-porphine, (b) Ni-porphyrin, and (c) Ni-phthalocyanine. Red and black lines indicate the two spin components. The isosurface plots correspond to charge densities associated with the states in the 0.2 eV energy range (indicated by dashed lines) around the Fermi level, which is set to zero.

porphyrin, and Ni-phthalocyanine cases, respectively. This is marked contrast to other carbon nanotreads, including those with nitrogen substitutions.⁶ Also, carbon and carbon nitride nanotreads with partially saturated bonds²⁷ present electronic behaviors which vary from semiconducting to insulating. The diamond-like structure of nanotreads drives them, in general, into an insulating state, so a question arises as to how the 2*H*-porphine are acquiring the metallic character. The answer relies on the hydrogenated nitrogen atoms. Nitrogen may replace a methine group (–CH) in carbon rings, as in the pyridine molecule, keeping its lone pair in a sp^2 orbital. Pyridine-based threads are semiconductors, as would be porphine-based threads without any ligands in their central core (neither hydrogen atoms nor metals). By binding hydrogen to the two nitrogen atoms, the additional electrons

reorganize the bonding configuration of the rings, and intermolecular interactions are effective to form dispersive bands crossing the Fermi level. The right panel of Figure 2a, which shows the isosurface plot of the charge density corresponding to states in the 0.2 eV energy range around the Fermi level, confirms this idea. In fact, it clearly shows extended states in the periodic direction, which, in the plane, are predominantly localized in the N–H bonds. As for the sp^3 -Ni-porphyrin-like compounds, the structures are magnetic, characterized by a magnetic moment of $2.8 \mu_B$. Figure 2b shows, on the left, the electronic bands for the two spin components, which are distinguished by black and red lines. In the right panel, the charge density isosurface plot (energy range indicated by dashed lines in the band structure) shows the nickel atomic wire and the nitrogen atoms as responsible for the metallic character of the compound. The results are similar to the phthalocyanine case, shown in Figure 2c, for which we found a magnetic moment of $1.9 \mu_B$. We could not find any indication of a possible Peierls-like transition. Such distortion could arise as the result of the competition between the cost of the elastic energy involved in a deformation and the energy gain associated with the electronic redistribution in the *k*-states when the Brillouin zone is changed due to increase in the lattice parameter. We have checked this possibility in our case, and we could not find any deformation (such as dimerization and trimerization) which could represent an energy gain. In fact, a distortion would involve a large elastic energy cost due to the carbon sp^3 network connected to the nitrogen atoms which, in turn, are bonded to the metallic element.

A question arises on the possibility of distinct conformations for the sp^3 -linked structures. We could not find any for the phthalocyanine case. However, for porphine systems, we did find one which turned out to be 0.2 eV per porphine molecule higher in energy compared to our lowest energy conformation. It was built by laterally translating one molecular unit relative to the other (by 2.49 Å) (see the Supporting Information for details). The result is that fewer carbon sp^3 bonds are formed, but it is still enough to hold the molecules together. With more sp^2 carbon atoms, the lattice vector tends to be larger (4.61 Å), weakening intermolecular interactions and driving the system to a semiconducting state.

Next, we turn to mechanical properties. Carbon nanotreads are known to possess high specific strength with Young's moduli similar to those of carbon nanotubes, of the order ~ 900 GPa. Would it be also true for porphyrin-like threads? To answer this question, we have performed a set of calculations in which the sp^3 covalently linked structures were submitted to tensile and compressive strains. We varied the length of the lattice vector in steps of 0.05 Å up to a 4% maximum strain in both directions. The energy \times strain plots for both hydrogenated-porphine (aligned configuration of N–H bonds in adjacent molecules, with similar results for the twisted one) and Ni-porphyrin are shown in Figures 3a and 3b, respectively. The parabolic behaviors indicate the harmonic regime in both cases and allow us to determine the Young's moduli from the second derivatives (we used the expression $Y = -(1/V_0)(\partial^2 E/\partial \epsilon^2)$, in which E is the energy, ϵ is the relative strain, and V_0 is the equilibrium volume). We found $Y = 601 \pm 8$ and $Y = 823 \pm 6$ GPa for porphine and Ni-porphyrin, respectively, which are comparable to those predicted for carbon nanotreads. In terms of 1D stress, these values are 543 and 669 nN, respectively.

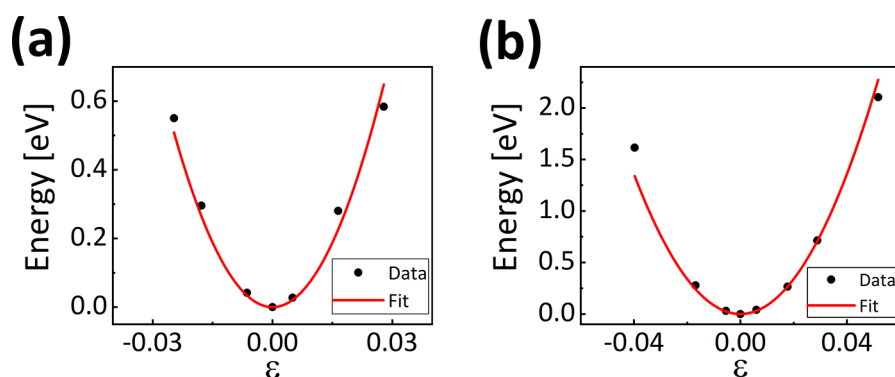


Figure 3. Plots of total energy as a function of the applied strain in (a) porphine and (b) Ni-porphyrin. DFT results are indicated by black dots, while the parabolic fits are represented by red solid curves. The strain is defined as $\Delta L/L_0$, in which ΔL is the change in the lattice vector and L_0 is the equilibrium value.

Finally, we show that the phenomenology is not restricted to periodic structures. Finite porphyrin-based threads may still remain stable. We showed that by relaxing, without any constraints, finite cuts in the periodic structure: [Figure 4a](#)

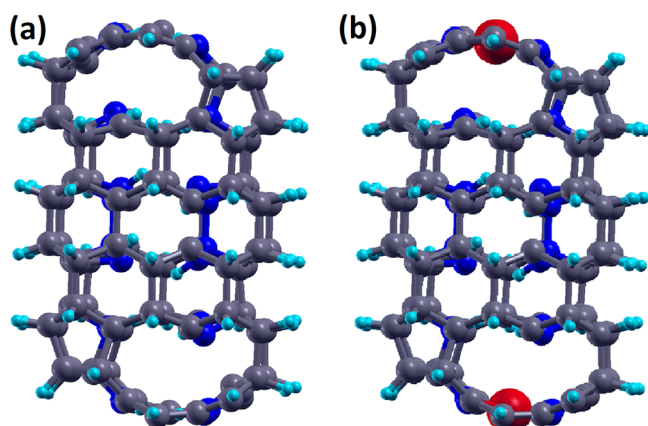


Figure 4. Relaxed geometries of finite porphyrin-based threads with six molecular units: (a) 2H-porphine case and (b) 2H-porphine structure with Fe substitutions in the upper- and bottom-most molecules.

shows the result of our calculations for six 2H-porphine molecules. The upper and lower units remained bonded to the structure by lateral bonds, while the central region in these units detached themselves and formed curved caps, like a canopy. This feature brings an interesting possibility, which we illustrate with the relaxed geometry shown in [Figure 4b](#): the upper- and bottom-most units of the hydrogenated-porphine may have their two hydrogen atoms replaced by a metallic element, such as iron, forming a mixed covalently linked structure. Besides, the iron insertions add a magnetic moment of $8.0 \mu_B$ to the system, and the metallic atoms may act as active sites for further functionalizations.

In summary, our calculations suggested a remarkable mechanical strength and conducting behavior for porphyrin-like molecules linked together via covalent bonds. The pressure required to achieve such rehybridization lies within the range observed in carbon nanowire syntheses. Importantly, the phenomenology is also observed for metal–porphyrin complexes, resulting in a central straight metallic wire. One-dimensional conductors may play important roles in nano-electronics, as nanowire connectors, and also allow for

investigation at a fundamental level of electron flow and correlations in low dimension. Besides, finite size structures with transition metal elements may act as molecular magnets and furnish functionalization sites to promote interface with biological molecules.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c03327>.

The choice of initial conditions, other possible conformations, the case of other metallic elements, the choice of exchange–correlation functional, table of coordinates of main structures ([PDF](#))

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Notes

The authors declare no competing financial interest.

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