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On-surface synthesis of indigo-based porphyrinoids and quadruply fused porphyrinoid oligomers with aromatic eight-membered rings

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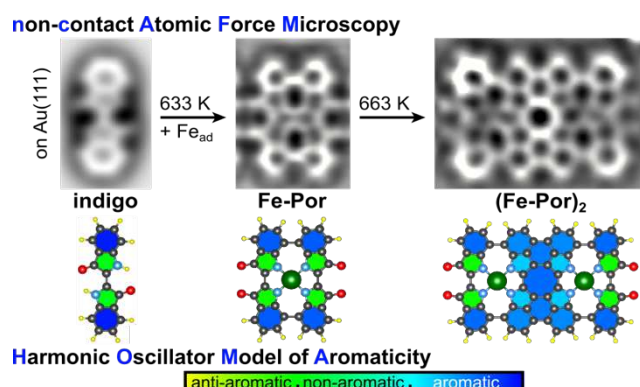
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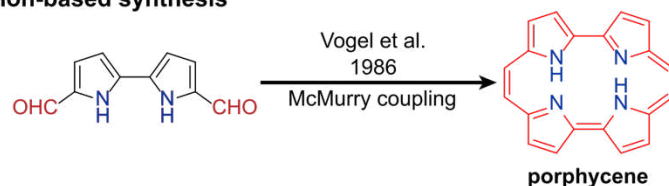
Abstract

Tailored porphyrinoid nanostructures are captivating and promising systems providing versatile optoelectronic and chemical properties or templates for complexed atoms. Here we report a novel Fe-porphyrinoid fabricated from indigo on Au(111). Its on-surface synthesis is mediated by Fe coordination driven isomerization affording a pocket template to position and spatially orient precursor moieties, facilitating a regiospecific reaction pathway. Further deoxygenative and dehydrogenative C–C couplings steps yield oligomers with quadruple linkages featuring fused six-membered as well as aromatic eight-membered rings. The reaction steps and products are thoroughly characterized by a combination of scanning tunnelling microscopy, bond-resolving atomic force microscopy, and density functional theory investigations. These findings introduce a distinct strategy to realize macrocyclic tetrapyrroles and quadruply fused porphyrinoids, paving the way for the fabrication of novel interfacial nanostructures.

Introduction

Porphyrins, consisting of four pyrrole subunits connected through methine bridges, are highly significant functional molecules in both biological processes and material science, as they possess appealing photophysical properties,¹ redox activity,² magnetochemistry³ and the ability to coordinate with metal atoms.⁴ In recent decades, substantial efforts have been devoted to enlarge this family by synthesizing various porphyrinoids (**Pors**)⁵⁻⁸ aiming at diverse conformations, cavity shapes, and π -electron systems. These structural variations bestow **Pors** with unique physical and chemical properties that differ markedly from those of conventional porphyrins. Among these, porphycene, being the first constitutional isomer of porphyrin, initially synthesized from bipyrrrole dialdehyde via McMurry coupling (Fig. 1a),⁹ has been extensively studied owing to its synthetic accessibility, chemical stability, and remarkable optical properties with enhanced absorption in the red region.¹⁰

a Previous work: Solution-based synthesis



b This work: On-surface synthesis

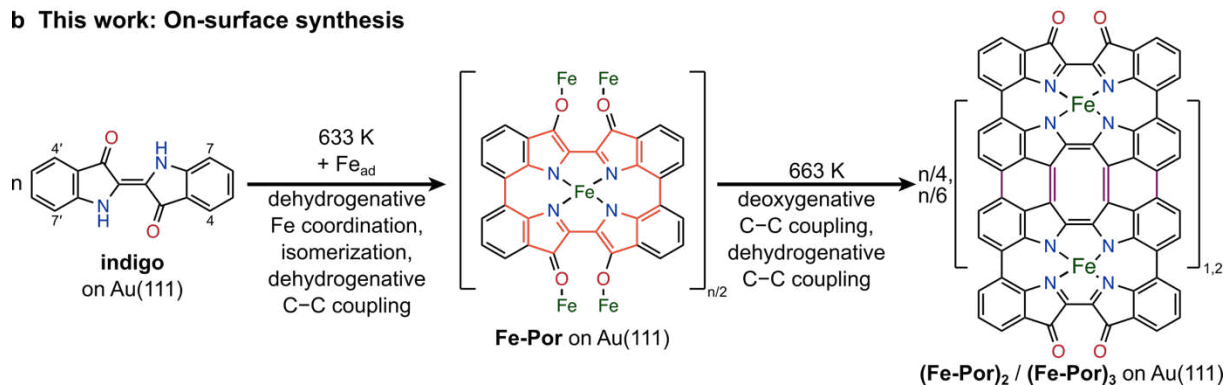


Fig. 1 | Selected synthesis schemes of porphycene and related porphyrinoid. a, Solution-based synthesis of porphycene. **b,** On-surface synthesis of **Fe-Por** coordination chains and **(Fe-Por)_{2,3}** adsorbed on Au(111). Shown in red in (a) the [18]porphyrin-(2.0.2.0) macrocycle of porphycene and in (b) the [0]porphyrin-(2.0.2.0) macrocycle of **Fe-Por**.

Porphyrin nanotapes¹¹ (e.g., β - β , *meso-meso* or β - β triply linked) have attracted considerable interest because their high degree of π -conjugation leads to strongly red-shifted absorption bands,¹² unusually small HOMO-LUMO gaps,¹¹ near-IR reverse saturable absorption,¹³ and high single-molecule conductance.¹⁴ In addition to porphyrin nanotapes, porphyrin nanobelts,¹⁵ **Pors**¹⁶ (e.g., corrole¹⁷⁻²¹ and subporphyrin)²² nanotapes, porphyrin-**Pors** (e.g., porphyrin-hexaphyrin)²³⁻²⁵ hybrid and porphyrin-graphene hybrid nanotapes²⁵⁻²⁸ have been successfully synthesized and explored. However, to date porphyrin-related nanotapes and nanobelts feature at most triple connections, reflecting a maximum of three fusing sites (β , *meso*, β) on one side of the used species. Quadruply (or higher) fused porphyrin-related nanotapes are particularly appealing because they promise larger π -conjugation networks and novel electronic properties. Realizing such structures requires the exploration of porphyrinoids that offer additional connection sites and reaction methodologies that enable their selective coupling.

Over the past decade, on-surface synthesis has become a versatile bottom-up strategy for constructing atomically defined nanostructures using rationally designed molecular precursors adsorbed on well-defined substrates.²⁹ Hitherto this method has yielded regular³⁰⁻³⁵ and expanded phthalocyanines,³⁵ triply fused porphyrin nanotapes,³⁶ and porphyrin-graphene hybrid nanotapes.^{25,26} Herein, we demonstrate the on-surface synthesis of a novel **Por** using a common natural pigment (indigo) with Fe atoms on Au(111), and their further processing

towards extended conjugated oligomers. The reaction products are identified by a combination of scanning tunnelling microscopy (STM), non-contact atomic force microscopy (nc-AFM), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) investigations.

Results

On-surface synthesis of porphyrinoid monomers, dimers and trimers. The deposition of a sub-monolayer of indigo molecules on Au(111) kept at room temperature (RT) results in linear chain-shaped structures stabilized by intermolecular hydrogen bonds ($\text{NH}\cdots\text{O}=\text{C}$, imino and carbonyl group: NH and $\text{C}=\text{O}$) (Supplementary Fig. S1a-c). Subsequent annealing to 473 K leads to the complete desorption of the molecules (evidenced by XPS in Supplementary Fig. S1d-f). However, a different scenario is observed when indigo and Fe are co-deposited upon annealing to 573 K, extended chain-like structures evolve (see Fig. 2a and Supplementary Fig. S2). They are associated with Fe-coordination polymers comprising dehydroindigo molecules, in analogy with our earlier work on $\text{Ag}(111)^{37}$ and supported by XPS data (Supplementary Fig. S3). To characterize the configuration of each molecule and determine whether dehydroindigo undergoes *trans-cis* isomerization on Au(111), similar to the behaviour on $\text{Ag}(111)^{37}$ we performed nc-AFM experiments using a CO-functionalized tip. The bond-resolving AFM image (Fig. 2b) reveals clearly the indole moieties and the relative positions of the $\text{C}=\text{O}$ groups (marked by arrows in Fig. 2b). Two distinct molecular interaction configurations can be identified, indicated by the orange and yellow brackets, respectively. In the segments marked by orange brackets, the signatures of the $\text{C}=\text{O}$ groups are observed on the same side of a single molecule. However, in the magenta-marked segment, the two protrusions are observed on both sides of a single molecule. Accordingly, the molecular units can be assigned to *trans*- or *cis*-dehydroindigo species within the Fe-dehydroindigo coordination polymer (CP).³⁷ In addition, a minority population of covalently linked *trans*- and *cis*-dehydroindigo monomers was observed within the CP (Supplementary Fig. S4). The linking observed in Fig. S4b-d can be attributed to the formation of a C7-C7 bond.

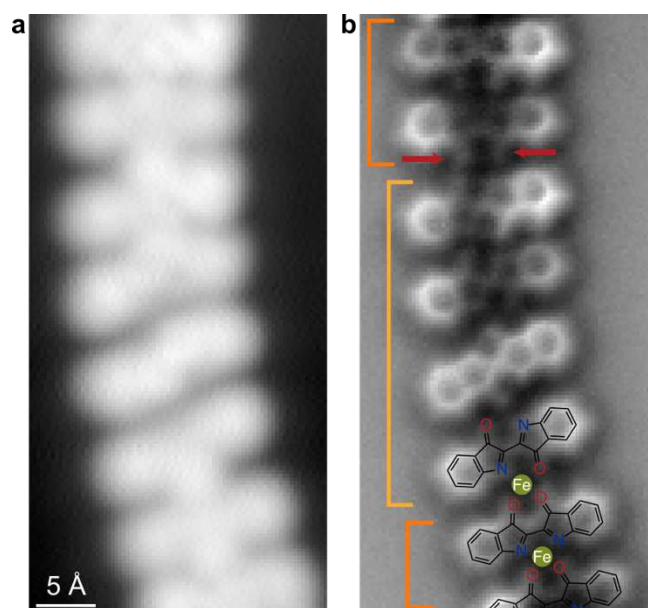


Fig. 2 | Identification of dehydroindigo molecular configurations. **a**, STM image ($U_b = -50$ mV, $I_t = 50$ pA) of a coordination polymer formed after annealing indigo and Fe on Au(111) at 573 K. **b**, Corresponding constant-height nc-AFM image ($U_b = 0$ V) revealing *trans*-dehydroindigo (orange brackets) and *cis*-dehydroindigo (yellow bracket) segments. A proposed structural model is overlaid in the lower region.

Surprisingly, upon annealing the sample to higher temperatures (633 K), homogenous coordination polymers (CPs) evolve (Fig. 3a and Supplementary Fig. 5a-b). They comprise a well-defined repeat unit with a characteristic rectangular shape and a bright central protrusion (example outlined in Fig. 3a, Supplementary Fig. 5c). The nc-AFM inspection of such rectangular products (outlined in Fig. 3b, Supplementary Fig. 5d-e) clearly reveals a macrocyclic skeleton formed by two covalently linked *cis*-dehydroindigo molecules (C7–C7 and C7'–C7' bonding), as illustrated by the structure model in Fig. 3c (new C–C bonds highlighted in red). Whereas the central region of the rectangular structure appears as a bright protrusion in low-bias STM measurements, a faint distorted cross is resolved by nc-AFM, similar to Fe centres of adsorbed phthalocyanine³⁸ and porphyrin species.³⁹ We therefore attribute these features to Fe complexed in a tetrapyrrole pocket and assign the rectangular product as the **Fe-Por**. Although the atomic model derived from the nc-AFM can be described by various resonance chemical structures (e.g., Supplementary Fig. S5f), for clarity in the following discussion we adopt the model shown in Fig. 3c, in which the Fe centre is coordinated in a porphyrin-like environment. Moreover, the on-surface synthesized tetrapyrrole core of **Fe-Por** is structurally similar to porphycene (highlighted in red in Fig.1).

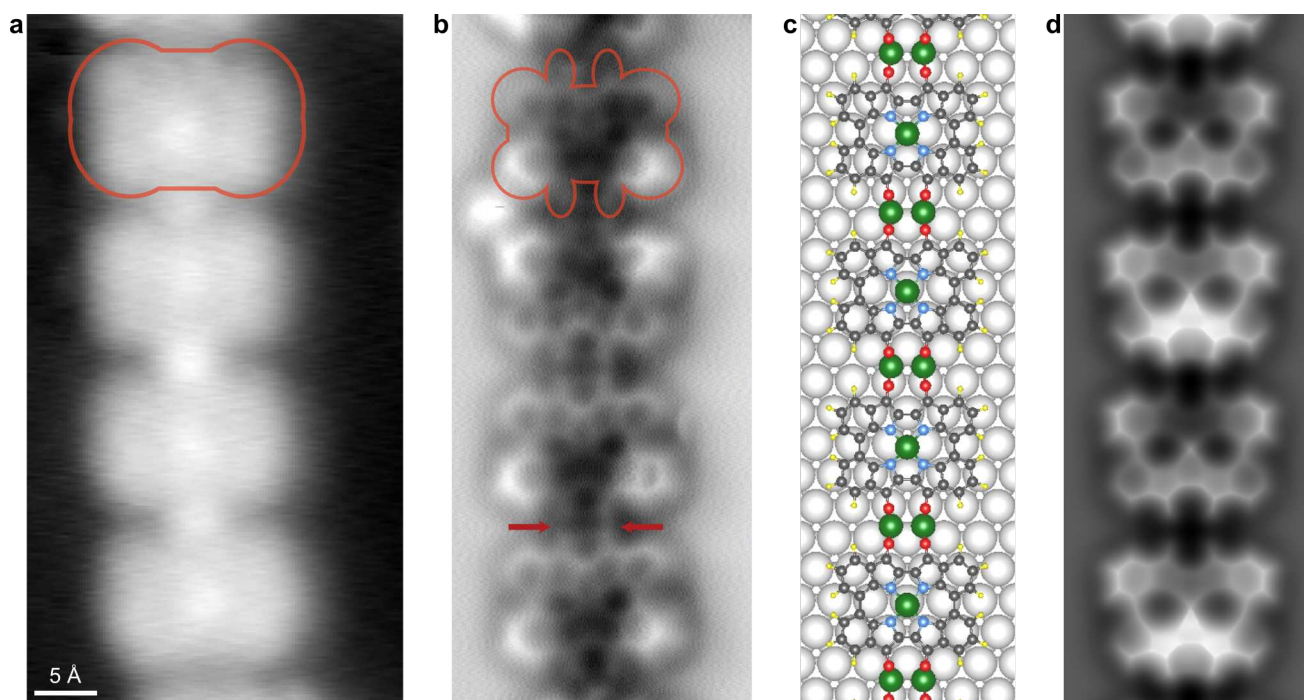


Fig. 3 | Structure of Fe-Por coordination polymers. **a**, STM image ($I_t = 10$ pA, $U_b = -50$ mV) of the coordination polymer consisting of chained porphyrinoids formed after annealing co-deposited indigo and Fe on Au(111) at 633 K. **b**, Corresponding nc-AFM image ($U_b = 0$ V). **c**, DFT-optimized geometry. **d**, nc-AFM simulation of the DFT model in **c**. Black, yellow, blue, red, green and white spheres denote C, H, N, O, Fe and Au atoms, respectively.

In the STM data, the coordination nodes between two adjacent **Fe-Pors** within these CPs appear as single bright protrusions (Fig. 3a, Supplementary Fig. S5b), similar to the imaging of the centres of the **Fe-Pors**. However, the corresponding nc-AFM image (Fig. 3b) reveals carbonyl groups facing each other between adjacent **Fe-Por** units (indicated by red arrows). The DFT modelling indicates that a linkage with two Fe atoms (Fig. 3c) is energetically favourable (as detailed in the SI section “Comparison of energetics of structural models”) and reproduces well the experimental data (Fig. 3d-f), unlike a model with a mononuclear node (see the comparison in the SI section “Comparison of AFM simulation of the two structural models considered”). The Fe centres are located 0.9 Å closer to the Au substrate than those of adsorbed **Fe-Por**, indicating stronger surface bonding. Indeed, a charge density analysis shows that these atoms largely account for the 1 e^- charge transfer from the CP to Au(111). The role of the identified defect nodes (Supplementary Fig. S6a, b, f and h) will be discussed below.

Moreover, upon annealing the sample to 663 K, a further reaction product is recognized in STM, reminiscent of two merged **Fe-Por** units (Fig. 4a and large-scale STM in Supplementary Fig. S7a), i.e., a dimer resulting from covalent fusion of two CP segments. The related experimental and simulated nc-AFM images unambiguously confirm this assignment (Fig. 4b, d).

Importantly, the central part of the **(Fe-Por)₂** appears remarkably flat and exhibits two fused six- and one eight-membered ring (Laplace filtered nc-AFM image in Supplementary Fig. 8), as a result of the quadruple linkages. Co-existing in the same area, a longer oligomer, **(Fe-Por)₃**, (Supplementary Fig. S7b-d) could be identified along with other interesting reaction side products (see Supplementary Fig. S9).

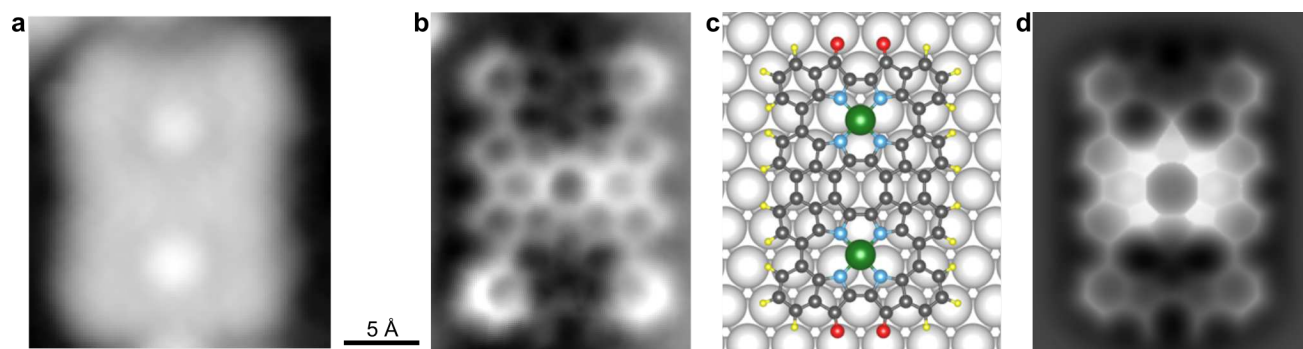


Fig. 4 | Structure of **(Fe-Por)₂.** **a-b**, High resolution STM and nc-AFM image of single **(Fe-Por)₂** after annealing the sample at 663 K. **c-d**, DFT relaxed structure and nc-AFM simulation of single **(Fe-Por)₂**. Scan parameters: $I_t = 10$ pA, $U_b = -1.2$ V (**a**); $U_b = 0$ V, constant height (**b**); colour coding as in Fig. 3.

Formation mechanism for Fe-Por and (Fe-Por)₂. Based on the combined analysis of the experimentally observed molecular species (Fig. 2, Supplementary Fig. S4) and the products described above, we propose the following reaction pathway (Supplementary Fig. S10) for the **Fe-Por** formation: First, the NH groups undergo dehydrogenation upon coordination with Fe atoms, yielding *trans*-dehydroindigo (Supplementary Fig. S10b).³⁷ A portion of these species then undergoes a thermally activated *trans*-to-*cis* isomerization (Fig. 2b and Supplementary Fig. S10c). At higher temperatures, a dehydrogenative C–C coupling assisted by an *N,O-N,N* chelating pocket occurs on one side of the *trans*- and *cis*-dehydroindigo molecules affords dimeric units (Supplementary Figs. S4 and S10e). Presumably, the *trans*-dehydroindigo within the dimer subsequently isomerizes into *cis*-dehydroindigo, generating an *N,N-N,N* chelating pocket (Supplementary Figs. 10f). Finally, a further dehydrogenative C–C coupling guided by this chelating pocket, closes the macrocycle and yields the **Fe-Por species** (Supplementary Fig. S10g). The chelating pocket has previously been demonstrated to facilitate dehydrogenative C–C coupling, albeit with a different regioselectivity.⁴⁰ With the present system it acts as a template that aligns the dehydroindigo in an appropriate spatial orientation for regioselective C–C bond formation, reminiscent of Ni-templated dipyrin synthesis in solution chemistry.⁴¹

The coordination directed regioselective C–C bond formation is likely promoted either by the Fe atom or possibly influenced by native Au adatoms.⁴⁰

The synthesis of **(Fe-Por)₂** involves both deoxygenative C–C coupling and dehydrogenative (4,4' C-H dehydrogenation) C–C coupling (Fig. 1b). The aforementioned defective **Por** coordination nodes (Supplementary Fig. S6) appear to be key intermediates in the **(Fe-Por)₂** fusion process. High-resolution nc-AFM images of these nodes (Supplementary Fig. S6d, g, and i) consistently reveal only three, rather than four, C=O groups pointing toward the same location. Given the **(Fe-Por)₂** observed, it is plausible to attribute these nodes to three carbonyl groups with a single Fe atom between them, whereas the missing carbonyl signature indicates deoxygenation prior to C–C coupling (Supplementary Fig. S6e). The coupling step involving 4,4' C–H dehydrogenation is presumably a surface-assisted intramolecular cyclodehydrogenation, a thermally activated process commonly observed for adsorbed substituted porphyrins.⁴² This mechanistic picture can be extended to account for the evolution of higher order oligomers such as **(Fe-Por)₃**, with yields decreasing from **Fe-Por** to **(Fe-Por)₂** to **(Fe-Por)₃**. Notably, the formation of **(Fe-Por)₂** with an eight-membered ring requires the cleavage of four C=O bonds and hence harsher reaction conditions. We propose that the Fe–O coordination acts as a directing template facilitating both C=O deoxygenation and 4,4' C-H dehydrogenation. Previous work⁴³ has reported the synthesis of graphene-like nanoribbons consisting of eight-membered rings through the assistance of a gold-organic hybrid intermediate product (C,C-C,C chelating pocket). The observation that the 7,7' C–H dehydrogenation process occurs at of 633 K, which is lower than the temperature required for deoxygenative C–C coupling (663 K), suggests that the 7,7' C–H dehydrogenation and the deoxygenative C–C coupling obey hierarchical reaction energetics and do not mutually compete.

Finally, it is essential to highlight the multifaceted role of Fe in the synthesis of both **Fe-Por** units and **Fe-Por** oligomers. Without Fe adatoms, indigo molecules on Au(111) desorb upon annealing at 473 K, as evidenced by XPS. In contrast, in the presence of Fe indigo remains adsorbed during annealing up to 673 K, which we attribute to a higher binding energy of Fe-indigo complexes or coordination polymers compared with that of individual molecules. Moreover, Fe induces indigo deprotoisomerization, entailing the formation of *cis*-dehydroindigo, serving as an essential precursor for the of **Fe-Por** synthesis pathway. Thirdly, Fe atoms participate in the formation of *N,O-N,N* and *N,N-N,N* coordination pockets acting as directing template. These pockets are crucial for guiding the selective positioning and spatial orientation of the reacting moieties and regiospecificity. Finally, Fe atoms are likely key for the

deoxygenative, McMurry-like C–C coupling, an essential step in the synthesis of **Fe-Por** oligomers. Notably, substituting Fe with the rare-earth element holmium (Ho), leads to markedly different regioselectivity at the coordination pocket and consequently different reaction products (Supplementary Fig. S11). This may reflect reduced propensity for *trans*-to-*cis* isomerization in the Ho case as well as size effects associated with the larger atomic radius. Overall, Fe stabilizes the adsorbates, enables key transformations, provides directing-template effects, and promotes specific coupling steps, all of which favor the synthesis of **Fe-Pors** and **Fe-Por** oligomers. Its reactivity and size are critical factors altogether favouring the observed synthesis.

Electronic properties. The electronic structure is assessed by differential conductance dI/dV measurements using scanning tunnelling spectroscopy (STS) combined with DFT calculations. In Supplementary Fig. S12, STS measurements on a single dehydroindigo and a single **Fe-Por** in their corresponding noncovalent CPs are presented. The absence of peaks within the bias range from -2 V to 2 V indicates that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of both species are outside this range (or elusive because of appreciable hybridization). Moreover, whereas porphycene (Fig. 1a) possesses 18π -electrons in its shortest conjugation pathway and thus is denoted as [18]porphyrin-(2.0.2.0) according to Hückel's rule and nomenclature, the corresponding synthesized **Por** macrocycle would be considered as a [0]porphyrin-(2.0.2.0) with no aromaticity due to the absence of a complete conjugation pathway.

STS measurements on both fused (**Fe-Por**)₂ (Fig. 5a) and (**Fe-Por**)₃ (Supplementary Fig. 13) reveal peaks appearing within the -2 V to 2 V region. DFT calculations show that the HOMO-LUMO gap decreases progressively as we go from a single indigo molecule to **Fe-Por** to (**Fe-Por**)₂. The (**Fe-Por**)₂ on Au(111) is found to be conducting in simulation (Fig. 5b). Fig. 5a displays characteristic local dI/dV spectra collected at the centre (depicted in purple), upper-Fe position (shown in green), and the upper-right position (represented in red) of adsorbed (**Fe-Por**)₂, along with the reference spectrum recorded on bare Au(111) (in yellow). At all points, a clear peak below the Fermi level is observed at -1.23 V. Additionally, two peaks in the unoccupied regime exist at 0.3 V and 1.22 V, respectively. The corresponding dI/dV maps are shown in Fig. 5c. The dI/dV map at -1.23 V resolves the two Fe centres within (**Fe-Por**)₂ as bright features. The dI/dV map at 1.22 V shows a "H"-shaped feature, possibly corresponding to the π -conjugated backbone of (**Fe-Por**)₂, whereby there is no contribution from Fe sites. Interestingly, at 0.3 V, the dI/dV map displays signatures of both the π -conjugated porphyrinoid

backbone and Fe, suggesting a mixed electronic state. It is important to note that, based on the available data, it is challenging to definitively identify which peaks correspond to the HOMO and LUMO of the investigated molecular structures. The experimental STS signature and dI/dV maps can be compared to the projected density of states (PDOS) and local density of states (LDOS) maps computed from DFT and shown in Fig. 5b,d. We see that though the match is not exact, as expected, overall trends and broad features correspond in experiment and theory. DFT calculations show that the Fe magnetic moments are preferentially aligned anti-ferromagnetically along the length of the NT: for **Fe-Por** CPs the moments on the single Fe atoms at the centres of the **Fe-Por** units are aligned opposite to those of the pair of Fe atoms that connect **Fe-Por** units. For **(Fe-Por)₂**, the moments on the two Fe atoms within the unit are preferentially aligned antiferromagnetically; these findings are of interest with regard to possible applications (Supplementary Tables S1, S2).

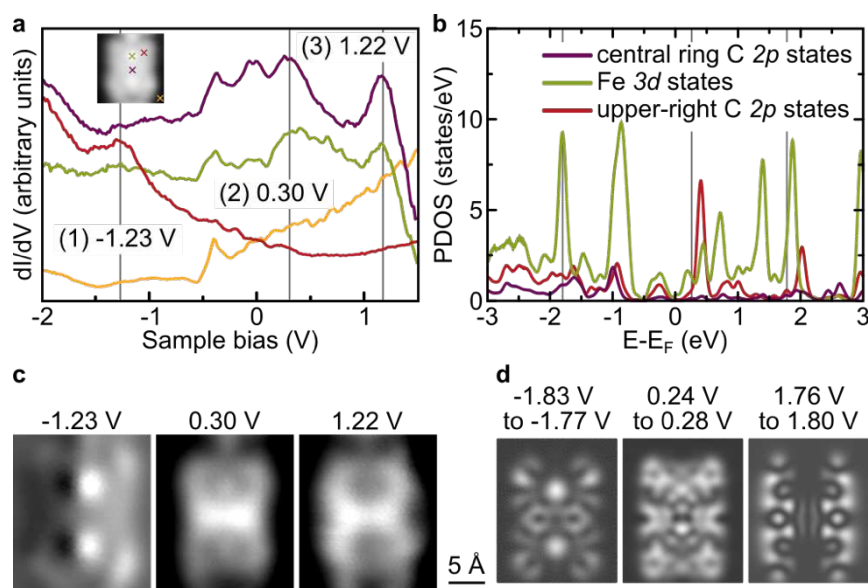


Fig. 5 | Electronic structure of **(Fe-Por)₂ on Au(111).** **a**, Characteristic dI/dV spectra acquired at the positions shown in the inset STM image by the crosses of the same colour. **b**, Experimental dI/dV maps at the sample biases indicated in constant-height mode with $I_t = 300$ pA. **c**, Calculated projected density of states on Fe d -orbitals (green curve) and total PDOS contributions from C $2p$ states of the central eight-membered ring (purple curve). **d**, Simulated constant-height dI/dV maps at the sample bias windows indicated. Grey lines in (a)/(c) indicate the biases/energies corresponding to the dI/dV maps in (c)/(d).

Analysis of aromaticity. To assess the aromaticity or anti-aromaticity of the synthesized porphyrinoids' components, we focus on isolated **Fe-Por** and **(Fe-Por)₂** molecules. Since their geometries are almost identical to those of surface-confined species, it is inferred that the

aromaticity is not significantly impacted by deposition on Au(111) (SI Fig. S19), as also seen by 0.23 electron charge transfer from overlayer to substrate. Specifically, we compute three aromaticity indices: the reformulated Harmonic Oscillator Model of Aromaticity (HOMA),⁴⁴ the Ring Current Density (RCD)⁴⁵⁻⁴⁷ and the Nucleus Independent Chemical Shift (NICS).⁴⁸⁻⁵⁰ The HOMA is a geometry-based index that examines the degree of bond length alternation in each conjugated ring. RCD and NICS compute the response when a magnetic field is applied perpendicular to the molecular plane, with the former indicating the magnitude and direction of induced ring currents, and the latter giving the value of the magnetic shielding tensor for a ghost atom placed at various positions near the molecule. Further details can be found in the Supplementary Information. Fig. 6 maps these three indices for the various rings in **Fe-Por** and **(Fe-Por)₂**, respectively. We note that a HOMA value > 0.5 indicates aromaticity, while HOMA < 0 indicates anti-aromaticity. With a magnetic field applied perpendicularly to the molecular plane and coming out of the page, (anti-)clockwise ring currents indicate (anti-)aromaticity, and (positive) negative RCD values indicate (anti-)aromaticity. For both molecules, all three indices agree on the aromaticity or anti-aromaticity of a given ring. For **Fe-Por**, all phenylene rings are aromatic, while the four pyrrole rings are anti-aromatic (Fig. 6a). Upon fusion two Fe-Por units to form **(Fe-Por)₂**, two of the four five-membered rings become aromatic, as a result of the newly formed linkages. Most strikingly, the central eight-membered ring is found to be aromatic. This appears to violate Hückel's $(4n+2)$ π -electron criterion for aromaticity, as a ring containing $4n$ π electrons ($n=4$) would nominally be expected to be antiaromatic. In fact, eight-membered rings embedded in a tetramer of fused porphyrins⁵² or a polycyclic aromatic hydrocarbon⁵³ were found to be antiaromatic.

Further insight into the aromaticity and resulting stability of **Fe-Por** and **(Fe-Por)₂** is obtained from Natural Bond Orbital (NBO) analysis.⁵⁴⁻⁵⁶ NBO analysis shows π -bond occupancies of 1.64 to 1.69 electrons per bond within the aromatic phenylene rings of Fe-Por, indicating substantial π delocalisation consistent with the local aromaticity established by HOMA, NICS, and RCD (Fig. 6a). On formation of **(Fe-Por)₂**, the quadruple linkage generates new conjugated pathways absent in the isolated monomers, resulting in the formation of the strongly aromatic 8-membered central ring. The π -electrons therein become even more delocalized, with the π -occupancies falling to 1.46 electrons per bond. Note that for a hypothetical planar structure of C₈H₈, modeled for comparison, these occupancies are close to 2. These 'lost' electrons are delocalized over the rest of the system, primarily affecting the neighbouring five-membered rings. We argue that this depletion in the number of p electrons in the central eight-membered ring is largely responsible for its unusual aromaticity: its total p electron occupancy is

significantly lowered, from the expected value of 8 to 5.84 electrons. Since 5.84 comes close to 6 (i.e., $4n+2$, for $n=1$), it can be argued that Hückel's rule remains valid also in this special macrocyclic environment.

We believe that on fusing two **Fe-Por** units by the quadruple linkages, the conversion of four five-membered rings from anti-aromatic to aromatic, and the three new aromatic rings formed, are favourable for stabilizing **(Fe-Por)₂**. The detailed analysis of evolution of the electronic structure and aromaticity from the monomer unit **Fe-Por** to dimer **(Fe-Por)₂** is included in SI. This electronic reorganisation from **Fe-Por** to **(Fe-Por)₂** has direct magnetic consequences. The monomer contains a single localised magnetic Fe centre, whereas the dimer contains two local $S = 1$ Fe centres connected by the newly formed aromatic bridge. The large $\pi(\text{C75-C76}) \rightarrow \text{LP}^*(\text{N96})$ (see Fig. S20 for the atomic indices) interaction and the weaker direct ring-to-Fe pathways on both sides enable antiferromagnetic superexchange through the central ring. Dimerisation thus transforms the electronic structure from a monomer with only locally (anti)aromatic rings into a fused aromatic system in which the central eight-membered ring mediates magnetic communication between the two Fe centres.

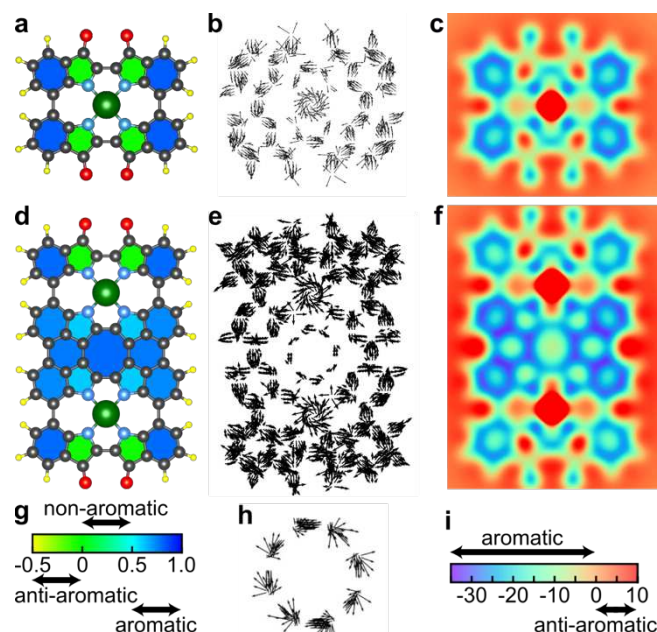


Fig. 6 | Computed aromaticity of Fe-Por (top row) and (Fe-Por)₂ (middle row). Three different indices have been computed: HOMA (left column), ring currents (middle column) and NICS (right column). All three indices agree on the properties of each ring, most notably the central eight-membered ring in **(Fe-Por)₂**, which is found to be aromatic. The colour of each ring in (a), (d) indicates the HOMA value for the ring according to the colour bar in (g), while the colour at each point in (c), (f) indicates the NICS value at that point, for a plane 1 Å above the molecular plane, according to the colour bar in (i). In (b), (e), (f), (anti-)clockwise ring

currents indicate (anti-)aromaticity. (h) is a zoomed-in view of the ring currents in the central eight-membered ring in **(Fe-Por)₂**.

Conclusions

We report the on-surface synthesis of novel indigo-based **Fe-Pors** and their quadruply fused oligomers, embedded in coordination chains. These **Fe-Pors**, akin to porphycene derivatives, are obtained with high yield through a series of thermally activated reaction steps, including Fe coordination, isomerization, and selective positioning and spatial orientation of reactant molecules, facilitating regiospecificity in the C–C couplings. Subsequently, deoxygenative and dehydrogenative C–C couplings fuse the **Fe-Pors** into **Fe-Por** oligomers, specifically **(Fe-Por)₂** and **(Fe-Por)₃**. These oligomers incorporate **Por** units connected by quadruple linkages, forming two new fused aromatic six-membered rings and one eight-membered ring. Notably, the fusion of two **Fe-Por** units into **(Fe-Por)₂** converts four previously anti-aromatic five-membered rings to aromatic systems. The formation of these new aromatic rings confers additional stability to **(Fe-Por)₂**. It is unambiguously established that the central eight-membered ring of **(Fe-Por)₂** is genuinely aromatic and serves as the conjugated pathway through which the two intermediate-spin Fe centres communicate antiferromagnetically. This work advances the synthesis of macrocyclic tetrapyrroles and introduces a class of quadruply fused **Fe-Por** elements which expand the synthetic toolbox in this field—particularly through the incorporation of an unusual eight-membered aromatic ring. These findings open avenues for the design of novel functional nanostructures with tailored properties.

Methods

Sample preparation. The Au(111) single-crystal substrate was cleaned by repeated cycles of Ar⁺ sputtering and annealing at up to 673 K. Indigo (TCI, exceeding 97% dye content) were deposited by heating the crucibles at 493–523 K. The substrate was held at room temperature during deposition. The deposition time was appropriately controlled to attain the desired molecular coverage. Transition metal atoms (Fe) were sublimated from a thin wire (Alfa Aesar, 99.995% purity for Fe), which was wound around a tungsten wire, resistively heated by direct current.

STM /AFM and dI/dV Measurements. The experiments were conducted at low temperature using a commercial Joule-Thomson STM (SPECS GmbH, 4.6 K) and a commercial STM/AFM (CreaTec, 5 K) instrument under a base pressure below 2×10^{-10} mbar. STM images were

recorded in constant-current mode, using an electrochemically etched tungsten tip. Tunnelling bias refers to the sample bias. Bond-resolved AFM measurements were acquired at a constant height and $V_s = 0$ V using a qPlus sensor with a tungsten tip decorated with a CO molecule (resonance frequency ~ 31 kHz, oscillation amplitude 60 pm, Q value > 100000 , stiffness $k \approx 1800$ Nm $^{-1}$) operated in frequency modulation mode. dI/dV measurements were recorded using a lock-in amplifier with a modulation frequency of 954 Hz and a modulation voltage (V_{mod}) of 20 mV. The data were analysed using SpmImage Tycoon.⁵⁷

X-ray Photoelectron Spectroscopy Measurement. The measurements were performed in a SPECS GmbH UHV system at the Technical University of Munich. Spectra were acquired with a monochromatic Al K α source ($h\nu = 1486.71$ eV) and a SPECS Phoibos 150 hemispherical analyzer in normal emission geometry. The energy scale was calibrated by setting the Au 4f $_{7/2}$ peak at a binding energy of 84.19 eV. A Shirley background was fitted to the O 1s and N 1s raw data. The XPS spectra represent electron intensity in arbitrary units after background subtraction and are offset for clarity.

Computational Methods. The adsorption geometry and electronic structure of the Fe-indigo coordinated structures on the Au(111) substrate were studied by performing spin-polarized density functional theory (DFT) calculations as implemented in the Quantum ESPRESSO software package.⁵⁸ using Projector Augmented Wave (PAW) pseudopotentials.⁵⁹ Wave functions and charge densities were expanded in a plane-wave basis set with cutoff energies of 60 Ry and 360 Ry, respectively. The gradient correction to exchange in conjunction with non-local interactions was incorporated using the vdW-DF2-B86R exchange-correlation functional.^{60,61} An onsite Hubbard correction $U = 1$ eV was applied to the Fe atoms.^{62,63}

Scanning tunnelling microscopy (STM) images were simulated using the Tersoff–Hamann approach.⁶⁴ Atomic force microscopy (AFM) simulations were performed using the probe-particle method developed by Hapala et al.,^{65,66} with a lateral stiffness of 0.25 N/m and an effective atomic radius $R_C = 1.5$ Å.

The gas-phase electronic structure of the Fe-Por and (Fe-Por) $_2$ molecules was computed using the GAUSSIAN 16 software package.⁶⁷ Calculations were performed with the 3-21G basis set and the B3LYP exchange-correlation functional. The results were found to be consistent with the use of higher order basis functions like def2-TZVP as well.

For HOMA analysis, we used the Multiwfn software,⁶⁸ which implements the reformulated-HOMA definition.⁴⁴ NICS⁴⁸ values were computed using GAUSSIAN 16. The planar molecules were placed in the yz -plane. A NICS $_{xx}$ scan was performed on a grid with 0.1 Å spacing in the y - and z -directions, at a height of 1 Å above the molecular plane.^{49,50}

Current density calculations were carried out using the GIMIC (Gauge-Including Magnetically Induced Currents) program,^{46,47} post-processing outputs from GAUSSIAN 16. Vector plots of ring currents were generated using the Matplotlib library.⁶⁹ Only the in-plane values of the current-density were plotted.

The σ and π electron count of each ring was analysed using the NBO program (NBO 3.1)^{54,55} as implemented in Gaussian 16 software package at the same B3LYP/3-21g level of theory. Delocalization interaction strengths within the pi system and between the ligand framework and Fe centres were quantified using the second order perturbation theory.⁵⁶

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Competing interests

The authors declare no competing interests.

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