

Supplementary Information

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

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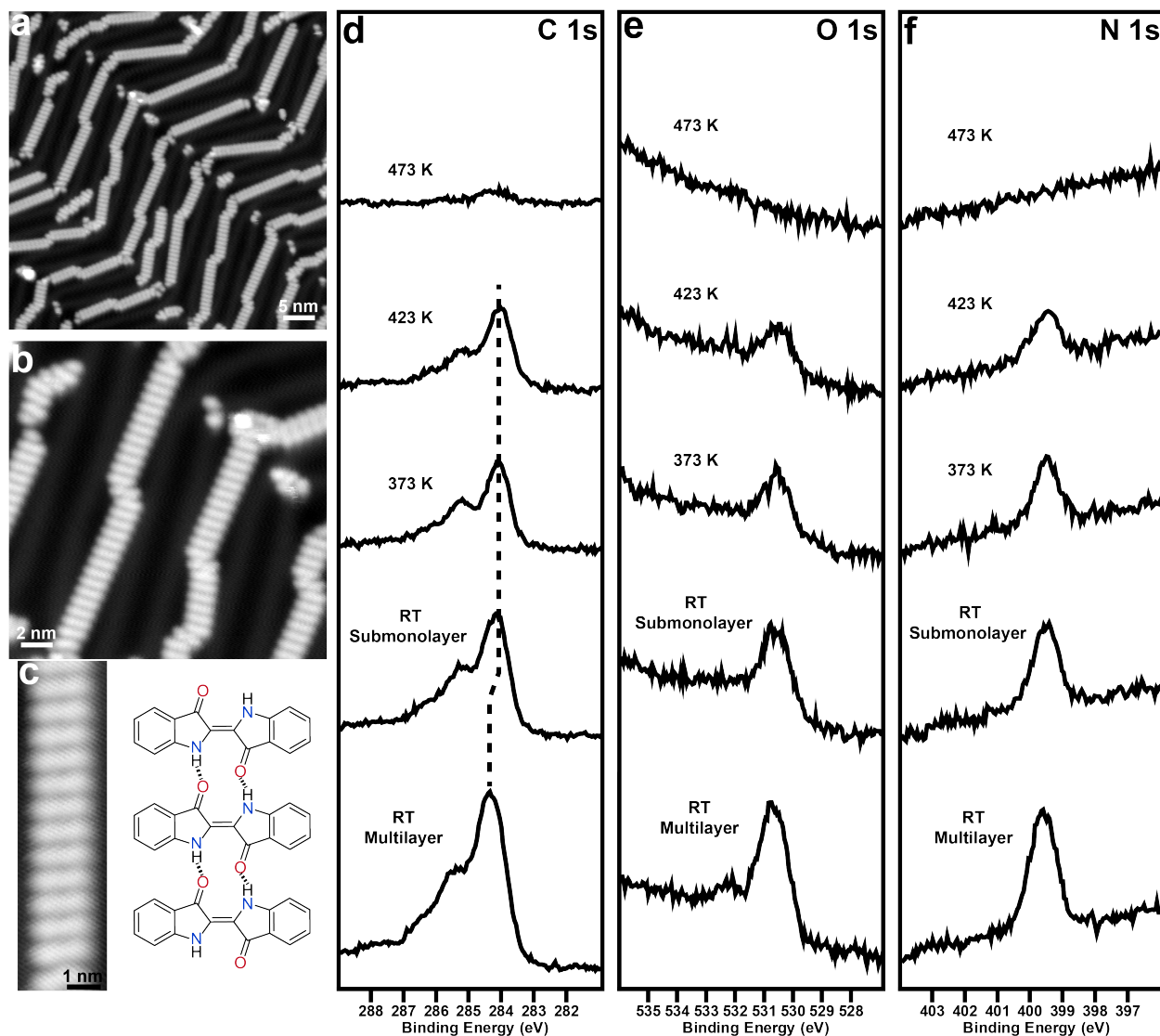


Figure S1: Indigo on Au(111) without Fe atoms. (a) An overview STM image of chain-like self-assemblies of indigo following room temperature (RT) deposition. (b) Zoom-in STM image. (c) High-resolution STM image and chemical structure model. The structure is stabilized by intermolecular hydrogen bonding. The structural interpretation is supported by XPS data. Core level spectra of (d) C 1s, (e) O 1s, and (f) N 1s for the indigo adsorbed on Au(111) at RT followed by subsequent annealing to 373 K, 423 K, and 473 K, respectively. (e-f) Both the O 1s and N 1s spectra show a single components each located at binding energies (E_B) 530.6 eV and 399.5 eV corresponding to C=O and –NH group, respectively. Hence it is deduced that C=O groups do not coordinate with Au adatoms and –NH groups are intact. (e-f) Desorption of indigo molecules after the sample was annealed to 473 K is evidenced by the lack of signal in the corresponding spectra. STM scan parameters: (a-b) $V_s = -1$ V, $I_t = 100$ pA; (c) $V_s = 100$ mV, $I_t = 100$ pA.

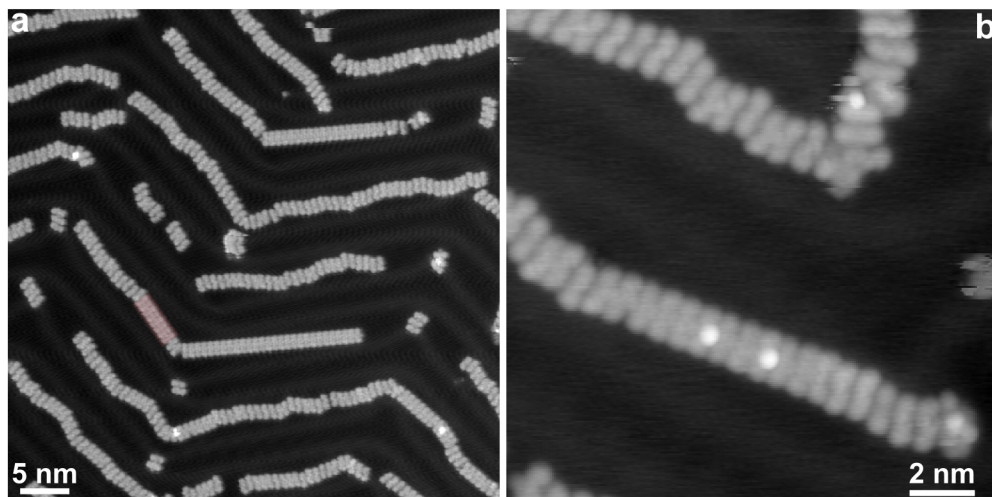


Figure S2: Coordination polymers (CPs) on Au(111) forming after annealing indigo with Fe adatoms at 573 K. (a) Overview STM image of CPs. (b) Zoom-in STM image of CPs. Scan parameters: (a) $V_s = -300$ mV, $I_t = 100$ pA; (b) $V_s = -100$ mV, $I_t = 10$ pA. All STM images were acquired at 4.6 K.

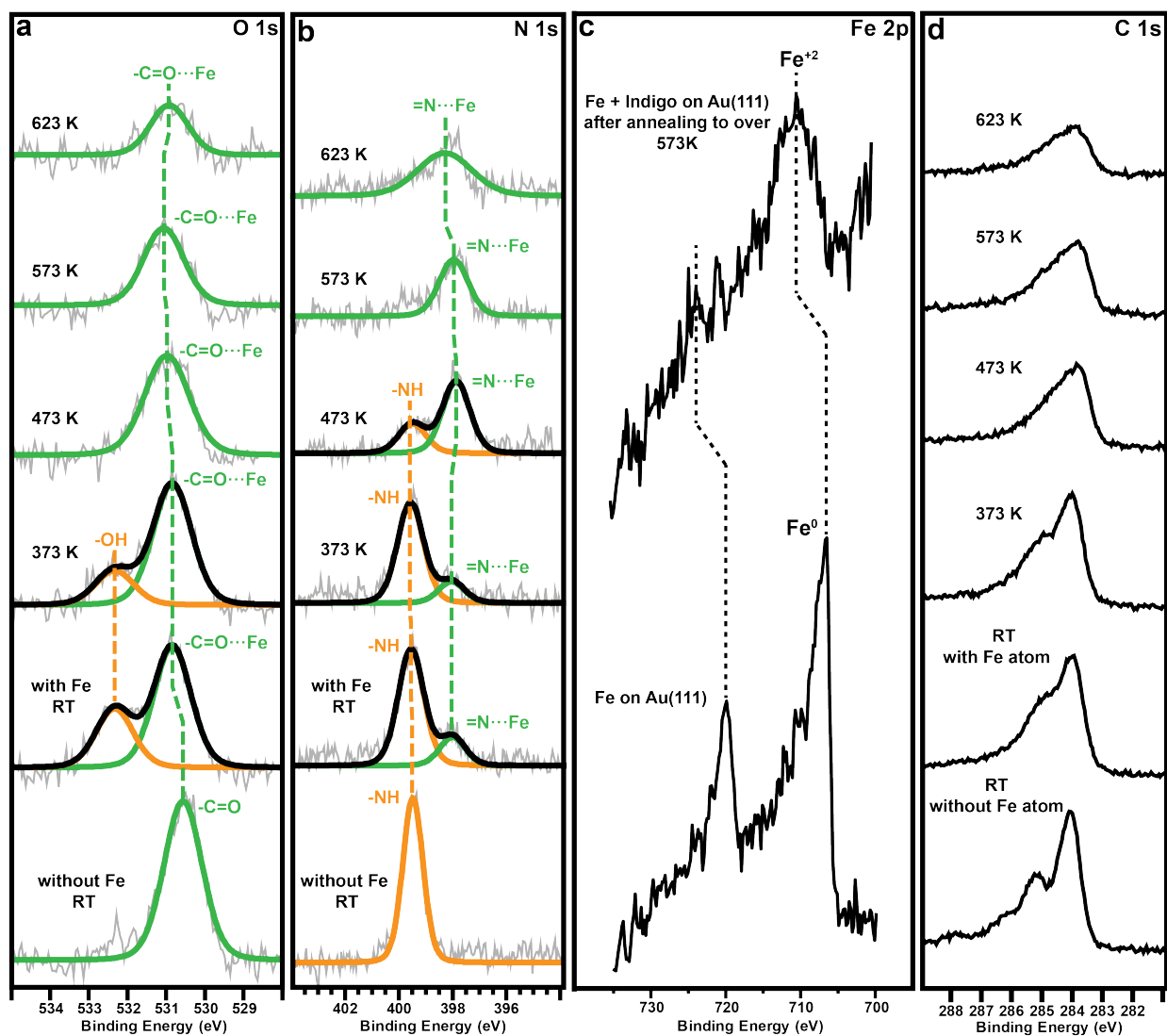


Figure S3: Core level spectra of O 1s, N 1s, Fe 2p, and C 1s for the indigo without Fe atoms on Au(111) at RT and indigo with Fe atoms on Au(111) at RT followed by subsequent annealing to 373 K, 473 K, 573 K, and 623 K, respectively. (a) The O 1s spectrum show the main peak located at $E_B = 530.6$ eV will shift to higher $E_B = 531.1$ eV at 573 K annealing temperature, implying to C=O...Fe coordination bond formation. (b) The N 1s spectra show that once introducing Fe atoms into the indigo/Au(111) surface, the main peak centered at $E_B = 399.5$ eV will be split off into an additional peak with weak intensity located at $E_B = 398.0$ eV, which indicates that partial -NH groups are catalyzed by Fe atoms and form partial =N...Fe coordination bonds. However, at 573 K sample annealing temperature, the weak peak becomes main and dominant peak located at $E_B = 398.3$ eV, implying that all -NH groups have been deprotonated and form =N...Fe coordination bonds. (c) The Fe 2p spectrum (at the bottom) displays two peaks at $E_B = 707.0$ and 720.0 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} of metallic Fe, respectively. In the underdosed Fe 2p spectrum (top), the Fe 2p_{3/2} and Fe 2p_{1/2} peaks are shifted to $E_B = 710.5$ and 724.0 eV, respectively, corresponding to the positively charged Fe(II) species in Fe...O coordination bonds. The Fe 2p spectra are in good agreement with the evolutions of N 1s and O 1s, demonstrating the formation of Fe...O coordinative bonds. (d) Corresponding C 1s spectra for reference.

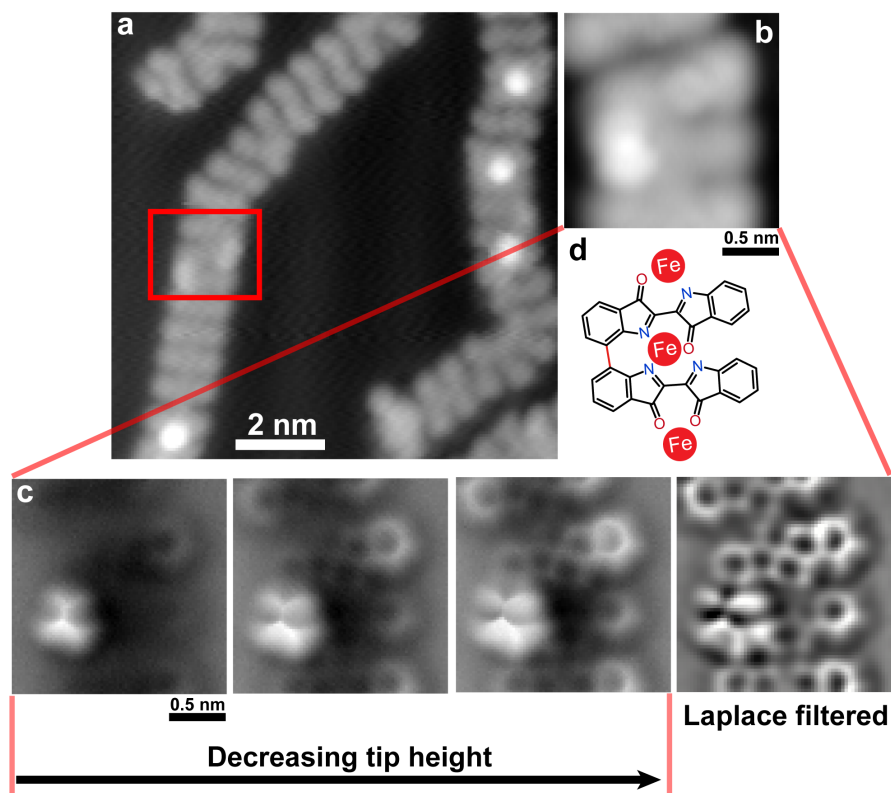


Figure S4: Reaction intermediate of the (Fe-Por) product formed through dehydrogenative C–C coupling between *trans*- and *cis*-dehydroindigo following RT sequential deposition of indigo and Fe and annealing at 573 K. (a-b) STM images. (c) nc-AFM images of the area shown in (b). (d) Proposed structural model. Scan parameters: (a) $V_s = 300$ mV, $I_t = 50$ pA; (b) $V_s = 50$ mV, $I_t = 50$ pA; (c) Constant height, $V_s = 0$ mV.

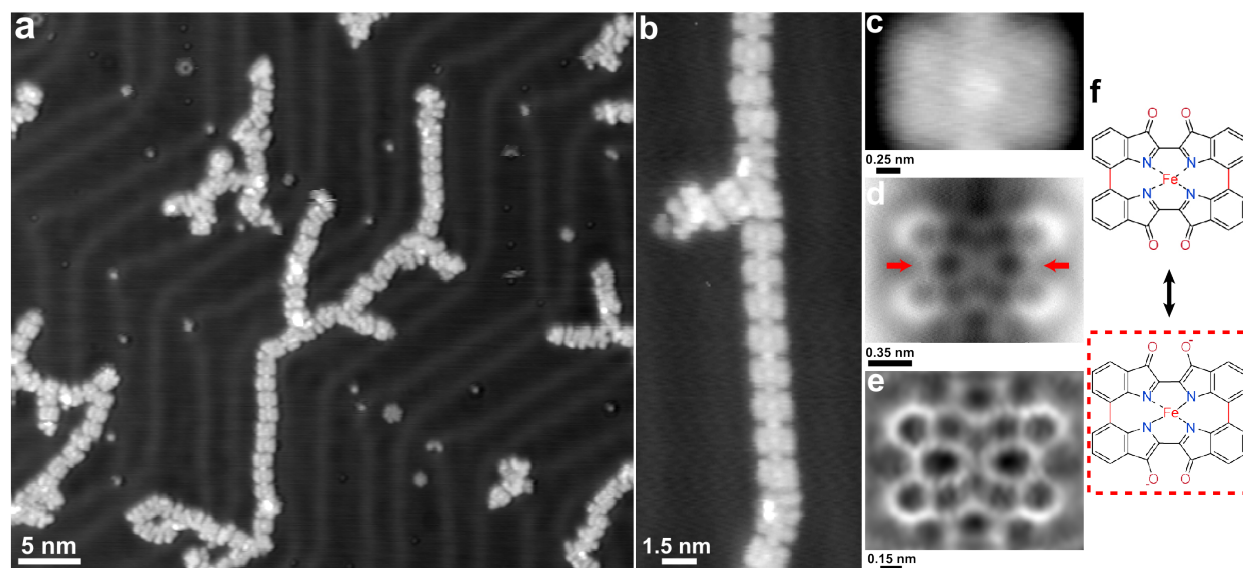


Figure S5: (a) Large-scale STM image after annealing indigo with Fe atoms at 633 K. (b) New CP consisting of porphyrinoids. (c) High-resolution STM, (d) high-resolution nc-AFM image, and (e) Laplace filtered image of (d) visualise a single (Fe-Por) molecule. The red arrows indicate new C–C bonds. (f) Two resonance chemical structures of Fe-Por. Scan parameters: (a, c) $V_s = -50$ mV, $I_t = 10$ pA; (b) $V_s = -100$ mV, $I_t = 100$ pA; (d) Constant height, $V_s = -2$ mV.

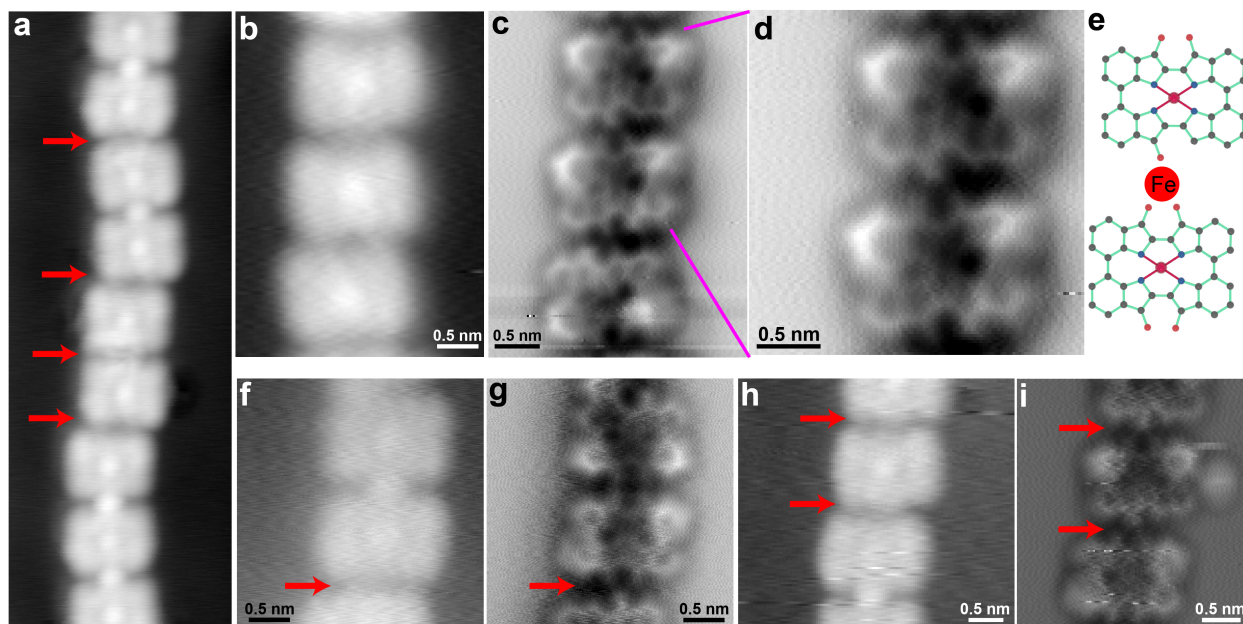


Figure S6: (a, b, f, h) High-resolution STM image of the new CPs containing of dark nodes. (c, d, g, i) High-resolution nc-AFM images of the new CPs presented in (b), (b), (g), and (i), respectively. (e) A possible model for the dark node. Scan parameters: (a) $V_s = -30$ mV, $I_t = 10$ pA; (b) $V_s = -50$ mV, $I_t = 10$ pA (f) $V_s = -20$ mV, $I_t = 10$ pA; (h) $V_s = -10$ mV, $I_t = 10$ pA; (c, d, g, i) Constant height, $V_s = -2$ mV.

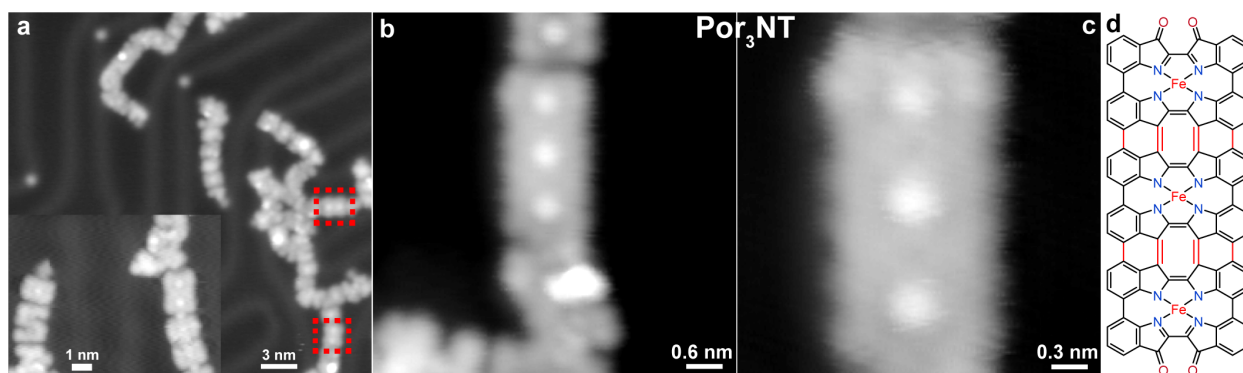


Figure S7: (a) Large-scale STM image containing $(\text{Fe-Por})_2$. (b-c) STM image of $(\text{Fe-Por})_3$. (d) Chemical structure of $(\text{Fe-Por})_3$. Scan parameters: (a) $V_s = -100$ mV, $I_t = 100$ pA; (b) $V_s = -200$ mV, $I_t = 100$ pA (c) $V_s = -133$ mV, $I_t = 100$ pA.

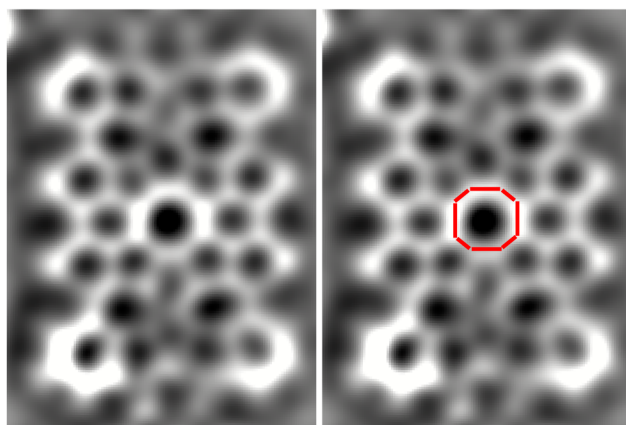


Figure S8: Laplace filtered nc-AFM image of $(\text{Fe-Por})_2$. Scan parameters: Constant height, $V_s = 0$ mV.

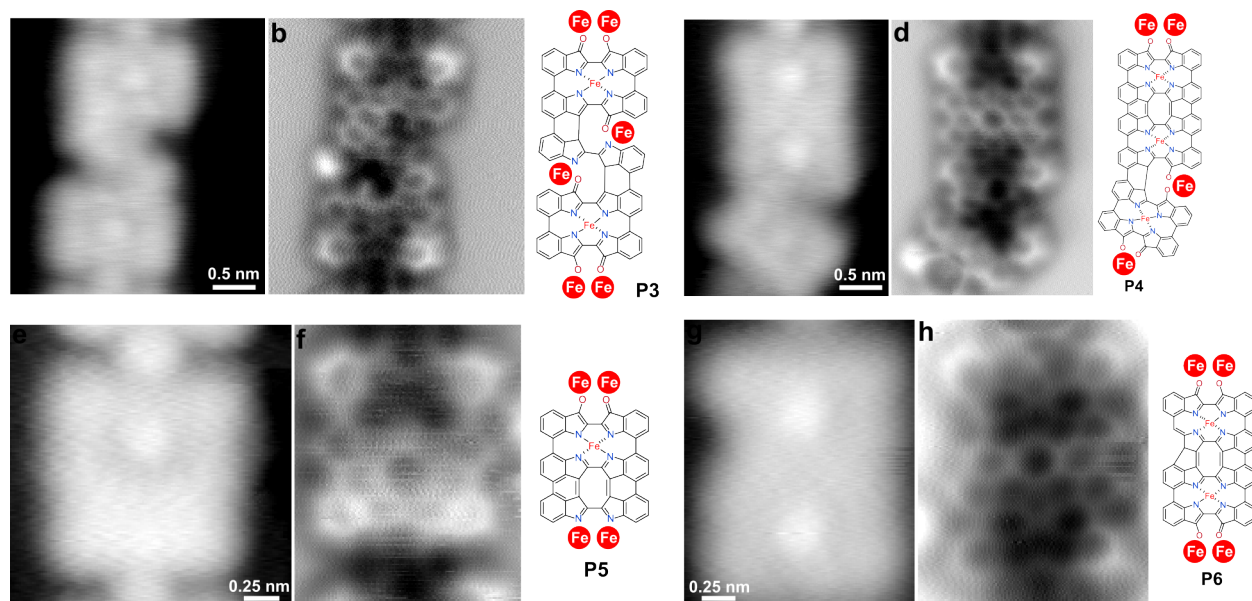


Figure S9: STM and nc-AFM images of side products following RT sequential deposition of indigo and Fe and annealing at 663 K. Scan parameters: (a) $V_s = 30$ mV, $I_t = 10$ pA; (c) $V_s = -10$ mV, $I_t = 10$ pA (e, g) $V_s = -20$ mV, $I_t = 10$ pA; (b, d, f, h) Constant height, $V_s = -2$ mV. The side products P3-P6 are also porphyrinoids. P3 consists of the two porphyrinoids, connected by a *trans*-dehydroindigo via McMurry-type coupling. The P4 could be an intermediate (or incomplete reaction) product in the formation of $(\text{Fe-Por})_3$. The P5 containing an eight-membered ring is formed by McMurry-type coupling between the porphyrinoid and a *cis*-dehydroindigo. The P6 is the $(\text{Fe-Por})_2$ with a defect that is three carbon atoms missing. It is worth noting that these side products are due to a variety of reactants including the two surface enantiomers of *trans*-dehydroindigo and *cis*-dehydroindigo.

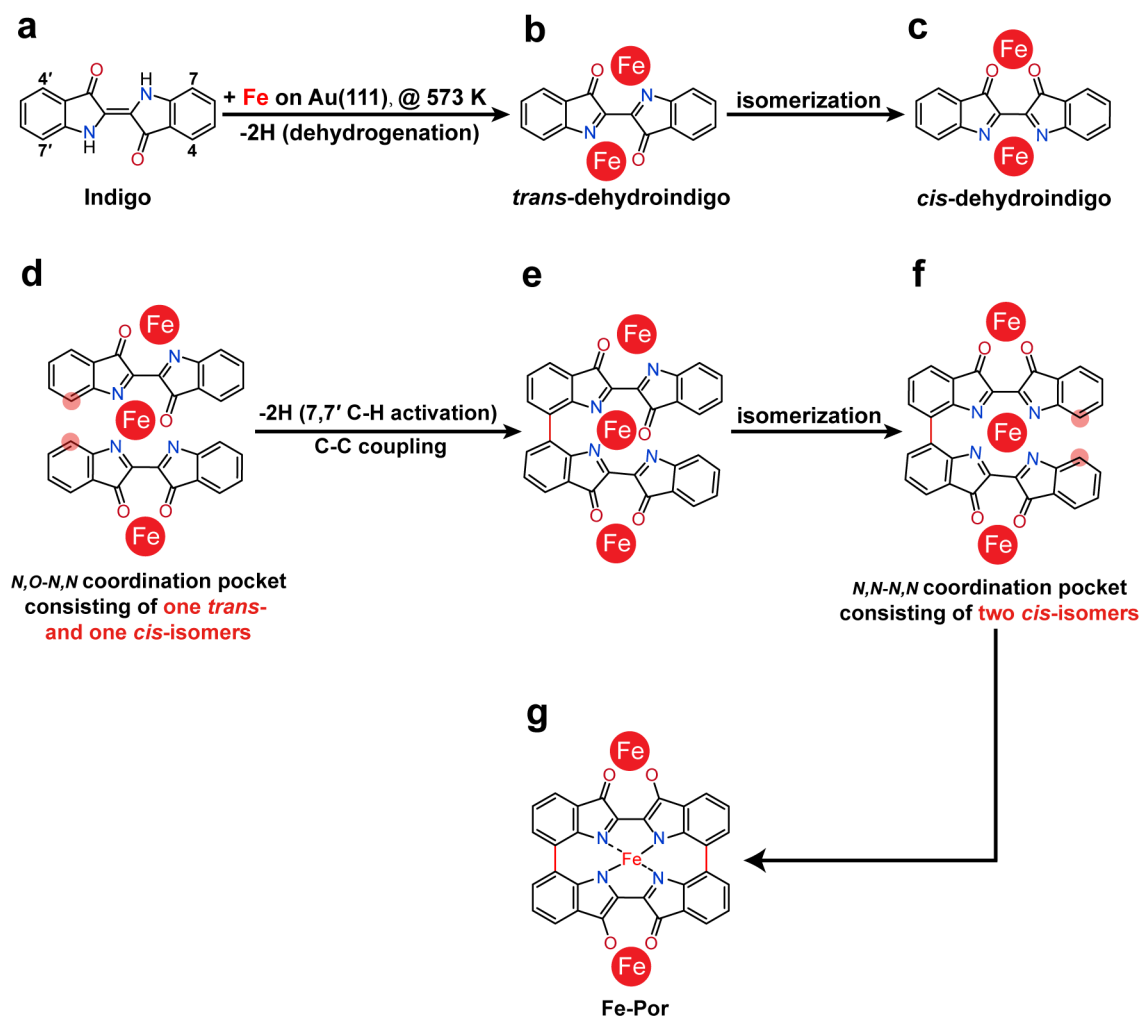
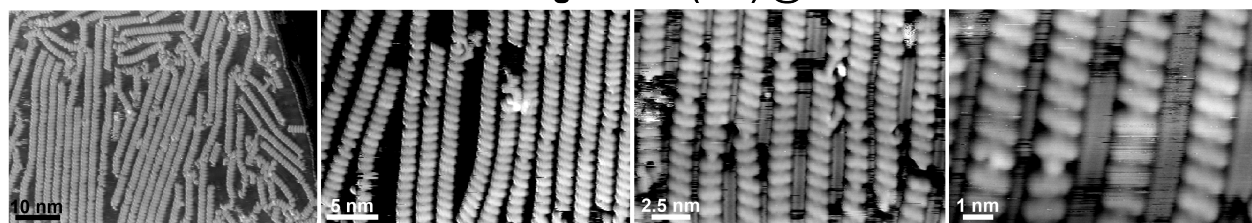


Figure S10: Proposed reaction pathway of synthesis of Fe-Por.

Ho + indigo on Au(111) @ 573 K



@ 673 K

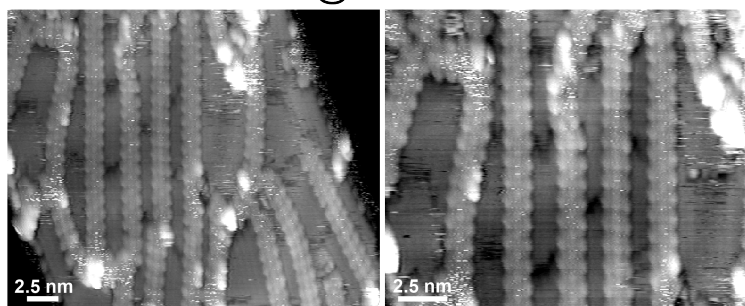


Figure S11: STM images of Ho-CPs. Scan parameters: $V_s = -1200$ mV, $I_t = 60$ pA.

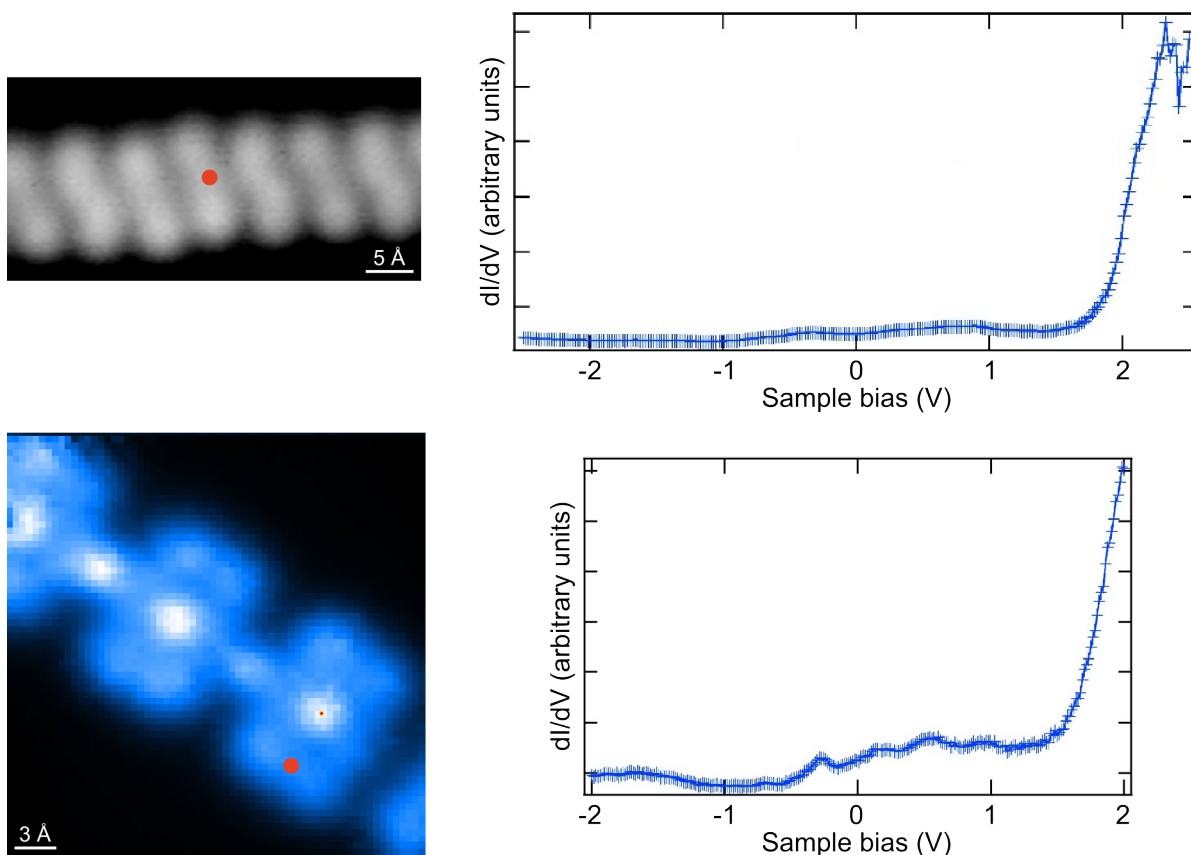


Figure S12: Scanning tunnelling spectroscopy (STS) (right) on the spots indicated by the red dots on the STM images (left) for dehydroindigo (top) and porphyrinoid (bottom).

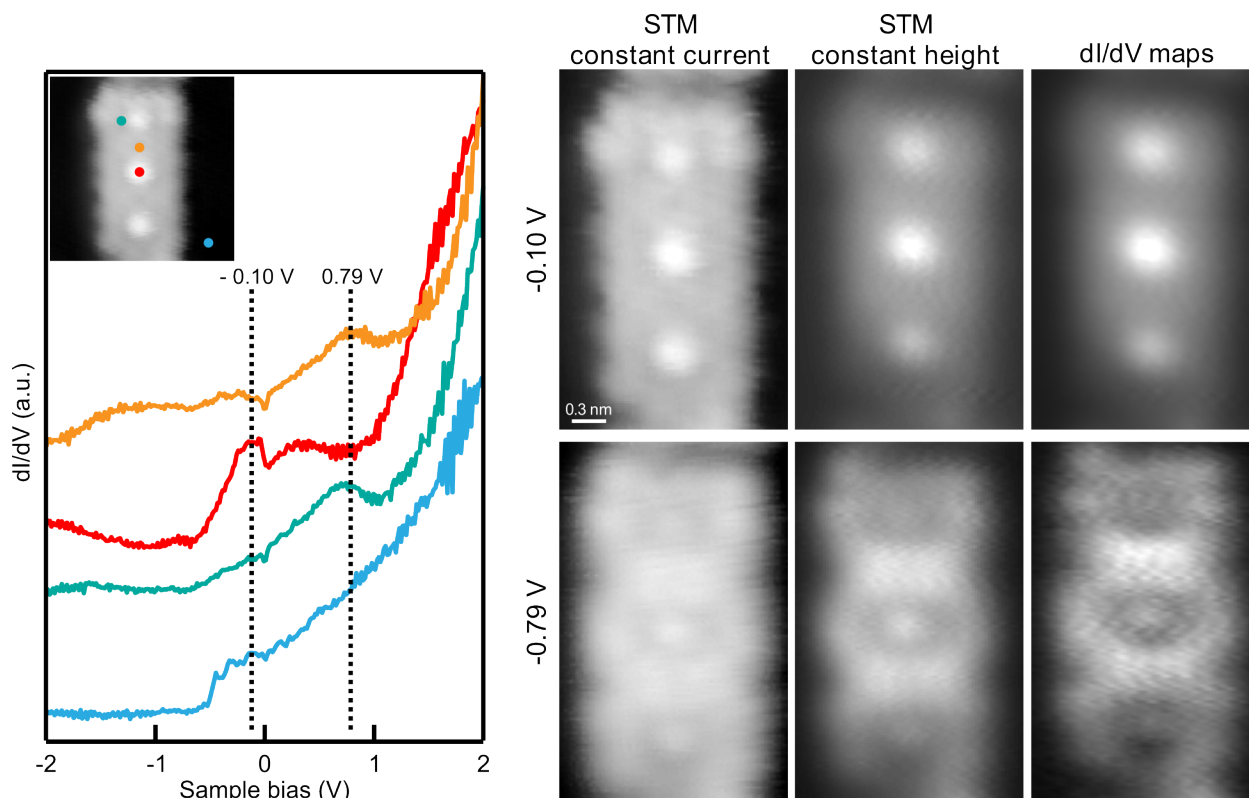


Figure S13: STS and dI/dV mapping of **Fe-Por₃**. On the left, characteristic dI/dV spectra collected at the positions indicated by the same coloured dots on the STM image inset: Center-Fe position (in red), upper-middle position (in orange), and the upper-left position (teal) of the **Fe-Por₃**, along with the reference spectrum recorded on bare Au(111) (blue). Two peaks are observed at -0.10 V and 0.79 V, respectively. The corresponding dI/dV maps are shown on the right. The dI/dV maps at -0.10 V reveal that the three Fe atoms within the **Fe-Por₃** also appear as bright features. The dI/dV map at 0.79 V displays a ladder-shaped feature. These two dI/dV maps are consistent with the dI/dV maps of **Fe-Por₃** located at -0.38 V and -0.30 V. However, it is also challenging to determine definitively whether these correspond to the HOMO or LUMO of **Fe-Por₃**.

DFT calculations

Comparison of energetics of structural models

DFT calculations were performed to find out how two adjacent **Fe-Por** molecules are joined within the CP. For investigating that, we considered two structural models: one (Model A) having one Fe atom bridging the subunits (see Fig. S14(a)) and the other (Model B) having two Fe atoms bridging the **Fe-Por** subunits (see Fig. S14(b)). We considered various possible collinear magnetic orderings for the two structural models considered, to find out the ground-state magnetic configuration of the chain structure that is formed; however, we note that the possibilities considered are not exhaustive. We then assumed the lowest energy configuration amongst the possibilities we considered to be the ground-state magnetic configuration of the linear chain. Tables S1 and S2 compare the total energies of the different magnetic orderings considered for the two structural models. We find that for Model A, the antiferromagnetic configuration u-d-u-d is the lowest in energy, where ‘u’ and ‘d’ refer to up-spin and down-spin, respectively. For Model B, a type of antiferromagnetic structure u-(d-d)-u-(d-d) is the lowest in energy; here, parentheses denote two Fe atoms in a dimer. In this configuration, there is an antiferromagnetic alignment between successive Fe atoms along the length of the chain. However, there is a ferromagnetic coupling between the two Fe atoms in a dimer, i.e., between Fe2 and Fe3, and between Fe5 and Fe6; see Fig. S14 for the labeling of Fe atoms.

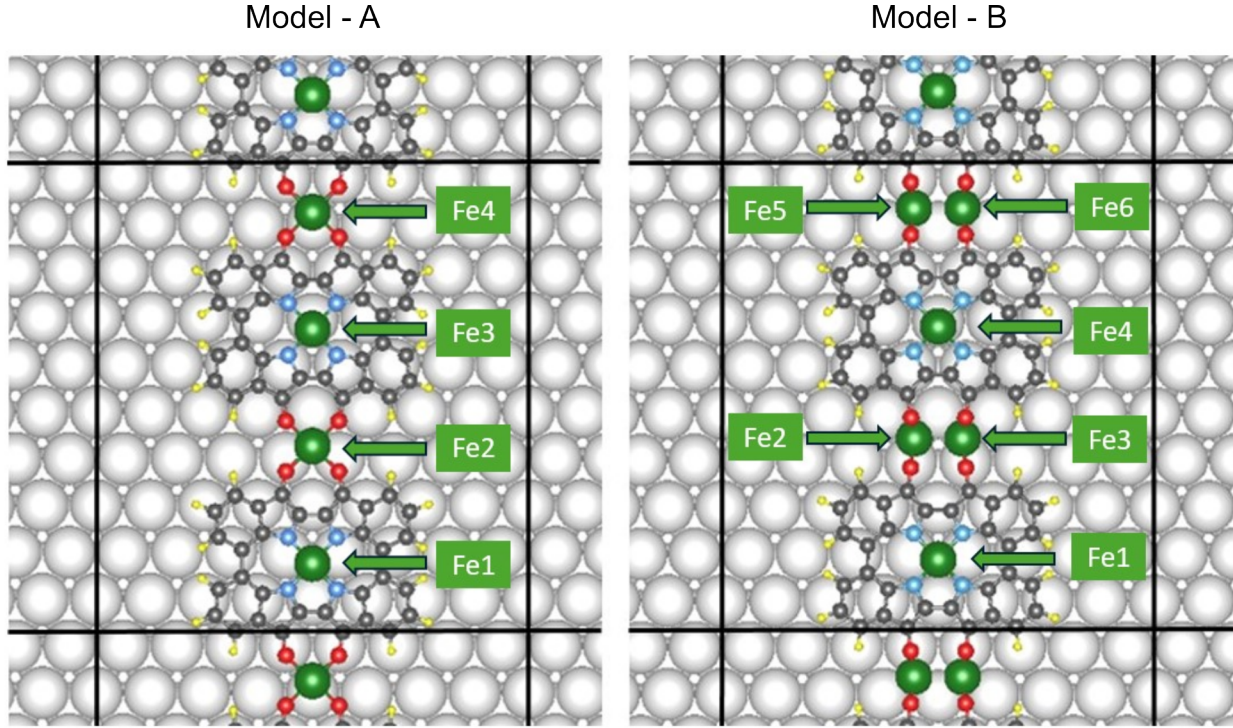


Figure S14: DFT optimized structure of **Fe-Por** CP, formed out of **Fe-Por** units. Two structural models were considered; (a) Model A, successive dimerized indigo units (**Fe-Por**) are connected by one Fe atom, and (b) Model B, successive dimerized indigo units (**Fe-Por**) units are connected by two Fe atoms. The black, yellow, blue, red, green and white spheres represent C, H, N, O, Fe and Au atoms, respectively. The different Fe atoms within the unit cell are labeled Fe1, Fe2,..., Fe6.

Table S1: Comparison of energies for different magnetic orderings using $U = 1$ eV. Fe1,..., Fe4 refer to the four different Fe atoms in the unit cell for Structure A. See Fig. S14 for labeling convention. 'u' refers to up spin orientation and 'd' refers to down spin orientation.

Magnetic Ordering Fe1-Fe2-Fe3-Fe4	ΔE (meV)
u-d-u-d	0.00
u-u-d-d	54.20
u-u-d-u	61.73
u-u-u-u	82.54

To compare the energetics of Model A and B, we consider the lowest-energy structure of Model A (which follows the u-d-u-d-... pattern) and the lowest-energy structure of Model B (which follows the u-(d-d)-u-(d-d)-... pattern). While making this comparison, for the chemical potential of the additional two Fe atoms present in Model B, we use the energy of a Fe adatom adsorbed on the lowest energy (fcc hollow) site on the Au(111) surface. The difference in free energy between Structural Models A and B is given by $\Delta\Omega = E_A - E_B + 2\mu_{\text{Fe}}$, where E_A and E_B are the total energies in Structural Models A and B, respectively. We then obtain $\Delta\Omega = 0.222$ Ry for $U = 1$ eV. Note that this result implies that Structure B is favored over Structure A.

Table S2: Comparison of energies for different magnetic orderings using $U = 1$ eV. Fe1, . . . , Fe6 refer to the six different Fe atoms in the unit cell for Structure B; see Fig. S14 for labeling convention. ‘u’ refers to up spin orientation and ‘d’ refers to down spin orientation.

Magnetic Ordering Fe1-Fe2-Fe3-Fe4-Fe5-Fe6	ΔE (meV)
u-(d-d)-u-(d-d)	0.00
u-(u-u)-d-(d-d)	25.94
u-(u-u)-d-(u-u)	63.64
u-(u-u)-u-(u-u)	82.06
u-(u-d)-u-(u-d)	451.27
u-(u-d)-d-(u-d)	459.60

Comparison of AFM simulation of the two structural models considered:

We compare the simulated AFM images of structural models A and B to see which one better matches the experiment (see Fig. S15). We focus on the region within the yellow rectangle in Fig. S15. In the experimental AFM image in the central panel, we see four bright rod-shaped features facing each other; these arise from four carbonyl groups from two adjacent (Fe-Por) subunits. This feature is correctly reproduced in the AFM simulation of only structural model B. We therefore again conclude that structural model B is the correct one, in agreement with the result obtained from DFT total energies.

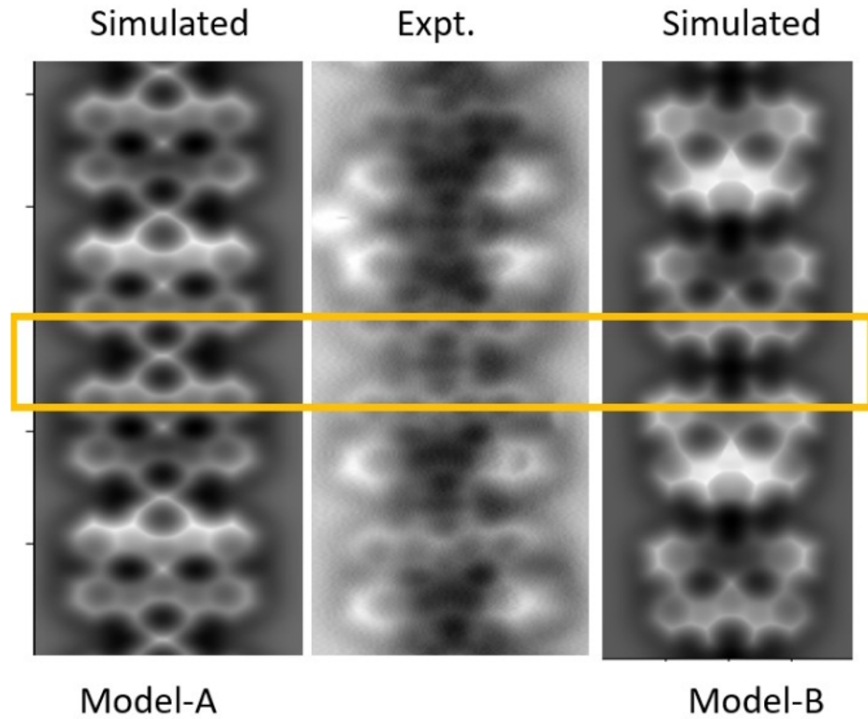


Figure S15: Comparison of experimental AFM image (central panel) with the simulated images (left and right panels) of the two structural models considered for the Fe-Por CP. We see that the rod-shaped features of the carbonyl groups (within the yellow rectangle in the three figures) are reproduced correctly only in the structural model B. The simulated images are generated using the relaxed structures of $U = 1$ eV calculations.

Charge Density Analysis of Fe-Por CP:

To calculate the amount of charge transferred between the CP and the substrate, we first calculated the charge density of the whole system (CP + substrate) using the Kohn-Sham wavefunctions obtained from our DFT calculation and then employed Bader's¹ charge partitioning scheme to compute the charges on the individual atoms. We found that 2.02 electrons/cell were transferred from the CP to the substrate. So, the Fe-Por CP acts as an electron donor on Au(111). The charge transferred per subunit constituting the CP is therefore 1.01 electrons. Also, we found that most of these electrons are donated from the bridging Fe atoms that connect adjacent Fe-Por units. This behavior of the CP acting as an electron donor, is markedly different from that previously observed for a Fe-indigo CP formed on Ag(111), which was found to act as an electron acceptor.²

For visualising this charge transfer, we have plotted the charge density difference between the CP and substrate (Figure S16). We calculated the charge density difference using the following formula: $\Delta\rho = \rho_{CP/Au(111)} - \rho_{CP} - \rho_{Au(111)}$ where, $\rho_{CP/Au(111)}$ is the charge density of the full system (CP + substrate) at the relaxed geometry, ρ_{CP} is the charge density of only the CP calculated at the relaxed geometry on the substrate and $\rho_{Au(111)}$ is the charge density of only the Au surface computed at the relaxed geometry of overlayer+ substrate. In this figure (Fig. S16), red lobes signify electron accumulation and blue lobes signify electron depletion upon being adsorbed on the substrate. Large red lobes are seen on the substrate, indicating that the substrate has gained electrons, corroborating the conclusions drawn from the Bader charge analysis.

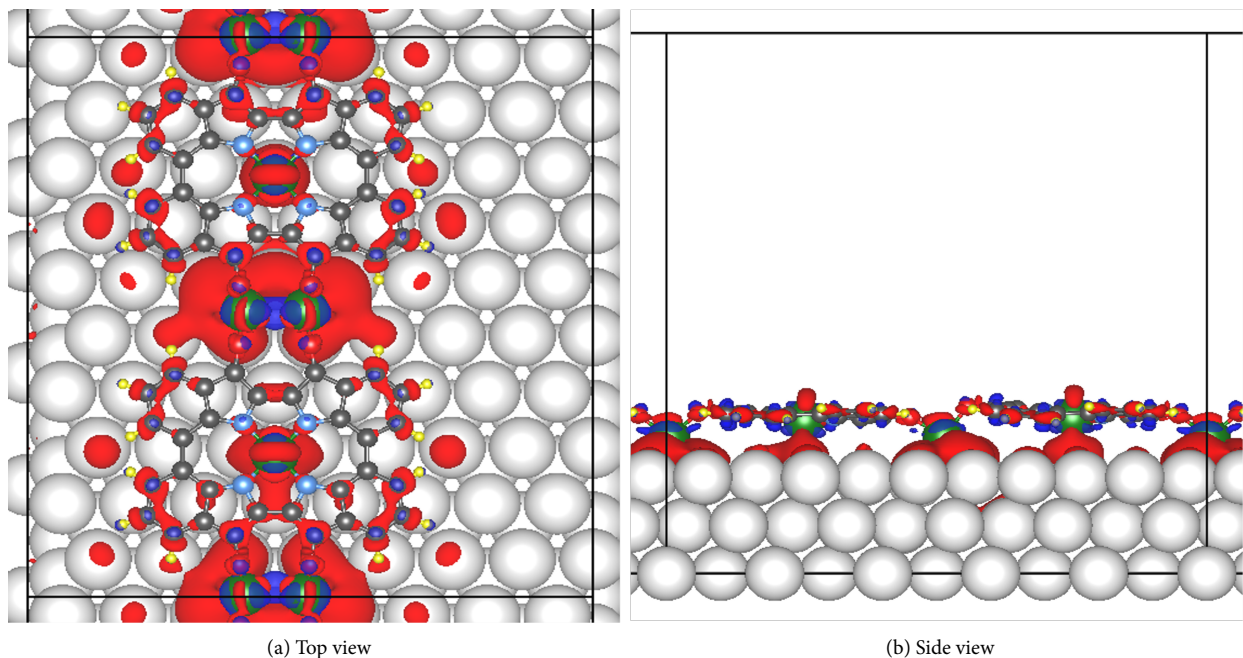


Figure S16: (a) Top and (b) side view of charge density difference plot of Fe-Por CP on Au (111). The red lobes signify electron accumulation and the blue lobes represent electron depletion. Isosurface value = ± 0.0005 electrons/Bohr³. We see that the CP is losing electrons, and the substrate is gaining electrons. The black, yellow, blue, red, green and white spheres denote the C, H, N, O, Fe and Au atoms respectively.

¹G. Henkelman, A. Arnaldsson & H. Jónsson. A fast and robust algorithm for Bader decomposition of charge density. *Comput. Mater. Sci.* 36, 354–360 (2006).

²H. Xu, R. Chakraborty, A. K. Adak, A. Das, B. Yang, D. Meier, A. Riss, J. Reichert, S. Narasimhan, J. V. Barth et al. On-surface isomerization of indigo within 1D coordination polymers. *Angew. Chem.* 136, e202319162 (2024).

We also plotted the spin polarized charge density distribution, showing the magnetic moments on the atoms constituting the CP (see Fig. S17). It is evident from the figure that the moments are primarily localized around the Fe atoms only. The up and down spin densities (shown by red and blue lobes in the plot) are so distributed because of the ground state magnetic ordering considered between the Fe atoms. In accordance with the results presented in Table S2, this corresponds to a u-(d-d)-u-(d-d) ordering of the moments on the Fe atoms within the unit cell. We note that the N atoms attached to the Fe atoms also gain some (small) magnetic moments.

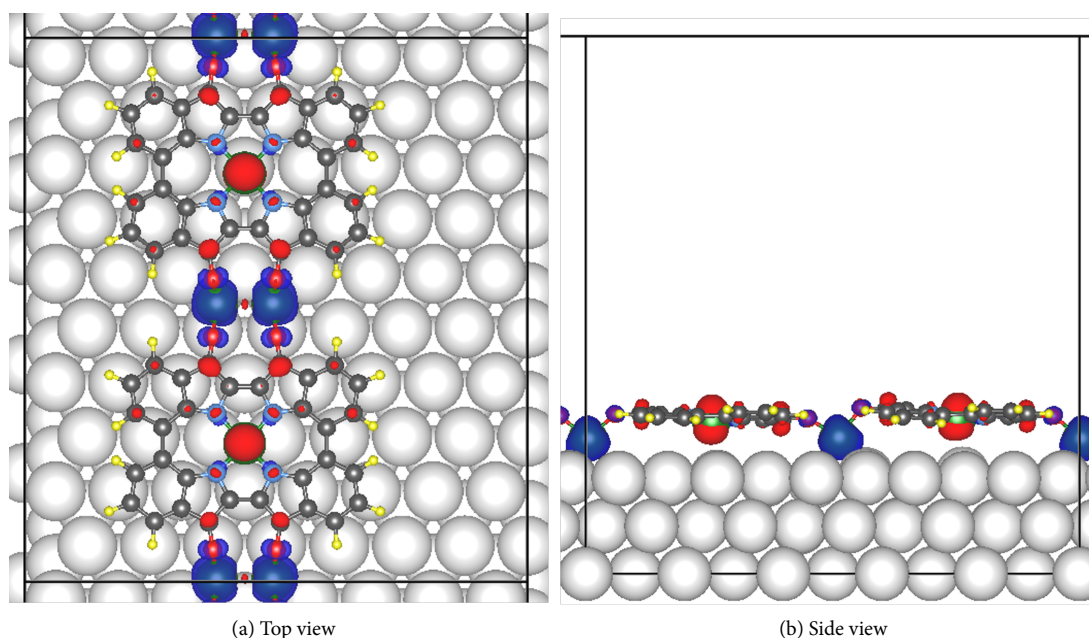


Figure S17: (a) Top and (b) side view of spin polarized charge density plot of **Fe-Por** CP on Au(111); the red lobes signify the up-spin and the blue lobes signify down-spin density. The magnetic moments are mostly localized on Fe atoms only. However, the N-atoms attached to the Fe atoms also gain some negligible magnetic moments. The isovalue used for the plot is ± 0.00005 electrons/Bohr³. The black, yellow, blue, red, green and white spheres denote the C, H, N, O, Fe and Au atoms respectively.

Choosing Hubbard- U parameter:

Choosing the appropriate value of the Hubbard U parameter in a DFT+ U calculation is a tricky question. We have chosen to determine it by looking for a match between the values of bias voltage at which experimental dI/dV maps (obtained from scanning tunnelling spectroscopy) image the Fe atoms as bright features, and the energies of the Fe d -orbitals (which vary as a function of U). Fig. S18 shows how the energies of the ten d orbitals (five up-spin and five down-spin) vary as a function of U . The five horizontal dashed lines in this figure correspond to the experimental peak positions obtained from STS (see Fig. 5(a) in the main manuscript). While the agreement is not exact (especially for the highest energy experimental peak, which may not arise from an Fe state), we see that the theoretical and experimental peak positions agree quite well for both $U = 0$ and $U = 1$ eV; we therefore conclude that either of these should be a good choice for U . In this paper, we choose $U = 1$ eV following our previous work on indigo coordination polymer on Ag(111) with the same exchange correlation functional.²

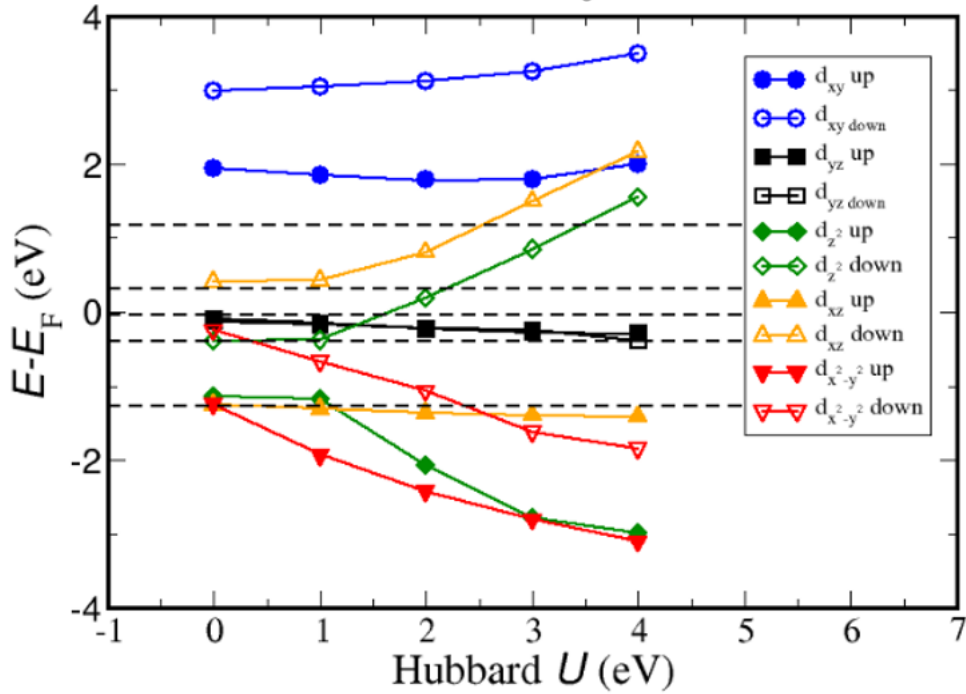


Figure S18: Determining value of U by matching Fe d -orbital energies with peak positions in STS. The curves show the variation of FeI (one of the two Fe atoms in the $(\text{Fe-Por})_2$ molecular unit) d -orbital energies with Hubbard U values, for Fe-Por_2 on the Au(111) surface. Each horizontal black dashed line denotes the position of a peak in the experimental spectrum obtained from STS. We see that $U = 1$ eV leads to a fairly good match between experiment and theory.

Aromaticity, magnetic response, and NBO analysis of Fe-Por and (Fe-Por)₂

Results for HOMA for (Fe-Por)₂ Using On-Surface Geometry

The aromaticity analysis of Fe-Por and (Fe-Por)₂ was performed on gas-phase structures. This approximation is justified by the negligible geometrical differences between the gas-phase and substrate-adsorbed geometries; deposition on Au(111) is therefore not expected to significantly alter the aromaticity trends. As a representative check, Fig. S19 shows the HOMA values of (Fe-Por)₂ computed using the on-surface geometry.

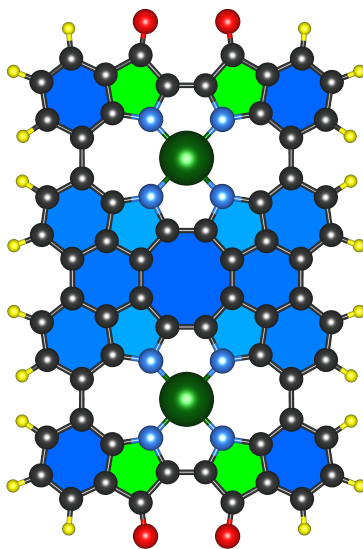


Figure S19: HOMA values of (Fe-Por)₂ computed at the on-surface geometry. The colour of each ring indicates its HOMA value according to the colour scale shown in panel (b). Very little change is observed in comparison with the gas-phase calculation, consistent with the small structural change upon adsorption on Au(111).

Broken-Symmetry Antiferromagnetic Calculation

For both Fe-Por and (Fe-Por)₂, the $S = 1$ state was found to be the lowest-energy local spin state. In (Fe-Por)₂, antiferromagnetic coupling between the two Fe centres was found to be favoured over ferromagnetic coupling. The magnetic coupling in (Fe-Por)₂ was therefore analysed using a broken-symmetry unrestricted DFT approach. Each Fe(II) centre was treated as an intermediate-spin local $S = 1$ centre. The antiferromagnetic solution corresponds to two local $S = 1$ Fe centres coupled antiparallel, rather than to a conventional closed-shell singlet.

The ferromagnetic state was first converged with the two Fe local spins aligned parallel. This converged ferromagnetic solution was then used to construct the antiferromagnetic broken-symmetry initial guess, following the Gaussian fragment-guess procedure for antiferromagnetic coupling.³ The molecule was divided into two magnetic fragments, each containing one Fe centre together with the corresponding porphyrinoid unit. The two fragments were assigned opposite spin orientations. The converged broken-symmetry solution was checked by inspecting the spin-density distribution, which confirmed opposite spin polarisation on the two Fe centres.

NBO Second-Order Perturbation Analysis

Natural Bond Orbital (NBO) second-order perturbation theory was used to quantify donor–acceptor interactions within the π system and between the ligand framework and the Fe centres. For a filled donor NBO i interacting with an empty or partially empty acceptor NBO j , the second-order stabilisation energy is given by^{4,5,6}

³L. Noodleman. Valence bond description of antiferromagnetic coupling in transition metal dimers. *J. Chem. Phys.* 74, 5737–5743 (1981).

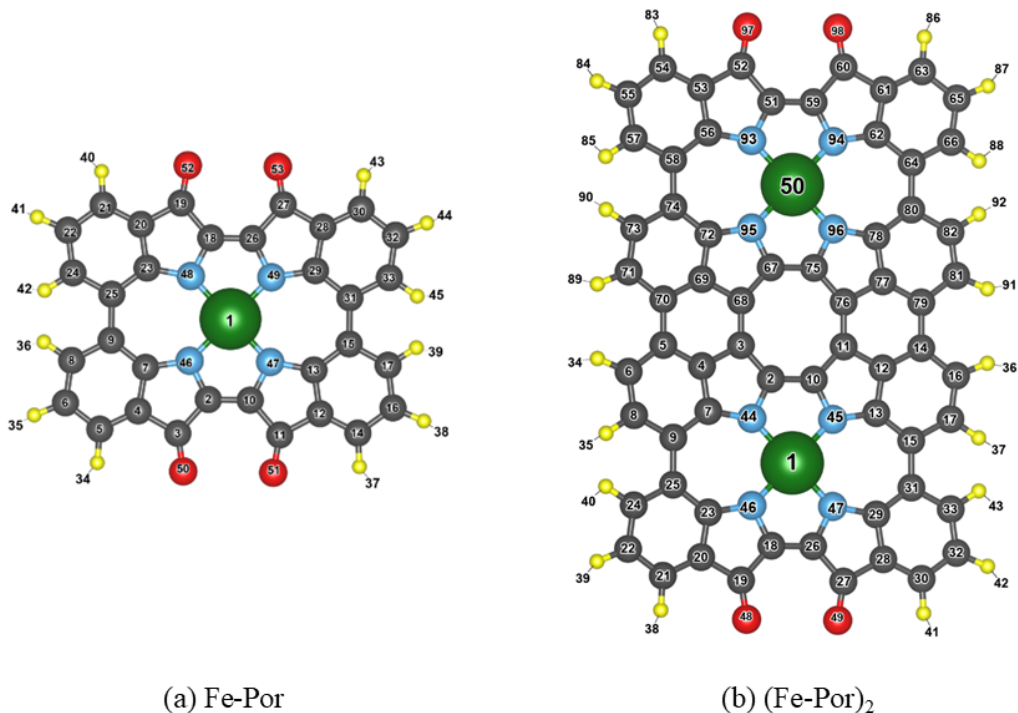


Figure S20: Gas phase relaxed molecular geometry with atomic indices of (a) **Fe-Por** and (b) **(Fe-Por)₂** as considered in the NBO analysis using Gaussian 16 software. The black, yellow, blue, red and green spheres denote C, H, N, O and Fe atoms respectively. All the following NBO analysis have been done referring to these atomic indices.

$$E_{i \rightarrow j}^{(2)} = \Delta E_{ij} = q_i \frac{F_{ij}^2}{\varepsilon_j - \varepsilon_i} \quad (1)$$

where q_i is the donor NBO occupancy, F_{ij} is the off-diagonal Fock matrix element between donor and acceptor NBOs, and ε_i and ε_j are the corresponding diagonal NBO energies. Larger $E^{(2)}$ values indicate stronger donor–acceptor mixing and greater electron delocalisation. The $E^{(2)}$ values were used qualitatively to identify dominant delocalisation pathways; they were not interpreted as directly additive total aromatic stabilisation energies.

Electronic Structure of Fe-Por

Natural Population Analysis of **Fe-Por** (see Fig. S20(a) for atomic indices) shows that the Fe centre carries a natural charge of +1.45 e , substantially smaller than a purely ionic Fe(II) value. This reflects strong donation from the surrounding porphyrinoid ligand field. The local spin moment on Fe is 2.79 μ_B , consistent with a localised intermediate-spin configuration.

The spin polarisation is also evident from the Fe d -orbital populations. The α -spin d_{z^2} orbital is nearly filled, with an occupation of 1.81 e , whereas the corresponding β -spin component contains only 0.86 e . Similar spin asymmetries are observed for d_{xz} , with $\alpha = 1.23 e$ and $\beta = 0.29 e$, and for $d_{x^2-y^2}$, with $\alpha = 1.08 e$ and $\beta = 0.13 e$. These occupancies confirm that the magnetic moment is primarily localised on the Fe centre.

The Fe centre is stabilised by a strong equatorial FeN₄ ligand field. The dominant NBO donor–acceptor interactions correspond to nitrogen lone-pair donation into Fe-centred acceptor orbitals. The representative interaction



⁴F. Weinhold. *Discovering Chemistry with Natural Bond Orbitals*. Wiley, 2012.

⁵E. D. Glendening, A. E. Reed, J. E. Carpenter & F. Weinhold. NBO, Version 3.1. Gaussian, Inc., Pittsburgh, PA, 2003.

⁶A. E. Reed, L. A. Curtiss & F. Weinhold. Intermolecular interactions from a natural bond orbital, donor–acceptor viewpoint. *Chem. Rev.* 88, 899–926 (1988).

has an $E^{(2)}$ stabilisation energy of 34.65 kcal mol⁻¹. Additional strong N→Fe σ -donation interactions of 30.63, 19.83, and 14.86 kcal mol⁻¹ are also observed. Summed over all donor-acceptor pairs, each nitrogen atom contributes approximately 100 kcal mol⁻¹ of stabilisation to the Fe centre. Weak but finite metal-to-ligand back-donation is also present; for example,



contributes 0.68 kcal mol⁻¹, electronically connecting the Fe centre to the conjugated macrocyclic framework.

Aromaticity of Fe-Por from NBO Analysis

Fe-Por exhibits delocalised π character within its aromatic phenylene rings, consistent with the local aromaticity assignment from HOMA, NICS, and ring-current density (main text, Fig. 6a); no continuous macrocyclic conjugation pathway is present, consistent with the [0]porphyrin-(2.0.2.0) designation. In a strictly localised Lewis picture, a formal π bond would contain approximately one electron per spin channel. In **Fe-Por**, the formal π -bond occupancies are depleted to approximately 0.80–0.87 e per spin channel, indicating substantial delocalisation away from individual formal double bonds. Representative π -bond occupancies are collected in Table S3.

Table S3: Selected formal π -bond occupancies in **Fe-Por**.

Bond	α -spin occupancy (e)	β -spin occupancy (e)
C2–C10	0.81	0.87
C7–C9	0.80	0.81
C13–N47	0.82	–
C18–C26	0.81	0.87
C23–C25	0.80	0.81
C29–C31	0.80	0.81

These values indicate that approximately 0.15–0.20 e per spin channel are delocalised away from the localised bonding regions into the extended π system of the aromatic phenylene rings.

The second-order perturbation analysis identifies the corresponding $\pi \rightarrow \pi^*$ delocalisation pathways. The dominant stabilisation energies fall in the range 7.1–13.8 kcal mol⁻¹. For example, the C13–N47 π bond donates into the adjacent C2–C10 π^* orbital with $E^{(2)} = 13.81$ kcal mol⁻¹. Within individual pyrrole subunits, C7–C9 donates into C6–C8 π^* with stabilisation energies of 8.72 kcal mol⁻¹ in the α channel and 9.71 kcal mol⁻¹ in the β channel. Extended conjugative communication between fused subunits is also present: C23–C25 donates into C7–C9 π^* with $E^{(2)} = 7.33$ and 7.14 kcal mol⁻¹, while C13–C15 donates into C29–C31 π^* with $E^{(2)} = 7.14$ kcal mol⁻¹. Together, these results confirm extended π delocalisation connecting the phenylene and pyrrole-type subunits, consistent with the ring-resolved aromaticity pattern in Fig. 6a–c of the main manuscript (aromatic phenylene rings, anti-aromatic pyrrole rings).

Electronic Reorganisation upon Dimerisation

The transition from **Fe-Por** to (**Fe-Por**)₂ (see Fig. S20(b) for any reference to the atomic indices) produces a significant redistribution of the conjugated π system. In the monomer, aromaticity is distributed over the entire macrocyclic porphyrinoid backbone. Upon dimerisation, the newly formed central eight-membered ring becomes the major site of π -electron delocalisation. This ring is composed of atoms C2, C3, C10, C11, C67, C68, C75, and C76, and bridges the two Fe-containing porphyrinoid units.

The central eight-membered ring has a HOMA value of 0.82, indicating strong bond-length equalisation and substantial aromatic character. This geometric result is fully consistent with the NICS and ring-current-density calculations, which show an aromatic magnetic response for the same ring, as shown in Fig. 6d–f of the main manuscript.

NBO bond occupancies provide a direct electronic explanation for this behaviour. The C–C σ bonds of the eight-membered ring remain highly localised, with α -spin occupancies of 0.98 e and β -spin occupancies of 0.98 e . Summed over both spin channels, each C–C σ bond retains approximately 1.96 e , confirming that the σ skeleton is structurally robust. In contrast, the formal π bonds of the eight-membered ring are strongly depleted to only 0.73 e per spin channel. Thus, each formal π bond contains only approximately 1.46 localised electrons rather than the ideal localised value of

2.00 e . Across the four formal π bonds of the ring, this corresponds to approximately 5.84 localised π electrons instead of 8.00, indicating a strong redistribution of electron density into the broader conjugated framework.

Cyclic $\pi \rightarrow \pi^*$ Delocalisation in the Eight-Membered Ring

Second-order perturbation analysis reveals a cyclic network of $\pi \rightarrow \pi^*$ interactions within the central eight-membered ring. Representative interactions and their stabilisation energies are listed in Table S4.

Table S4: Selected intra-ring $\pi \rightarrow \pi^*$ NBO interactions in the central eight-membered ring of $(\text{Fe-Por})_2$.

Donor $\rightarrow$ Acceptor	Spin channel	$E^{(2)}$ (kcal mol $^{-1}$)
$\pi(\text{C2-C3}) \rightarrow \pi^*(\text{C10-C11})$	α and β	10.80
$\pi(\text{C2-C3}) \rightarrow \pi^*(\text{C67-C68})$	α and β	12.94
Range of intra-ring interactions	–	9.6–13.0

These interactions form a closed donor–acceptor network around the central ring and demonstrate continuous conjugative communication between its formal double bonds. However, the planar C_8H_8 reference also exhibits comparably strong local $\pi \rightarrow \pi^*$ interactions while remaining antiaromatic. The $E^{(2)}$ values therefore establish the presence and connectivity of the conjugative pathway, but do not alone define its aromatic character. For $(\text{Fe-Por})_2$, the aromatic assignment follows from the HOMA, NICS, and ring-current-density results, while the NBO analysis shows how the cyclic pathway is incorporated into the extended polycyclic π framework.

Comparison of Aromaticity Indices of Planar C_8H_8 and $(\text{Fe-Por})_2$

As discussed in the main manuscript, some of the pyrrole rings that are anti-aromatic in **Fe-Por** become aromatic in $(\text{Fe-Por})_2$. In addition, a central eight-membered ring is formed, which is (unexpectedly) aromatic.

Below we present details of further analysis regarding the aromaticity of the rings.

As an initial step, we compare the aromaticity of a planar isomer of C_8H_8 (cyclooctatetraene) with that of the central 8-membered ring in $(\text{Fe-Por})_2$. We first compute the geometric HOMA index (see main text for discussion). The HOMA value for the former is -0.31 , indicating that the ring is anti-aromatic, as expected from the Hückel rule. In contrast, for the latter we recall it was 0.82 , indicating that the 8-membered ring in $(\text{Fe-Por})_2$ is aromatic, in seeming violation of Hückel’s rule.

Next, we compare 2D maps showing the Nucleus Independent Chemical Shift (NICS) for C_8H_8 and $(\text{Fe-Por})_2$. The NICS(1) values are plotted in Fig. S21; the color indicates the NICS value calculated at a height of 1 Å above the molecular plane, according to the color bar on the right. The figure on the left shows the results for C_8H_8 . The interior of the ring is strongly red (positive), indicating anti-aromaticity. This can be compared with the results for $(\text{Fe-Por})_2$, plotted on the right below. The interior of the central 8-membered ring is seen to be light blue/green (negative), indicating aromaticity.

Thus, both the geometric HOMA index and the electronic NICS index confirm that planar C_8H_8 is anti-aromatic, as expected, whereas the central 8-membered ring in $(\text{Fe-Por})_2$ is aromatic, in seeming violation of Hückel’s rule.

Charge Re-distribution Visualisation in $(\text{Fe-Por})_2$

In Fig. S22, we display the isosurfaces of the charge redistribution, defined as $\Delta\rho = \rho_{(\text{Fe-Por})_2} - \rho_{\text{C}_8\text{H}_8}$, where ρ_i denotes the electronic charge density for the system i . The blue lobes localized over the central 8-membered ring clearly indicate a depletion of charge density from this region, while an accumulation of electron density occurs in the neighboring rings (not shown in this figure for clarity).

Connection between Aromaticity and Antiferromagnetic Superexchange

The central eight-membered ring is not only aromatic; it also provides the electronic bridge for antiferromagnetic superexchange between the two Fe centres in $(\text{Fe-Por})_2$. In the broken-symmetry solution, the two Fe(II) sites retain local intermediate-spin $S = 1$ character but couple antiparallel. The NBO analysis elucidates three distinct channels through which the aromatic bridge couples to the Fe coordination environment.

First, the Fe centres remain stabilised by strong nitrogen-to-iron σ -donation interactions. For example,

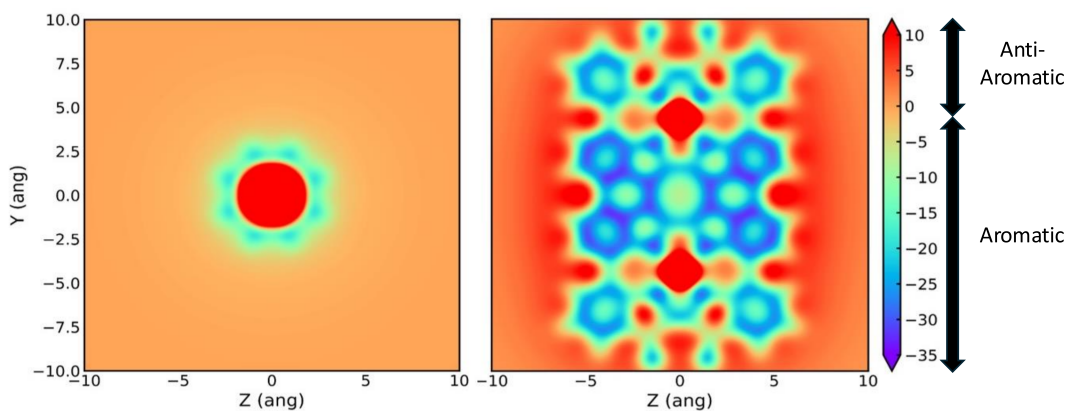


Figure S21: NICS(1) values calculated on a two-dimensional grid 1 Å above the molecular plane. Planar C_8H_8 (left) exhibits strongly positive NICS values inside the ring, indicating antiaromaticity. In contrast, the central eight-membered ring in the complete $(Fe-Por)_2$ framework (right) exhibits negative NICS values, indicating aromaticity.

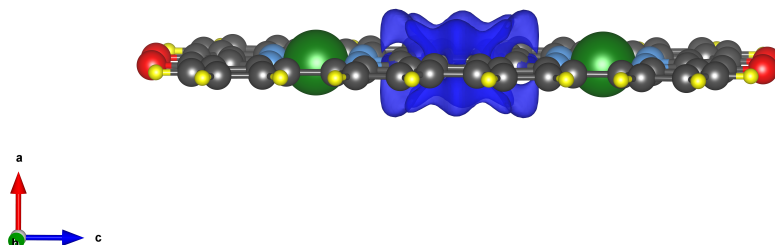


Figure S22: Charge-density-difference isosurface plot comparing planar C_8H_8 with the central eight-membered ring of $(Fe-Por)_2$, shown at an isovalue of $-0.0005 e/Bohr^3$. The blue lobes denote electron depletion from the central eight-membered-ring region, visualising the redistribution of approximately 2.16 π electrons to the adjacent rings. The red lobes corresponding to charge accumulation are not shown for simplicity. The black, yellow, blue, red, and green spheres denote C, H, N, O, and Fe atoms, respectively.



has an $E^{(2)}$ stabilisation energy of $32.04 \text{ kcal mol}^{-1}$, comparable to the corresponding interaction in the monomer. Second, the central eight-membered ring couples strongly to a coordinating nitrogen atom through the interaction



with an exceptionally large $E^{(2)}$ value of $65.33 \text{ kcal mol}^{-1}$. Since N96 belongs to the Fe coordination environment, this interaction links the aromatic π system of the central ring directly to the local ligand field of one Fe centre.

Third, direct ring-to-metal donor-acceptor interactions are observed on both sides of the dimer. On one side, the C2-C10 bond donates into an Fe1-centred acceptor orbital with $E^{(2)} = 0.67 \text{ kcal mol}^{-1}$, supplemented by a $0.52 \text{ kcal mol}^{-1}$

contribution from C2–C3. On the other side, C67–C75 donates into an Fe50-centred acceptor orbital with $E^{(2)} = 0.74 \text{ kcal mol}^{-1}$, supplemented by $0.57 \text{ kcal mol}^{-1}$ from C67–C68. Although these direct ring-to-Fe interactions are weaker than the primary Fe–N coordination interactions, their simultaneous presence on both sides of the molecule demonstrates that the two Fe centres are electronically connected through the same aromatic bridge. The central eight-membered ring therefore acts as a conjugated superexchange pathway: its delocalised π system links both metal coordination environments and enables antiferromagnetic communication between the local $S = 1$ Fe centres.