How to cite: *Angew. Chem. Int. Ed.* **2025**, e21922
doi.org/10.1002/anie.202521922

On-Surface Synthesis *Very Important Paper*

Combined In-Solution and On-Surface Synthesis of a Fully Fused Cross-Shaped Phthalocyanine Pentamer

Luis M. Mateo+, Tzu-Chao Hung+, Andreas Rank, Raffael Spachtholz, Felix Giselbrecht, Jonas Schön, Leo Gross,* Jascha Repp,* and Diego Peña**

Dedicated to Professor Tomás Torres

Abstract: Phthalocyanines (Pcs) are a class of technologically relevant tetrapyrrolic macrocycles that offer rich photophysical properties as well as excellent tunability by means of chemical functionalization. Among such functionalization strategies, the synthesis of multinuclear, fully fused Pcs – adjacent macrocycles seamlessly fused through a shared aromatic ring into a continuous π-system – is particularly appealing for the preparation of new, exotic, atomically precise carbon frameworks. However, the notoriously low solubility of Pcs typically impedes the synthesis of oligomers beyond trimers. In addition, the positional control for specific units in large low-symmetry frameworks is particularly challenging. In this work, taking advantage of the benefits of on-surface synthesis under ultra-high vacuum (UHV) conditions, we present a strategy that allows the on-surface synthesis of cross-shaped Pc pentamers. This pentamer, which bears two different metal ions with pre-defined positional control, shows a small transport gap of 1.15 eV on Au(111).

Introduction

Phthalocyanines (Pcs) possess a palette of unique photophysical properties, such as strong absorption in the UV–Vis/NIR spectrum, tunable redox activity, good electrochemistry, and rich chelation chemistry.[1] Owing to these features, which arise from their planar aromatic core of 18 highly delocalized π-electrons,[2,3] Pcs hold a privileged position in molecular materials sciences, with applications in photodynamic therapy,[4] chemical sensors,[5] solar cells,[6] nonlinear optics[7] and many more. Apart from their intrinsically interesting properties, Pcs can further be fine-tuned to meet the requirements for specific applications through the introduction of chemical modifications. These modifications range from structurally simple approaches (e.g., the introduction of electron withdrawing/donating moieties)[8] to more complex ones, such as the extension of the Pc's π-system. The latter can be achieved by introducing π-conjugated moieties[9] or through the construction of multinuclear systems.[10]

Multinuclear compounds are abundant in porphyrin (Por)-based systems, giving rise to fascinating structures and complex photophysical properties.[11] However, despite the structural similarity of Pcs and Pors, Pc-based multinuclear systems are comparably much less explored, probably due to the difficult synthetic accessibility of the required Pc building blocks, combined with the notoriously low solubility of Pcs.[12] Nonetheless, a few examples of multinuclear Pc systems have been reported, mainly consisting in the covalent linkage of Pcs through spiro-bridges[13] and rigid π-conjugated linkers (such as alkynes[14,15] and benzene rings[16]). Another strategy, which is synthetically more demanding, consists in the fusion of the corresponding heterostructure to the Pc core through multiple π-bonds, leading to fully planar structures with optimal π-orbital overlap and therefore strong π-conjugation. In this context, Pcs have been fused to Pors[17] and other porphyrinoids[18–20] as well as to additional Pcs.[10,21] These latter fused multinuclear Pc systems (Figure 1a, Wöhrle's trimers) showed exceptionally large onset wavelengths in the UV–Vis/NIR spectra (as large as 942 nm, corresponding to 1.32 eV) and decreasing highest occupied molecular orbital (HOMO)—lowest

---

[*] L. M. Mateo+, D. Peña
Centro de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, Santiago de Compostela 15782, Spain
E-mail: luismanuel.mateo@usc.es
diego.pena@usc.es

T.-C. Hung+, A. Rank, R. Spachtholz, F. Giselbrecht, J. Schön, J. Repp
Institute of Experimental and Applied Physics, University of Regensburg 93053, Regensburg, Germany
E-mail: jascha.repp@ur.de

L. Gross
IBM Research Europe–Zurich, Rüschlikon 8803, Switzerland
E-mail: LGR@zurich.ibm.com

D. Peña
Oportunius, Galician Innovation Agency (GAIN), Santiago de Compostela 15702, Spain

[+] Both authors contributed equally to this work.

Additional supporting information can be found online in the Supporting Information section

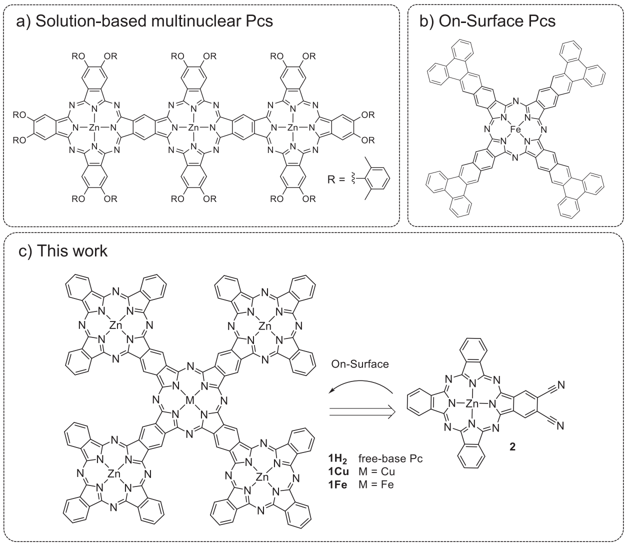


Figure 1. In-solution and on-surface synthesis of multinuclear and extended Pc systems a) In-solution synthesized multinuclear Pc,[21] b) On-surface synthesized Pc,[22] and c) the herein proposed combination of in-solution and on-surface synthesis to obtain a cross-shaped multinuclear Pc pentamer.

unoccupied molecular orbital (LUMO) gaps upon increasing the conjugation from dimers to trimers.[21] These reports have motivated the search for larger oligomers (with an increased number of fused Pc units), which can be expected to show further reduced HOMO–LUMO gaps and intriguing photophysical properties. However, as pointed out before, synthetic access to such oligomers is restricted by solubility issues and very low yields. In fact, the reported Pc trimer shown in Figure 1a could only be prepared in 0.9% yield, using bulky 2,6-dimethylphenoxy groups to reduce the π–π stacking and confer solubility to the target compound.[21]

In the context of the preparation of such large, aromatic, and poorly soluble nanostructures, on-surface synthesis under ultra-high vacuum (UHV) conditions has proven to be a particularly useful approach over the last decade. Indeed, this strategy allowed the synthesis of a plethora of planar and poorly soluble π-conjugated systems,[23–28] including several porphyrinoid-based examples.[29–35]

Apart from allowing the preparation of otherwise inaccessible structures,[36–38] on-surface synthesis enables the direct characterization of the obtained nanostructures by means of local-probe techniques, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM). The combination of these techniques allows the detailed in situ structural and electronic characterization with atomic resolution.[39,40]

In fact, Pcs have widely been studied in the context of on-surface chemistry, where the focus was mainly laid on structural aspects, aggregation behavior and the photophysical properties of surface-supported Pcs.[41] Interestingly and in stark contrast to Pors, which to date have not been synthesized on-surface, the direct on-surface synthesis of Pcs, by cyclotetramerization of 1,2-benzodinitrile (*phthalonitrile*) precursors, has been reported. Piantek and coworkers (using co-deposited Mn),[42] and Bucher and coworkers (using co-deposited Fe)[43] demonstrated that Pcs can be synthesized by on-surface cyclotetramerization of 1,2,4,5-tetracyano-benzene.[42–45] Later, reports by Lobo–Checa and coworkers,[46] Wang and coworkers,[47] and Gottfried and coworkers,[22] showed that this methodology can be employed with structurally more complex phthalonitriles, giving rise to sophisticated Pc derivatives, see, e.g., Figure 1b.[22]

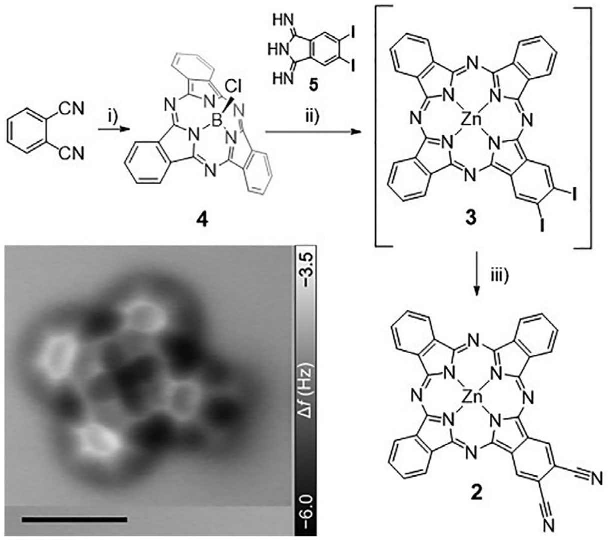
Bearing the successful on-surface cyclotetramerization of phthalonitriles in mind, we envisioned the preparation of a cross-shaped Pc pentamer **1**, starting from dicyano Pc **2** (Figure 1c). The goal of this strategy is the preparation of customized nanosized Pc oligomers, in which two different metals may be introduced at atomically defined positions in an exact 4:1 stoichiometric ratio. Furthermore, this pentamer **1** would overcome the (solubility-imposed) limits of classical in-solution Pc chemistry, giving access to fused multinuclear Pcs beyond Wöhrle's trimers (Figure 1a).[21] To that end and using solution-based chemistry, we prepared an A_3B-type Pc **2** that bears a phthalonitrile moiety, which in turn can act as an on-surface Pc precursor. This precursor is intended to be cyclotetramerized on Au(111), in presence of co-deposited Fe atoms, to form a Pc pentamer **1Fe** (Figure 1c). Using bond-resolving AFM imaging with a CO functionalized tip,[39] we unambiguously demonstrate the formation of the target Pc pentamer **1Fe**, in which the central FePc moiety is flanked by four ZnPc macrocycles. Through a combination of differential conductance (dI/dV_s) mapping and density functional theory (DFT) calculations, we assign the frontier orbitals and estimate a HOMO–LUMO transport gap of about 1.15 eV for **1Fe**, which is notably reduced compared to the individual ZnPc (~1.8 eV on Au(111)).

Results and Discussion

Solution-Based Synthesis of Dicyano Pc 2

The synthesis of unsymmetrically substituted Pcs, such as the target dicyano Pc **2**, is inherently challenging, giving rise to complex mixtures and low yields.[12,48] As shown in Figure 1c, compound **2** comprises three equal (A) unsubstituted isoindoline units and one different (B) 5,6-dicyanoisoindoline moiety, and is thus an A_3B-type Pc.[12]

Inspired by the work of Torres and coworkers,[12] we first attempted the most direct and straightforward strategy, consisting of the statistical cyclotetramerization of phthalonitrile and 4,5-dicyano-phthalonitrile. Unfortunately, instead of **2,** this approach yielded the symmetrically unsubstituted A_4 Pc, along with highly polar, insoluble, and unidentified side-products. We attribute this to the electron-withdrawing character of the cyano groups in 4,5-dicyano-phthalonitrile, decreasing the reactivity of this phthalonitrile in cyclotetramerization reactions. We thus decided to enhance the reactivity of 4,5-dicyano-phthalonitrile by transforming it into the corresponding 1,3-diiminoisoindoline, which is a commonly used synthetic strategy for the use of poorly reactive phthalonitriles in mixed cyclotetramerization reactions.[2] However, we only obtained trace amounts of **2**, which could



Scheme 1. Preparation of **2** by means of a SubPc ring-expansion reaction of **4**. Reagents and conditions: i) BCl_3, *o*-dichlorobenzene, reflux, 3 h; ii) $Zn(OAc)_2$, *N,N*-dimethylaminoethanol, 90 °C, 72 h; iii) KCN, CuI, PPh_3, $Pd(PPh_3)_4$, THF, 70 °C overnight. Bond-resolved AFM image of **2** on bilayer NaCl/Au(111) ($V_S = 0$ V, $\Delta z = +0.9$ Å, scale bar = 1 nm).

not be isolated due to the, again, large amount of the symmetric A_4-type Pc as undesired main product.

In view of these limitations, we decided to switch to the subphthalocyanine (SubPc) ring-expansion approach, which was shown to allow the synthesis of A_3B-type Pcs (Scheme 1).[49,50] Furthermore, we decided to introduce the two cyano groups *after* the formation of the Pc macrocycle to i) enhance the reactivity of the corresponding isoindoline, ii) enhance the solubility of the resulting product and iii) suppress the formation of undesired cyclization side-products.

To this end, we first prepared the unsubstituted Cl-SubPc **4**,[51] which we then reacted with 5,6-diiodo-1,3-diiminoisoindoline **5** and zinc acetate, giving rise to a mixture of **3**, A_4 Pc, and highly polar side-products. After performing flash column chromatography to remove the polar side-products, the (inseparable) mixture of **3** and A_4 Pc was directly subjected to a twofold Pd-catalyzed cyanation reaction, affording a mixture of **2** and A_4 Pc, which could be separated by column chromatography. The successful preparation and purification of **2** was demonstrated by means of ^{1}H NMR and MALDI-TOF MS (see Supporting Information) as well as by bond-resolving AFM imaging (see Scheme 1). The AFM image reveals the cyano groups as linear bright features. The connected isoindoline group appears with slightly darker contrast compared to the other isoindoline groups, which we assign to a non-planar adsorption geometry. Likely interaction of the cyano groups with the surface pulls the corresponding arm of the molecule toward the surface.

On-Surface Cyclotetramerization: Synthesis of 1

With dicyano Pc **2** in hand, we began exploring its on-surface cyclotetramerization to obtain cross-shaped Pc pentamer **1**. To this end, Pc **2** was sublimed onto a clean Cu(111) surface, kept at a temperature of around 8 K and under ultra-high vacuum (UHV) conditions. Figure 2a shows the overview STM image of such a sample after annealing to ~520 K for 5 min, where several distinct features can be found, among which the Pc pentamer **1Cu** stands out thanks to its characteristic cross shape. Bond-resolved AFM imaging was carried out to confirm the formation of a new central Pc core, which connects to each of the four adjacent ZnPc moieties through one benzene ring (Figure 2a, inset). Notably, some of the acquired AFM images reveal a slightly different pattern at the central metal ion position, possibly suggesting the coexistence of **1Cu** and **1H$_2$** (Figure S1). Looking at the AFM data (Figure 2a, inset), a markedly different brightness of the peripheral benzene rings of the four ZnPcs becomes apparent, which indicates that **1Cu** does not absorb planarly on the Cu(111) surface. Furthermore, one can see the lower ZnPc moiety is slightly tilted with respect to the surface plane. This suggests that **1Cu** interacts strongly (and therefore hybridizes) with the underlying substrate, as commonly observed for molecules on Cu(111),[52] which hampers the study of the electronic properties of **1Cu** on Cu(111).

Wang and coworkers recently reported the direct on-surface synthesis of AuPcs from dicyano derivatives on Au(111),[47] which is less reactive than Cu(111). Using Au(111) as substrate and after thermal annealing ~570 K for 5 min, we could not identify any cross-shaped cyclotetramerization products. Instead, the sample showed a large amount of dimer-like structures, in which two units of **2** are facing each other through their dicyano-bearing isoindoline moieties, as revealed by the overview STM image (Figure 2b) and the bond-resolved AFM image (Figure 2b, inset and Figure S2). Because of the high affinity of the cyano group toward gold, cyano-bearing compounds are known to form stable metal–organic structures which, in some cases, show very low mobility and poor reactivity.[53–55] Interestingly, the constituents of these dimer-like structures are *not* covalently coupled and the reaction did not evolve toward the desired Pc pentamer, which is in contrast to other dicyano derivatives.[47,56] In this context, and given that the noncovalent interaction between nitrogen atoms (N···N) is rather unusual, we hypothesize that the two units of **2** are linked via coordination to gold adatoms.

To suppress the formation of dimers of **2** and thereby enable the formation of **1Fe**, we performed the cyclotetramerization in presence of co-deposited Fe atoms.[22,44] Single Fe atoms were therefore co-deposited onto a sample of **2** on Au(111) (see Figure S3), which was then annealed to ~520 K for 10 min. Figure 2c shows an overview STM image after annealing, in which several four-fold symmetric cross-shaped structures, identified as **1Fe** (see next paragraph) are observed. We estimated a yield of 18% for the on-surface synthesis of **1Fe**. The yield showed some variations, depending on the exact sample preparation conditions (see Figure S4). Notably it represents a substantial improvement with regard to the yield in solution-based preparation methods, which are typically in the range of 1%–2%.[10] Besides **1Fe**, some presumable cyclotetramerization intermediates, such as dimers, trimers, and other oligomers, were observed (see Figure S5 as example). The bond-resolved AFM image of

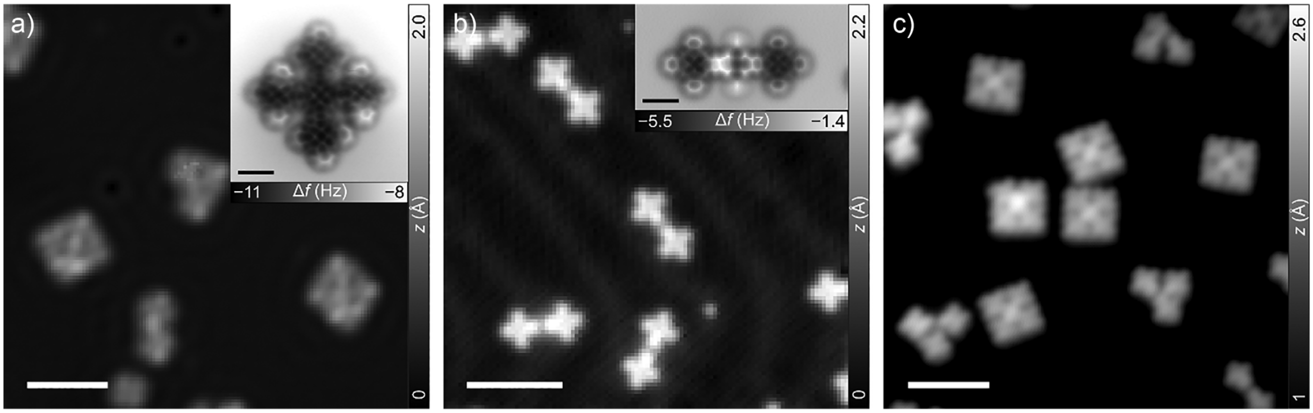


Figure 2. a) Overview STM image of a sample of **2** on Cu(111) after annealing to ~520 K for 5 min, showing the successful on-surface synthesis of **1Cu** ($V_S = 0.2$ V, $I = 7$ pA). Inset: Bond-resolved AFM image of **1Cu** ($V_S = 0$ V, $\Delta z = -2.15$ Å). The AFM image suggests that the overall pentamer structure is non-planar and distorted, which we attribute to its interaction with the substrate. b) Overview STM image of a sample of **2** on Au(111), without co-deposited Fe atoms, after annealing to ~570 K for 5 min. Only dimers of **2** can be found on the surface ($V_S = 0.2$ V, $I = 1$ pA). Inset: bond-resolved AFM image of one such dimer ($V_S = 0$ V, $\Delta z = -1.50$ Å). c) Overview STM image of a sample of **2** on Au(111), with co-deposited Fe atoms, after annealing to ~520 K for 10 min. Several pentamers **1Fe** can be found on the surface. Metal tips were used for STM images. Scale bars in STM images 5 nm. Scale bars in AFM images (insets) 1 nm.

1Fe (Figure 3a), which proves the formation of a central Pc moiety, shows similar brightness of all phenyl moieties, indicating a planar geometry of the molecule, in contrast to **1Cu** on Cu(111). With a closer look, the core of the central Pc shows a cross-like feature, whereas the cores of the outer Pc moieties show hollow-square-like features. These distinct features indicate that the inner and outer Pc cores bear, as expected, different central metal ions, namely Zn^{2+} in the peripheral Pcs and Fe^{2+} in the central Pc, respectively.[57,58] Finally, a differential conductance (dI/dV_S) map (Figure 3b) which was simultaneously acquired during the constant-height AFM image, reveals a zero-bias resonance localized at the center of the newly formed Pc, which can be attributed to the interaction between the non-zero spin located at the Fe atom and the conduction electrons of the Au(111) surface substrate, i.e., a Kondo peak.[59–61]

Electronic Properties of 1Fe

After the successful on-surface synthesis of **1Fe**, we turned our attention toward its electronic properties. Considering **1Fe** a π-extended pentameric counterpart to Wöhrle's trimers (Figure 1a), we expect a reduction of the HOMO–LUMO gap with respect to these compounds.[10,21] To elucidate the electronic properties and thereby estimate the HOMO–LUMO gap, we combined scanning tunneling spectroscopy (STS) and constant-current dI/dV_S mapping with DFT calculations.

We measured STS at different positions of the molecule (see Figure S6). However, we observed that the spectra are very similar and are largely dominated by the features of Au(111), such that the Kondo peak is the only clearly distinguishable feature. We attribute this finding to the hybridization of the large π-system of **1Fe** with the underlying surface. To resolve the electronic features of

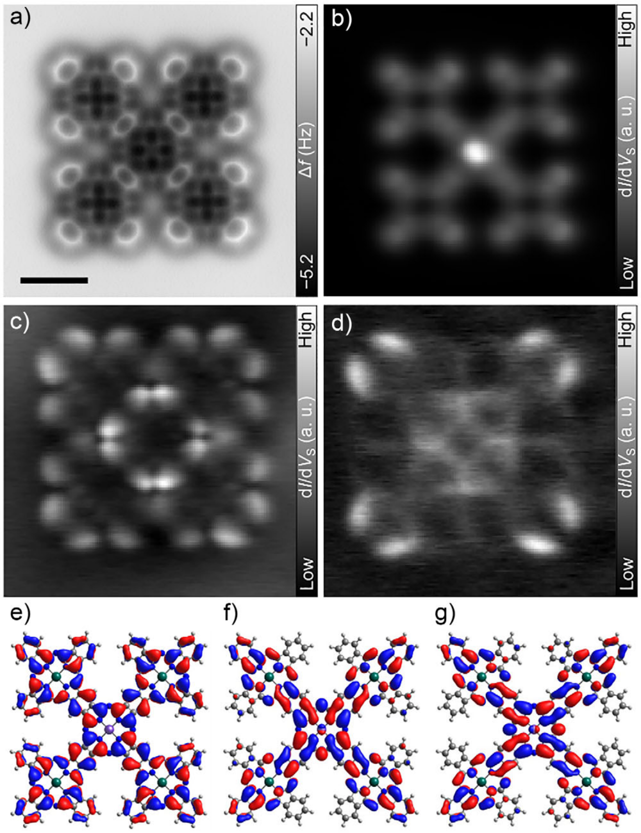


Figure 3. a) Bond-resolved AFM image of **1Fe** on Au(111). b) Constant-height differential conductance map, acquired simultaneously with a), showing zero-bias-resonance at the center of pentamer, demonstrating the formation of a FePc moiety ($V_S = 0$ V, $\Delta z = -1.5$ Å). c) and d) Constant-current differential conductance maps, acquired at $V_S = -0.35$ V and $+0.80$ V, respectively. e) DFT-derived HOMO, f), and g) DFT-derived degenerate LUMOs of **1Fe**. Scale bar = 1 nm, applying to panels a)–d).

1Fe, we performed dI/dV_S mapping in which the spatial contrast indicated ion resonances. We found a positive ion resonance (PIR)[62] at $V_S = -0.35$ V (Figure 3c), in which 16 intensity maxima are observed at the periphery and further eight maxima appear at the center of the cross-shaped pentamer. The corresponding DFT-derived HOMO, which is shown in (Figure 3e), matches with the experimental dI/dV_S map, where nodal planes can be observed along the two (perpendicular) molecular axis lie *along* the three Pc cores (Zn–Fe–Zn), respectively. On the other hand, we found a negative ion resonance (NIR) at $V_S = 0.80$ V (Figure 3d), in which a faint feature is observed at the central Pc, together with eight distinct lobes at the outermost benzene rings (two lobes per benzene ring). The excellent agreement of NIR with the superposition of corresponding DFT-derived degenerate LUMOs (Figure 3f,g), allows the assignment of this state to the LUMO of **1Fe**. Therefore, the resulting on-surface HOMO–LUMO transport gap can be estimated to be $\Delta E_{\text{HOMO–LUMO}} \sim 1.15$ eV, which is significantly reduced with respect to ZnPc on Au(111) (~1.8 eV, see Figure S7), thus indicating a strong and efficient conjugation between the π-systems of the individual Pcs.

In fact, the correspondence between gap size and extension of π-conjugation can be followed in the series of ZnPc, over the dimer of **2**, an incomplete cyclotetramerization byproduct (see Figures S2 and S5, respectively) to the final product **1Fe**, which is summarized in Table S1. Specifically, the gaps of ZnPc and the dimer of **2** are similar (1.8 eV), while the gap of the incomplete cyclotetramerization byproduct is reduced to 1.45 eV. This trend suggests a lack of conjugation in the dimer in accordance with the noncovalent coupling within the dimer of **2**, a partial conjugation in the incomplete byproduct and an excellent conjugation in **1Fe**, leading to a reduction of the HOMO–LUMO gap by more than 30%, from 1.8 to 1.15 eV.

Observed Side-Product: Pentamer with Two Fe Atoms

As mentioned above, several side-products were observed in the on-surface cyclotetramerization of **2** on Au(111). One of these products is particularly interesting and will be discussed herein in more detail.

As can be seen in Figure 4a, the low-voltage STM image of some of the cross-shaped pentamers does not show the same brightness in the center of all four peripheral Pcs. In fact, one of these presumable ZnPcs (top left) shows a bright spot in the central cavity. The bond-resolved AFM image, shown in Figure 4b, reveals a cross-like structure in the center of the top left Pc, just as for the central Pc. While these differences are subtle, making it difficult to identify the substituted metal core, the corresponding zero-bias dI/dV_S map (Figure 4c) clearly indicates that one of the peripheral Pcs hosts a Fe^{2+} metal ion instead of Zn^{2+} (Figure 4d) as mentioned above (cf. Figure 3). The most likely source of this structure is the presence of traces of **$2H_2$** in the sample of **2**, which could not be detected by NMR or MALDI-MS (see Figures S17–S20), and have undergone self-metalation with co-deposited Fe atoms.[63]

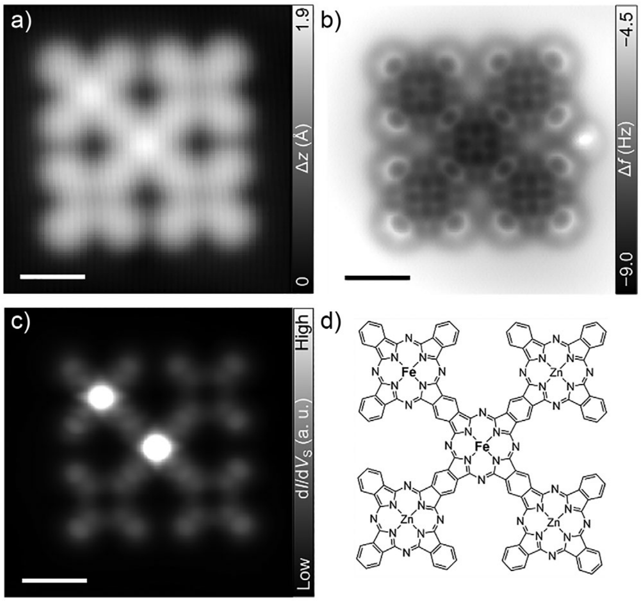


Figure 4. a) Low-voltage STM image ($V_S = 0.2$ V, $I = 1$ pA), b) Bond-resolved AFM image and c) Constant-height differential conduction map, acquired simultaneously with b), showing that the upper-left moiety of the pentamer hosts an iron metal ion instead of zinc ($V_S = 0$ V, $\Delta z = -1.75$ Å). d) Chemical structure of the di-iron pentamer. All scale bars refer to 1 nm.

Another possible source is the on-surface transmetalation from ZnPc to FePc, which to the best of our knowledge remains unreported to this date, making this hypothesis rather unlikely. Interestingly, we did not find any examples with three Fe^{2+} metal ions, thus stressing the low likelihood of the trans-metalation scenario. Regardless of its origin, the detection and characterization of such a structure with Zn:Fe ratio 3:2, whose targeted synthesis seems quite difficult, opens the possibility of studying exotic Pc-based architectures.

Conclusions and Outlook

In this work, we present a combined in-solution and on-surface approach toward cross-shaped pentameric Pc nanostructures **1**, which consist of five fused Pc cores. These compounds are substantially π-extended counterparts of Wöhrle's trimers and, to the best of our knowledge, the largest well-defined and fused Pc oligomers with positional control of different metal cores.

The unsymmetrically substituted dicyano Pc **2**, which acts as on-surface Pc precursor, is obtained by means of a SubPc ring expansion reaction, followed by a twofold Pd-catalyzed cyanation reaction. The so-obtained Pc **2** could then be cyclotetramerized both on Cu(111) and on Au(111). While the tetramerization reaction on Cu(111) proceeded in absence of co-deposited atoms, yielding **1Cu**, the corresponding reaction on Au(111) required the presence of co-deposited Fe atoms, yielding the Fe^{2+}-metalated analogue **1Fe**. Using a combination of constant-current dI/dV_S mapping with DFT calculations, we were able to identify the PIR and NIR, respectively, and we thus extracted an estimated on-surface HOMO–LUMO transport gap of $\Delta E_{\mathrm{HOMO-LUMO}} \sim 1.15$ eV, which is significantly reduced with respect to ZnPc on Au(111) (~1.8 eV). The strategy presented herein allows, in principle, the on-surface synthesis of a variety of Pc pentamers by simply exchanging the central metal ion of **2**, or by employing a different co-deposited metal on Au(111). In doing so, distinct pentamers could be obtained — with an *à la carte* choice of the metal ions — in an exact 4:1 stoichiometric ratio.

Furthermore, this work opens the possibility for the synthesis of larger Pc oligomers by introducing two additional cyano groups at the *trans*-position of **2**. In particular, two-dimensionally expanded analogues of **1** can be envisioned, whose on-surface polymerization might result in a molecular Lieb lattice.

Supporting Information

The authors have cited additional references within the Supporting Information.

Acknowledgements

The authors thank Dr. Elena Cañizares for valuable discussions. The authors acknowledge financial support from the Spanish grant PID2022-140845OBC62 (MICIU/AEI/10.13039/501100011033 and ERDF), from the Xunta de Galicia (Centro de Investigación do Sistema Universitario de Galicia, 2023–2027, ED431G 2023/03) and from the European Union (ERC Synergy Grant MolDAM no. 951519). L.M.M. acknowledges financial support from MCIN/AEI, with co-funding from the European Union (NextGenerationEU/PRTR), through the Juan de la Cierva Fellowship (FJC2021-047965-I).

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Cyclotetramerization • In-solution synthesis • On-surface synthesis • Phthalocyanine • Scanning probe microscopy

---

[1] L. Breloy, O. Yavuz, I. Yilmaz, Y. Yagci, D.-L. Versace, *Polym. Chem.* **2021**, *12*, 4291–4316. https://doi.org/10.1039/D1PY00462J.

[2] N. B. McKeown, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, Amsterdam, **2003**, pp. 61–124.

[3] R. P. Linstead, *J. Chem. Soc.* **1934**, 1016. https://doi.org/10.1039/jr9340001016.

[4] P.-C. Lo, M. S. Rodríguez-Morgade, R. K. Pandey, D. K. P. Ng, T. Torres, F. Dumoulin, *Chem. Soc. Rev.* **2020**, *49*, 1041–1056. https://doi.org/10.1039/C9CS00129H.

[5] D. Gounden, N. Nombona, W. E. van Zyl, *Coord. Chem. Rev.* **2020**, *420*, 213359. https://doi.org/10.1016/j.ccr.2020.213359.

[6] M. Urbani, M.-E. Ragoussi, M. K. Nazeeruddin, T. Torres, *Coord. Chem. Rev.* **2019**, *381*, 1–64. https://doi.org/10.1016/j.ccr.2018.10.007.

[7] M. Yahya, Y. Nural, Z. Seferoğlu, *Dyes Pigm.* **2022**, *198*, 109960. https://doi.org/10.1016/j.dyepig.2021.109960.

[8] E. A. Kuzmina, T. V. Dubinina, L. G. Tomilova, *New J. Chem.* **2019**, *43*, 9314–9327. https://doi.org/10.1039/C9NJ01755K.

[9] H. Ali, J. E. van Lier, *Tetrahedron Lett.* **1997**, *38*, 1157–1160. https://doi.org/10.1016/S0040-4039(97)00013-0.

[10] S. G. Makarov, O. N. Suvorova, D. Wöhrle, *J. Porphyr. Phthalocyanines* **2011**, *15*, 791–808. https://doi.org/10.1142/S1088424611003835.

[11] T. Tanaka, A. Osuka, *Chem. Soc. Rev.* **2015**, *44*, 943–969. https://doi.org/10.1039/C3CS60443H.

[12] M. S. Rodríguez-Morgade, G. De La Torre, T. Torres, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, Amsterdam, **2003**, pp. 125–160.

[13] W. A. Nevin, W. Liu, S. Greenberg, M. R. Hempstead, S. M. Marcuccio, M. Melnik, C. C. Leznoff, A. B. P. Lever, *Inorg. Chem.* **1987**, *26*, 891–899. https://doi.org/10.1021/ic00253a023.

[14] M. J. Cook, M. J. Heeney, *Chem. - Eur. J.* **2000**, *6*, 3958–3967. https://doi.org/10.1002/1521-3765(20001103)6:21⟨3958::AID-CHEM3958⟩3.0.CO;2-Y.

[15] E. M. Maya, P. Vázquez, T. Torres, *Chem. - Eur. J.* **1999**, *5*, 2004–2013. https://doi.org/10.1002/(SICI)1521-3765(19990702)5:7⟨2004::AID-CHEM2004⟩3.0.CO;2-P.

[16] G. Bottari, T. Torres, *Chem. Commun.* **2004**, 2668. https://doi.org/10.1039/b411960f.

[17] Y. Zhang, Z. Xue, D. Qi, K. Wang, H. Liu, J. Jiang, *Chem. - Eur. J.* **2017**, *23*, 15017–15021. https://doi.org/10.1002/chem.201703787.

[18] G. de la Torre, M. V. Martínez-Díaz, P. R. Ashton, T. Torres, *J. Org. Chem.* **1998**, *63*, 8888–8893. https://doi.org/10.1021/jo981118p.

[19] Y. Zhang, J. Oh, K. Wang, C. Chen, W. Cao, K. H. Park, D. Kim, J. Jiang, *Chem. - Eur. J.* **2016**, *22*, 4492–4499. https://doi.org/10.1002/chem.201504837.

[20] Y. Zhang, L. Zhao, K. Wang, J. Jiang, *Inorg. Chem. Front.* **2017**, *4*, 104–109. https://doi.org/10.1039/C6QI00496B.

[21] S. G. Makarov, O. N. Suvorova, C. Litwinski, E. A. Ermilov, B. Röder, O. Tsaryova, T. Dülcks, D. Wöhrle, *Eur. J. Inorg. Chem.* **2007**, *2007*, 546–552. https://doi.org/10.1002/ejic.200600843.

[22] L. J. Heuplick, Q. Fan, D. A. Astvatsaturov, T. V. Dubinina, J. M. Gottfried, *Commun. Chem.* **2024**, *7*, 292. https://doi.org/10.1038/s42004-024-01351-8.

[23] S. Clair, D. G. de Oteyza, *Chem. Rev.* **2019**, *119*, 4717–4776. https://doi.org/10.1021/acs.chemrev.8b00601.

[24] R. Lindner, A. Kühnle, *ChemPhysChem* **2015**, *16*, 1582–1592. https://doi.org/10.1002/cphc.201500161.

[25] Q. Sun, R. Zhang, J. Qiu, R. Liu, W. Xu, *Adv. Mater.* **2018**, *30*, 1705630. https://doi.org/10.1002/adma.201705630.

[26] R. Zuzak, J. Castro-Esteban, P. Brandimarte, M. Engelund, A. Cobas, P. Piątkowski, M. Kolmer, D. Pérez, E. Guitián, M. Szymonski, D. Sánchez-Portal, S. Godlewski, D. Peña, *Chem. Commun.* **2018**, *54*, 10256–10259. https://doi.org/10.1039/C8CC05353G.

[27] C. Moreno, M. Vilas-Varela, B. Kretz, A. Garcia-Lekue, M. V. Costache, M. Paradinas, M. Panighel, G. Ceballos, S. O. Valenzuela, D. Peña, A. Mugarza, *Science* **2018**, *360*, 199–203. https://doi.org/10.1126/science.aar2009.

[28] K. Eimre, J. I. Urgel, H. Hayashi, M. Di Giovannantonio, P. Ruffieux, S. Sato, S. Otomo, Y. S. Chan, N. Aratani, D. Passerone, O. Gröning, H. Yamada, R. Fasel, C. A. Pignedoli, *Nat. Commun.* **2022**, *13*, 511. https://doi.org/10.1038/s41467-022-27961-1.

[29] L. M. Mateo, Q. Sun, S.-X. Liu, J. J. Bergkamp, K. Eimre, C. A. Pignedoli, P. Ruffieux, S. Decurtins, G. Bottari, R. Fasel, T. Torres, *Angew. Chem. Int. Ed.* **2020**, *59*, 1334–1339. https://doi.org/10.1002/anie.201913024.

[30] Q. Sun, L. M. Mateo, R. Robles, P. Ruffieux, N. Lorente, G. Bottari, T. Torres, R. Fasel, *J. Am. Chem. Soc.* **2020**, *142*, 18109–18117. https://doi.org/10.1021/jacs.0c07781.

[31] Q. Sun, L. M. Mateo, R. Robles, N. Lorente, P. Ruffieux, G. Bottari, T. Torres, R. Fasel, *Angew. Chem. Int. Ed.* **2021**, *60*, 16208–16214. https://doi.org/10.1002/anie.202105350.

[32] Q. Sun, L. M. Mateo, R. Robles, P. Ruffieux, G. Bottari, T. Torres, R. Fasel, N. Lorente, *Adv. Sci. (Weinh)* **2022**, *9*, e2105906.

[33] J. Li, N. Merino-Díez, E. Carbonell-Sanromà, M. Vilas-Varela, D. G. de Oteyza, D. Peña, M. Corso, J. I. Pascual, *Sci. Adv.* **2018**, *4*, eaaq0582.

[34] S. Kawai, A. Ishikawa, S.-i. Ishida, T. Yamakado, Y. Ma, K. Sun, Y. Tateyama, R. Pawlak, E. Meyer, S. Saito, A. Osuka, *Angew. Chem. Int. Ed.* **2022**, *61*, e202114697. https://doi.org/10.1002/anie.202114697.

[35] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, S. Hecht, *Nat. Nanotechnol.* **2007**, *2*, 687–691. https://doi.org/10.1038/nnano.2007.346.

[36] S. Mishra, D. Beyer, K. Eimre, S. Kezilebieke, R. Berger, O. Gröning, C. A. Pignedoli, K. Müllen, P. Liljeroth, P. Ruffieux, X. Feng, R. Fasel, *Nat. Nanotechnol.* **2020**, *15*, 22–28. https://doi.org/10.1038/s41565-019-0577-9.

[37] N. Pavliček, A. Mistry, Z. Majzik, N. Moll, G. Meyer, D. J. Fox, L. Gross, *Nat. Nanotechnol.* **2017**, *12*, 308–311.

[38] T. Wang, A. Berdonces-Layunta, N. Friedrich, M. Vilas-Varela, J. P. Calupitan, J. I. Pascual, D. Peña, D. Casanova, M. Corso, D. G. de Oteyza, *J. Am. Chem. Soc.* **2022**, *144*, 4522–4529. https://doi.org/10.1021/jacs.1c12618.

[39] L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, *Science* **2009**, *325*, 1110–1114. https://doi.org/10.1126/science.1176210.

[40] L. Gross, B. Schuler, N. Pavliček, S. Fatayer, Z. Majzik, N. Moll, D. Peña, G. Meyer, *Angew. Chem. Int. Ed.* **2018**, *57*, 3888–3908. https://doi.org/10.1002/anie.201703509.

[41] J. M. Gottfried, *Surf. Sci. Rep.* **2015**, *70*, 259–379. https://doi.org/10.1016/j.surfrep.2015.04.001.

[42] M. Piantek, D. Serrate, M. Moro-Lagares, P. Algarabel, J. I. Pascual, M. R. Ibarra, *J. Phys. Chem. C* **2014**, *118*, 17895–17899. https://doi.org/10.1021/jp506652j.

[43] S. Kezilebieke, A. Amokrane, M. Abel, J.-P. Bucher, *J. Phys. Chem. Lett.* **2014**, *5*, 3175–3182. https://doi.org/10.1021/jz5015696.

[44] Y. Zhao, B. Yuan, C. Li, P. Zhang, Y. Mai, D. Guan, Y. Li, H. Zheng, C. Liu, S. Wang, J. Jia, *ChemPhysChem* **2019**, *20*, 2394–2397. https://doi.org/10.1002/cphc.201900238.

[45] M. Koudia, M. Abel, *Chem. Commun.* **2014**, *50*, 8565–8567. https://doi.org/10.1039/C4CC02792B.

[46] A. Domínguez-Celorrio, C. Garcia-Fernandez, S. Quiroga, P. Koval, V. Langlais, D. Peña, D. Sánchez-Portal, D. Serrate, J. Lobo-Checa, *Nanoscale* **2022**, *14*, 8069–8077. https://doi.org/10.1039/D2NR00721E.

[47] Z. Wang, X. Liu, Y. Lu, Z. Wang, C. Bortolini, M. Chen, S. Wei, W. Li, J. Zhu, H. Ju, F. Rosei, M. Dong, L. Wang, *Mater. Chem. Front.* **2019**, *3*, 1406–1410. https://doi.org/10.1039/C9QM00070D.

[48] G. de la Torre, C. G. Claessens, T. Torres, *Eur. J. Org. Chem.* **2000**, *2000*, 2821–2830. https://doi.org/10.1002/1099-0690(200008)2000:16⟨2821::AID-EJOC2821⟩3.0.CO;2-2.

[49] A. Weitemeyer, H. Kliesch, D. Woehrle, *J. Org. Chem.* **1995**, *60*, 4900–4904. https://doi.org/10.1021/jo00120a038.

[50] N. Kobayashi, T. Ishizaki, K. Ishii, H. Konami, *J. Am. Chem. Soc.* **1999**, *121*, 9096–9110. https://doi.org/10.1021/ja983325c.

[51] G. E. Morse, T. P. Bender, *ACS Appl. Mater. Interfaces* **2012**, *4*, 5055–5068. https://doi.org/10.1021/am3015197.

[52] J. Schaffert, M. C. Cottin, A. Sonntag, C. A. Bobisch, R. Möller, J. P. Gauyacq, N. Lorente, *Phys. Rev. B* **2013**, *88*, 075410. https://doi.org/10.1103/PhysRevB.88.075410.

[53] C. Dobler, C. Tönshoff, H. F. Bettinger, T. Chassé, M. B. Casu, *J. Phys. Chem. C* **2017**, *121*, 13660–13665. https://doi.org/10.1021/acs.jpcc.7b02077.

[54] Z. Yang, M. Corso, R. Robles, C. Lotze, R. Fitzner, E. Mena-Osteritz, P. Bäuerle, K. J. Franke, J. I. Pascual, *ACS Nano* **2014**, *8*, 10715–10722. https://doi.org/10.1021/nn504431e.

[55] J. Meyer, A. Nickel, R. Ohmann, Lokamani, C. T., D. A. Ryndyk, Y. Garmshausen, S. Hecht, F. Moresco, G. Cuniberti, *Chem. Commun.* **2015**, *51*, 12621–12624. https://doi.org/10.1039/C5CC02723C.

[56] Q. Wang, X. Liu, T. Lu, M. Fu, M. Zhang, T. Wang, L. Yu, L. Wang, Z. Wang, *J. Chem. Phys.* **2024**, *161*.

[57] B. de la Torre, M. Švec, P. Hapala, J. Redondo, O. Krejčí, R. Lo, D. Manna, A. Sarmah, D. Nachtigallová, J. Tuček, P. Błoński, M. Otyepka, R. Zbořil, P. Hobza, P. Jelínek, *Nat. Commun.* **2018**, *9*, 2831. https://doi.org/10.1038/s41467-018-05163-y.

[58] P. Chen, D. Fan, A. Selloni, E. A. Carter, C. B. Arnold, Y. Zhang, A. S. Gross, J. R. Chelikowsky, N. Yao, *Nat. Commun.* **2023**, *14*, 1460. https://doi.org/10.1038/s41467-023-37023-9.

[59] L. Colazzo, C. Urdaniz, Y. Jung, L. Fang, S.-h. Phark, C. Wolf, W.-D. Schneider, A. Heinrich, W.-J. Jang, *Nano Lett.* **2025**, *25*, 1883–1889. https://doi.org/10.1021/acs.nanolett.4c05391.

[60] E. Minamitani, N. Tsukahara, D. Matsunaka, Y. Kim, N. Takagi, M. Kawai, *Phys. Rev. Lett.* **2012**, *109*, 086602. https://doi.org/10.1103/PhysRevLett.109.086602.

[61] L. Gao, W. Ji, Y. B. Hu, Z. H. Cheng, Z. T. Deng, Q. Liu, N. Jiang, X. Lin, W. Guo, S. X. Du, W. A. Hofer, X. C. Xie, H. J. Gao, *Phys. Rev. Lett.* **2007**, *99*, 106402. https://doi.org/10.1103/PhysRevLett.99.106402.

[62] J. Repp, G. Meyer, S. M. Stojković, A. Gourdon, C. Joachim, *Phys. Rev. Lett.* **2005**, *94*, 026803. https://doi.org/10.1103/PhysRevLett.94.026803.

[63] D.-L. Bao, Y.-Y. Zhang, S. Du, S. T. Pantelides, H.-J. Gao, *J. Phys. Chem. C* **2018**, *122*, 6678–6683. https://doi.org/10.1021/acs.jpcc.8b00086.

Manuscript received: October 07, 2025
Revised manuscript received: November 05, 2025
Manuscript accepted: November 07, 2025
Version of record online: ■■, ■■