This article can be cited before page numbers have been issued, to do this please use: A. Sarmah and P. Hobza, Mater. Adv., 2020, DOI: 10.1039/D0MA00461H.

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Directly linked metalloporphyrins: A quest for the bio-inspired materials

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Abstract: The directly-linked iron-diporphyrin complexes are appealing candidates and a fundamental precursor for an extended metalloporphyrin array that could potentially mimic the biological design of an energy harvesting material. This impulse us to appraise the layout for the modular fusion of two iron-porphyrin units. Herein, DFT based calculations suggested that the electronic environment of diporphyrin systems could be tuned according to the topological attachment between the porphyrin units. Subsequently, a gradual increase in the electronic interaction between the constituent porphyrin units triggers a decrease in the HOMO–LUMO gap. This is essential to achieve higher electric conductivity. The spin-polarized electronic transmission is another interesting aspect of these iron-diporphyrin systems and promising for spintronic applications. The successive theoretical interpretation of the existence of two dimensional (2D) metalloporphyrin arrays could be the route to design a graphene analog of the covalent metal-organic framework.

Keywords: Metalloporphyrin, molecular electronics, DFT, photophysics, spintronics
Introduction:

The overwhelming success in the field of nanoscience inspired cumulative trials to mimic the natural photosynthetic system at molecular levels. This new concept developed the foundation for molecular photonic and electronic devices and incited the quest towards molecular electronics.\cite{1-5} There is a wide range of known molecular pigments that are strong contenders for building block elements in molecular devices. Indeed, the versatile optical (absorption and emission), redox, and photochemical behavior of porphyrin and their derivatives manifest great potential as the component of nanostructures.\cite{6-8} The global scientific community working hard to execute sensible laboratory protocols for the photosynthetic light-harvesting antenna complexes along with their possible applications in molecular conductive wires and optoelectronic devices.\cite{9} An efficient low bandgap material is the fundamental requirement of nanoelectronics. Consequently, the porphyrin macrocycles are ideal candidates due to the polarisability, optical oscillator strength, and extensive coordination chemistry of the complexes. There are plenty of scopes to develop a better understanding of the relationship between the structure of porphyrinoids and their spectroscopic and photophysical properties.\cite{10}
The unparalleled electronic behavior along with their optical linear and non-linear properties, the π-extended porphyrinoid molecules came to prominence and open up new horizons for technology and medical applications.11-13 In terms of sophisticated technological applications, the π-extended porphyrins are also potential precursors for the fabrication of electron- and energy-transfer devices. Certain important measures need to be tuned for the design and development of such functional porphyrin-based dyes are the nature of the bridges between aromatic components, distance and relative orientation between each chromophore, structural conformation, and the extent of steric interactions.14 It is important to note that, in comparison to the native porphyrins, the π-extended porphyrins display substantial changes in their optical and electrochemical properties. The implications of the covalent linker between essentially coplanar chromophores improve direct conjugation that induces split Soret and intensively red-shifted Q bands.15

The operational synthetic gateway to sculpt the multiporphyrin arrays have been realized with different types of shorter linkers that are suitable for preparing linear or extended architectures either via a meso or β position attachment.16 The fused porphyrin arrays show upbeat technological advantages such as the rigid and co-planar structures and low HOMO–LUMO gaps. In principle, several different approaches have been adopted to extend a porphyrin chromophore without changing the actual number of pyrrole units and methine bridges. The outcome of a practical implementation of this idea is tetrabenzoporphyrin.17-19 The increment in every single benzene unit included in the macrocycle results in a bathochromic shift of about 30 nm. Subsequently, Lash et al. rendered the synthetic strategy for the extension of the conjugated aromatic unit in the porphyrin array.20 Along these same lines, an important break-through was the preparation of a cross-shaped dye comprising five conjugated porphyrin units reported by Vicente and co-workers.21 In another interesting study, Crossley et al. reported the laboratory synthesis of porphyrin arrays containing one or more pyrazine units.22 Thompson and co-workers based on their prior experiences on synthetic protocols of fused porphyrins concluded that one should start from the meso–meso, β–β, β–β diporphyrin, bearing pyrene moieties, as the appropriate substrate for intramolecular oxidation reactions.23

The feasibility of the tetrameric metalloporphyrin sheet has recently been realized,24 indicating the possible existence of a 2D infinite metalloporphyrin sheet in experimental conditions.
For the first-time, Abel et al. reported the fabrication of a novel two-dimensional (2D) Fe embedded phthalocyanine (poly-FePc) organometallic porous sheet. These newly categorized 2D material exhibit promising conduction and magnetic properties, however, restricted to variable grain boundary conditions. In these 2D systems, the TM (transition metal) atoms are uniformly and separately distributed without clustering and display well-defined geometry and magnetic properties. Subsequently, different TM-Pc monolayers find sophisticated applications in spintronics and gas capture. Indeed, the unique and regular structural orientation of the TM atoms in these TM-Pc monolayers makes these 2D architectures an appealing candidate for single-atom-catalysts. In this direction, the DFT based theoretical modeling predicted the application of not-yet-synthesized Co-Pc and Cr-Pc monolayers can be good catalysts for CO oxidation. However, to date, the electronic properties of the basic building blocks of the 2D metalloporphyrin sheet i.e., the porphyrin-dimers units have been addressed scarcely.

In this study, we have extended a systematic investigation to develop a better understanding of the electronic behavior of fused metalloporphyrin moiety based on density functional theory (DFT). Taking the analogy from previous reports, there could be significant modulation in the electronic properties of the hybrid system depending on the fusion mode between porphyrin units. Subsequently, we have also traced the relative changes in the electronic properties of the systems during the transformation from one-dimensional to two-dimensional arrays i.e., sheet-like structure. The manuscript is organized in the following way. In section 2, we have addressed the computational methodologies. The results and discussions, section 3 (a) consist of an analysis of the DFT results on fused porphyrins at the molecular level along with their photophysical behaviors. The essence of electronic transport through the porphyrin dimers in different fusion modes are assayed in section 3(b). A comprehensive theoretical pursuit of the electronic behavior of the 2D arrays is featured in section 3(c). Finally, we have summarized the key findings of our theoretical simulation along with some futuristic applications of the model systems in the concluding remarks, section 4.

2. Theoretical Methods

The quantum mechanical (QM) calculations at the molecular level are undertaken using Gaussian09 software package. All structures were optimized with Becke’s three-parameter
hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)\(^{36,37}\) without symmetry restriction, employing the correlation-consistent polarized, cc-pVTZ basis set\(^{38}\) for all atoms. Additional single-point calculations are performed at CAM-B3LYP39/cc-pVTZ level to account the long-range energy correction in optimized structures. This specific DFT functional effectively coalesces the hybrid qualities of B3LYP and the long-range correction showcased by Tawada et al. Excitation energy calculations were carried out using TDDFT,\(^{40-42}\) as implemented in the Gaussian09 programs. TDDFT calculations, carried out at the CAM-B3LYP structures, were done utilizing the same basis sets like those used in the ground-state DFT calculations. The Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM)\(^{43}\) is the default SCRF method to simulate an H\(_2\)O solvent environment. The dielectric constant was set as 78.54 for the H\(_2\)O solvent. All data were obtained under this method unless mentioned otherwise. Multiwfn\(^{44}\) software is employed for the analysis and visualization of various electronic properties of the ground and excited states.

The periodic calculations are executed using spin-polarized density functional theory (DFT) under the generalized gradient approximation (GGA)\(^{45}\) in the form envisaged by Perdew, Burke, and Ernzerhof (PBE) as deployed in the Vienna \textit{ab initio} simulation package (VASP).\(^{46}\) The projected augmented wave (PAW) method\(^{47,48}\) with a plane-wave basis set was used. Subsequently, the spin-polarized calculations are performed under the Vosko-Wilk-Nusair (VWN) modification\(^{49}\) scheme to interpolate the correlation energy. We enforced periodic boundary conditions and a vacuum space of 15 Å along the z-direction in order to avoid interactions between two FeP (iron-porphyrin) images in nearest-neighbor unit cells. All of the structures were relaxed using the conjugate gradient method without any symmetric constraints. To investigate the magnetic coupling between the TM atoms, we have considered a 2x2 surface unit cell. A 3×3×1 Monkhorst-Pack\(^{50}\) k-point grid centered on the Γ point are used for the calculations. The energy cutoff and convergence criteria for energy and force are set to be 400 eV, 1×10\(^{-4}\) eV, and 0.01 eV/Å, respectively.

3. Results and discussion:
(a) i. Electronic structure calculation:

In an excellent review article Tanaka et al. exclusively discussed the synthetic strategies for different directly linked porphyrin arrays. According to the study, the linked porphyrins are broadly categorized into three types, namely, (a) singly-linked porphyrin oligomers, (b) fused porphyrin oligomers, and (c) triply-linked porphyrin oligomers. These classifications are primarily based on the different modes of chemical attachment between the porphyrin units. In our present study, we have chosen four types of porphyrin oligomers with different bonding patterns. Further, the selected Iron-porphyrin oligomers have well defined synthetic protocols and the promising high-end application prospects are thoroughly explored.

Fig. 1: The optimized structures of the systems studied in the present report. According to the standard notations (based on the point of attachments) system 1 is meso-to-meso linked, system 2 is β, meso, β fused and system 3 and 4 are α-β fused oligomers. The geometry optimization is done at B3LYP/cc-pVTZ level of theory. The yellow, blue, gray and white balls represent the Fe, N, C and H atoms, respectively.
Here, system 1 consists of a porphyrin dimer linked through 1,3-butadiyne bridge. Similarly, triply and doubly linked attachment features are explored with system 2 and system 4. Again, a fully conjugated porphyrin dimer is attributed to system 3. The aromatic character of porphyrin containing 26 delocalized $\pi$ electrons is well established. The 1,3-butadiyne bridge between the metallloporphyrin units forms the planar Fe-PP dimeric structure. Perhaps, the planner structural arrangement increases the possibility of both porphyrin and butadiyne moieties contribution to the extended $\pi$-electron conjugation over the entire system. Subsequently, the extended $\pi$-electron conjugation also improves the performance of electrical conduction. A relatively higher consistency between experimental findings and calculated values for the planner porphyrin arrays as compared to that of its non-planner analogs is evident from the recent report, which encourages us to concentrate on the planner systems. Similarly, the higher degree of extended $\pi$-electron conjugation in the other three fused Fe-PP dimer systems also opens up new avenues to tune and manipulate the characteristic electronic properties of the systems by means of structural orientation. The linked M-PP (M= Cr, Mn, Fe, Zn, Cu) dimer is the simplest building-block for the one-dimensional metallloporphyrins nanowires. Embedding 3d TM (transition metal) atom, i.e., Fe into the porphyrin cores can significantly modulate the electronic properties of the system. The Fe centers are in +2 valence states and coordinated to the nitrogen atoms. The combination of strong coordination interactions and relatively large distances between the two Fe centers (due to the rigid covalent bridging) effectively prevent the aggregation of these atoms. As a result, the Fe atoms can be incorporated separately to the individual porphyrin units, which can induce the intrinsic magnetic properties to Fe-PP dimer, making them promising probes in the fabrication of nanodevices for spintronics application.
Fig. 2: The total density of states (TDOS) plots (a)-(d) for the system 1-4, respectively. The position of HOMO and LUMOs are indicated with red arrows. The electronic charge densities at the HOMO and LUMO levels are represented with the colored isosurface maps in the figure.
The computed Total density-of-states (TDOS) plots along with the location of occupied and virtual orbitals for the four systems are reported in Fig. 2. The green and red lines indicate the occupied and virtual orbitals. The blue line in the plots represents the TDOS of the system.

As we have observed from Fig. 2, the electronic states of the first three systems have close similarities with one-another except small variation near the HOMO level. However, the fourth molecule exhibits significant changes in the electronic states around the HOMO level. A systematic analysis of the plots provides useful insights into the electronic structure. The significant electronic contribution from the p-type atomic orbitals of carbon and nitrogen atoms to the frontier molecular orbitals (FMOs) of the system is evident from the isosurface plots reported in Figure 2. Subsequently, the corresponding PDOS plots for the model systems are included in the supporting information. The substantial contribution of iron d-orbitals toward the total density of states along with the bonding nature of MOs constituted from its overlap with the carbon p-orbitals near the HOMO region can be distinguished from the plots. It is important to note that the electronic charge densities on the iron centers at the FMO levels are consistent for all the systems. However, there are some observed deviations from this ideal nature of metallic centers at the HOMO of the first and LUMO of the fourth systems. The visual graphics of the corresponding isosurface plots for the frontier molecular orbitals (FMO) (Fig. 3) further confirmed the above observations. Subsequently, we have also performed the calculations with a higher spin-multiplicity of the systems. The existence of unpaired spins on the central metal atom is clearly evident from the spin-density maps reported in the supporting information section.
Fig. 3: The visual graphics of Frontier molecular orbital (FMO) of the systems. The value in the box represents the HOMO-LUMO gap.

The gradual increase in the electronic interaction between the constituent porphyrin units triggers a decrease in the HOMO–LUMO gap. This is essential to achieve higher electric conductivity. Subsequently, a large number of bridging structures that can enhance the inter-porphyrin conjugation have been intensively exploited.\textsuperscript{56-58} The 1,3-butadiyne-bridged porphyrin oligomers, i.e., system 1 showed positive cooperative self-assembly (i.e. all-or-nothing assembly) as well as the moderate increase in planarity and conjugation, consequently reduction in the HOMO–LUMO band gaps. A higher degree of conjugation in the system 2 facilitated greater electron delocalization that minimizes the HOMO-LUMO gap. The preferential $\sigma$-bonding characteristic in the highest occupied MO level of the system 1 and 2 are evident from Fig. 2. However, $\pi$-bonding and $\pi$-antibonding nature of the HOMO and LUMO orbitals, respectively, in system 3 associated with an increase in the HOMO-LUMO energy gap. A seemingly different FMO picture is observed for the system 4. Here, the HOMO and LUMO are primarily located at the metal centers associated with an extremely small electronic bandgap refers to the profound metallic nature of the molecule that correlates well to the DOS plot in Fig. 2.

So-called “fused diporphyrin” is an excellent and straightforward synthetic protocol to connect two porphyrins units directly through multiple covalent bonds. Within a coplanar geometrical arrangement, the systems should be quite favorable for the electronic $\pi$ conjugation. As we have seen, diporphyrin is the fundamental unit of an extended 1D metalloporphyrin array. These 1D structures have compelling electronic and magnetic properties and considered as molecular wire or porphyrin-taps by virtue of their rigid shape and extended electronic conjugations.\textsuperscript{59} It is now well understood that the extraordinary electronic properties of the metalloporphyrin array are the consequence of a modular sequence of the diporphyrin units. So, it is important to develop a better understanding of the chemical nature as well as the electronic structure of the ‘linking-zone’ between two single units.
Fig. 4: The Shaded surface map with the projection of the localized-orbital locator (LOL) maps for the four systems. The bridge or fused region between two porphyrin units is represented in the red box and the corresponding LOL map of that particular region is designated inside the black square. The cut–plane (LOL values from 0.0 to 0.8) is along the y-axis with a distance of 0.0 Å from the xz plane. Localized electrons was shown in yellow-red (LOL > 0.5); The pale green basins (LOL ≈ 0.5) indicates the delocalized electrons; the electron depletion regions are shown by the blue circles (0.0 < LOL < 0.5).

In the preceding sections, we have addressed the findings of different theoretical tools to account a quantitative recognition of the chemical bonding in the diporphyrin systems. It would have been great to obtain some qualitative interpretations of the results in terms of visual graphics. The localized-orbital locator (LOL) is an emergent descriptor of chemical bonding. According to the general convention of LOL, the gradients of localized orbitals are maximized with the increasing extent of overlap in localized orbitals. Additional theoretical details about LOL is included in supporting information. Moreover, LOL has a simpler interpretation in terms of fast and slow electron regions. Qualitatively the high/low LOL values are associated with slow/fast electrons and slow electrons attributed the characteristic of localized electrons, such as in bonds or
lone-pairs. The light red and yellow regains in the 1,3-butadiene bridge represent two weak covalent C-C π-bonds along with the strong σ-bonding character of the C-C single bond. The bright red spot in the map depicted the higher electron localization due to the presence of a C-C single bond. The projection shows spikes around the atomic zone in the 3D surface and distinguishes the blue circles in the 2D map. There are some distinct differences in the nature of chemical bonding for the fused diporphyrin systems. Apparently, the benzofused (system 3) and triple-bridge (system 2) complexes exhibit the aromatic ring current due to the fast π-electron cloud at the center of the six-member ring (the blue region). However, the α-β bridge complex (system 4) does not have this aromatic character, although it has some effective π-conjugations at the four-membered ring. Again, the benzofused and triple-bridge systems showing similar bonding characteristics, but a critical analysis of the bonding pattern on the basis of LOL map at the fused position reveals certain differences. The regular distribution of blue and red zones for the triple-bridge system is the indication of a fully conjugated behavior of the π-electrons and the regular valley shaped 3D projection also supports this observation. On the other hand, the benzo-fused system has a lower degree of electron delocalization as evident from the sharp spikes in the 3D projection along with the non-uniform distribution of blue and red zones in the 2D color map. The anti-aromatic characteristic of the meso-meso bridge system is also realized from the LOL map.

ii. Excited state dynamics: A TDDFT analysis

It is important to understand the photophysical behavior to account the suitable application prospects of a system. The DFT based simulated UV-VIS absorption spectra of the four complexes in water solvent along with the relevant parameters are executed in graphical form and included in Fig. 5. The details of the different electronic transitions corresponding to each of the peaks that appeared in the absorption spectra are reported in Table 1.
Fig. 5: Simulated absorption spectra of the complexes in water solvents obtained at CAM-B3LYP/cc-pVTZ level. The charge density difference (CDD) isosurface plot represents the difference in electronic charges associated with the preferred electronic transition (most intense peak) in the spectrum. Here, the electron accumulation and depletion zones are evident from the red and green regions in the plot. The molecular orbitals associated with the particular transitions are distinguished with the black arrow in the figure.

Table 1: The critical details of the electronic transitions appeared in the absorption spectrum.
It is observed that in the 1,3-butadiene linked diporphyrine complex (system 1) the low-energy Q-band is a sharp peak as compared to that of the other three systems, where the Q-band appeared to be a broad-peak. The Q-band at \( \lambda_{\text{max}} = 618 \text{ nm} \) for system 1 is mainly the result of a HOMO\( \rightarrow \)LUMO type of electronic transition with a significantly high oscillator strength.60 Similarly, the Q-bands for system 2 and 4 are largely red-shifted (\( \lambda_{\text{max}} = 806 \) and \( 1137 \text{ nm} \), respectively) due to the increased in delocalized \( \pi \)-electrons and the enlargement of the conjugate

| System   | Peak Maxima (nm) | Oscillator strength | Major Orbital Contributions              |
|----------|------------------|---------------------|------------------------------------------|
| System 1 | 618 (\( S_0 \rightarrow S_7 \)) | 1.41                | HOMO\( \rightarrow \)LUMO (94%)          |
|          | 449 (\( S_0 \rightarrow S_{30} \)) | 1.06                | HOMO-1\( \rightarrow \)LUMO+4 (27%)      |
| System 2 | 806 (\( S_0 \rightarrow S_8 \)) | 0.208               | HOMO-1\( \rightarrow \)LUMO+1 (83%)      |
|          | 523 (\( S_0 \rightarrow S_{22} \)) | 1.43                | HOMO\( \rightarrow \)LUMO (76%)         |
| System 3 | 548 (\( S_0 \rightarrow S_{12} \)) | 0.570               | HOMO\( \rightarrow \)LUMO+1 (83%)       |
|          | 445 (\( S_0 \rightarrow S_{31} \)) | 1.1927              | HOMO-1\( \rightarrow \)LUMO (81%)       |
| System 4 | 1137 (\( S_0 \rightarrow S_{17} \)) | 0.3081              | HOMO\( \rightarrow \)LUMO (93%)         |
|          | 560 (\( S_0 \rightarrow S_{40} \)) | 1.8699              | HOMO-5\( \rightarrow \)LUMO+2 (60%)     |
surface. However, in the benzo-fused system 3, the Q-band is blue-shifted by 70 nm relative to that of the system 1 is the consequence of a strong interporphyrin interaction mediated by the benzenoid unit.\textsuperscript{61,62} The substantial Q-band peak broadening in the fused porphyrin complexes are induced by the relative increase in the electronic interaction between the porphyrin units. The characteristic Soret-band of the porphyrin is observed at $\lambda_{\text{max}} = 449$ and 445 nm for the system 1 and 3, respectively, associated with the high oscillator strength. However, this particular band seems to be exceedingly red-shifted at $\lambda_{\text{max}} = 523$ and 560 nm, for system 2 and 4, respectively. The red-shifted absorption bands associated with fused structures suggest the presence of unusually large electronic interaction between the $\pi$ orbitals on the two macrocycles. The unobtrusive and efficient intramolecular charge transfer (CT), including CT from metal to ligand, the ligand to metal, or intramolecular CT within ligands is evident from the electron density difference map. It is affirmative to observe a small amount of $\pi-\pi^*$ of electron transition, which is the main reason for the organic molecules with large nonlinear optical (NLO) response.

\textbf{iii. AFM and IETS simulations:}

The development of very sophisticated analytical tools like High-resolution atomic force microscopy (HR-AFM) and inelastic tunnelling microscopy (IETS) provide access to distinctly imaged chemical structures within conjugated molecules. Recently, different techniques are evolved to simulate these analytical images based on the information generated from quantum mechanical calculations.\textsuperscript{63-64} We have simulated the AFM and IETS images with CO probes based on classical forcefields formalism proposed by Hapala et al.\textsuperscript{63} According to this model, probe-particle, which represents a CO molecule, is connected to a tip with spring and is used to determine the interaction between tip and sample in AFM measurements. The simulation parameters will be obtained from a specific molecular adsorption geometry of the model system is defined by DFT beforehand. The simulated images are presented in Fig. 6.
Fig. 6: Simulated constant-height AFM and IETS-STM images for different tip-sample distances \( z = 10.0 \) and 9.6 Å. (a) Red dots indicate the relaxed xy position of the probe particle, (b) distance at which probe experiencing the modulations in the local electrostatic field around the molecule due to the presence of tip apex (c)AFM and (d) IETS-STM channels are shown.

Initially, the molecules are deposited on a Ag(111) surface and total energy DFT calculations are performed with the VASP package to obtain the relaxed geometry of the adsorbed molecule. The adsorbed molecule is found to located around 2.75 Å above the metal surface and it seems to be a remain planner. More details about the DFT calculations are included in the supporting information section. To the best of author’s knowledge, one-to-one correlation between simulated images and experimental data for all the model system included in our study is non-viable. However, we explored various experimental reports with similar porphyrin motifs to account the relevance of our theoretical modeling.

In the reported literature, the 8-hydroxyquinoline tetramer is extensively investigated from both the experimental and theoretical prospects. For this particular system, the high-resolution AFM and STM images based on the experiment as well as DFT calculation is well
documented.\textsuperscript{65,66} The bond contrast in the AFM images has been qualitatively compared to the bond order, where the higher local electron density leads to stronger Pauli repulsion exerted on the tip. Subsequently, it is conclusive to reach out qualitative interpretations to the nature of the existing bonding pattern in the system. It is evident from the Zhang \textit{et al.} study\textsuperscript{66} that the electron localization function (ELF) is directly related to the contrast of a chemical bond appeared in the AFM image. The computed ELF

![ELF maps of dimers](image)

Fig. 7: Electron localization function (ELF) maps of dimer. The DFT calculations are performed at CAM-B3LYP/cc-pvTZ level. The ELF analysis and visualization is generated with Multiwfn package.

maps of the four systems are depicted in Fig. 7. A significantly localized electron density donation from N to Fe in the ELF of dimers is evident from the graphics, whereas the electrons between the \(\beta-\beta\) and \textit{meso-meso} position bonding are rather delocalized. These attributed the bonding features in the central regions of the dimer is dative and the fused or linked positions are covalent in nature. On the basis of ELF, it can be argued that the Fe-N bond is significantly polarized, and the shared electrons are preferably localized near the N atom, thus, the AFM contrast is negligible at the metal center.
Inelastic Electron Tunneling Spectroscopy (IETS) has re-emerged as an efficient analytical tool in the understanding of nanoscale and molecular junctions. Subsequently, the mapping of the intensity of the IETS feature can contribute to the understanding of the spatial distribution of functional groups. According to our theoretical model, a CO molecule is attached to the tip, and the bonding between two atoms in the porphyrin dimer could be sensed by a particular vibrational mode of the tip CO. Once we performed a gradual scanning of the adsorbed molecule with the CO-terminated tip, there should be a significant modulation in the energy and intensity of the hindered translational vibration of CO which can be traced by inelastic electron tunneling spectroscopy (IETS) with the STM. A systematic account on the relative variation in low-energy CO vibration can manipulate the potential energy landscape of the molecule and its surroundings. The primary advantage of the IETS-STM technique is the real-space spectroscopy and imaging of the probe. The AFM technique basically detects the local density of states (LDOS), whereas, IETS based on STM has proven to be a versatile technique for the real-space imaging of molecular structure and chemical bonding of single molecules on surfaces. Comparison between experiments and simulations on IETS spectral features offers detailed information about chemical conformation, electron–vibration coupling, etc.

The comprehensive discussions on the two sophisticated analytical techniques in terms of computer simulation provide useful insights into the chemical structures of the porphyrin dimers.

(b) Electronic transport behavior of the porphyrine dimers:

In the recent years, density-functional theory (DFT) and nonequilibrium Green’s function (NEGF) formalism provide an excellent interface for the theoretical modeling of molecular transport properties in connection to the accomplishments of single-molecule nanodevices. It is encouraging to note that the NEGF+DFT formalism, at the GGA level of theory, showing promising results for transport in the strongly coupled regime and through off-resonant transport levels.
Fig. 8: The relative variations in the zero biased electronic transmission computed using the DFT-NEGF approach for different porphyrin dimers connected through two semi-infinite gold electrodes. Here, (a) a general pictorial representation of the device and (b)-(e) the corresponding zero-biased transmission plots for system 1-4, respectively. The spin-polarized transmission for the two spin-channels ($\alpha$ and $\beta$) is represented by the red and black colored lines in the plot. The important changes around the Fermi level are represented by the shaded region in the plots.

The transport calculations are performed based on NEGF+DFT formalism as implemented in the ADF-BAND periodic DFT code.$^{72,73}$ Comprehensive details about the calculations are available in the supporting information. This is indeed an efficient tool to investigate the electronic transport behavior of a novel single-molecular junction with metallic electrodes. In our present
study, we have modeled a gold–(porphyrin dimer)–gold (Au–PorD–Au) junction. The contacts are
designed with Au (111) faces consisting of 3 × 3 atoms, represented in Figure 8. The calculations
are performed at PBE level with an SZ basis on the Au contacts and a TZP basis on the molecule,
except where stated otherwise. More theoretical details are available in the supporting information.

The foremost observation from the plots reported in Fig. 8 is that there are substantial
variations in the electronic transmission with the changes in the position as well as the orientation
of attachment between the two porphyrin units. Another important observation is the manifestation
of spin-polarized electronic transmission, i.e., electronic transmission through the two spin-
channels is different. The extensive research works of Harmann et. al. on the spin-resolved
transport through organometallic complexes reveal important implications of electron transport in
nanoscale devices.\textsuperscript{74} In a molecular bridge, the decrease in conductance due to the appearance of
destructive quantum interference (DQI) favors the ferromagnetic coupling between two spin
centers while the increased conductance through the bridge can favor antiferromagnetic coupling.\textsuperscript{75}
It was observed that in the case of a $\pi$-conjugated system the destructive interference could block
the electronic transmission, contrary to that of a partial cancellation for the saturated system.\textsuperscript{76}
Similarly, the local transmission through the complexes and their molecular orbitals show
substantial dependencies on the various components of the molecular structure that mediate
electron transport.\textsuperscript{77} It is worth mentioning here that the electronic behavior of a system around
the Fermi level determines the versatility of that molecule for nanoscale device fabrication. The
present study accounts for a significant modulation of electronic transmission at the two spin states
around the Fermi level for all the systems. From Figure 8, it can be assumed that the origin of spin-
dependent electronic transport in the system is due to the spin asymmetry of the electronic
structure caused by the presence of paramagnetic metal centers in each porphyrin unit. The
findings of spin-polarized calculations in the next segment suggested the presence of spin
asymmetry in the model systems. It suggested that the spin-filtering capacity is inherent in the
hybrid systems, not in the interface. All systems show the metallic nature of transmission
associated with a sharp kink around the Fermi level. The first three systems exhibit an intense peak
for the down-spin electrons close to the Fermi zone, whereas, the fourth system defines the
possibility of a sharp increase in the transmission through the up-spin channel at the Fermi level.
The shape and position of these transmission peaks signify the low-bias electronic conductance for
these junctions. The analysis of NEGF-DFT based findings in terms of transmission plots uncovers certain important interpretations. Another striking feature is the quantum interference effects in the electronic transport of these systems.\textsuperscript{78-81} It appears that the electronic transmission through the spin-down channel exhibits significant quantum interference around the Fermi level. The transmission spectrums exhibit a smooth regression around the Fermi energy for spin-up (red line in Figure 8), while for spin-down (black line in Figure 8), the transmission exhibits a sharp dip near the Fermi energy suggesting a destructive pattern of quantum interference.\textsuperscript{82} The interference features are dramatic and in many cases dominated the characteristic transmission spectrum around the Fermi level. Here, the quantum interference patterns are different according to the topological changes in the model systems. It is worth mentioning here that the interference features arise from antiresonances (sharp dips in the transmission). The interference pattern, an antiresonance, exclusively associated with the down-spin electronic current and affects the system transmission close to the Fermi energy. Antiresonances are nothing but the opposite of a transmission resonance and consequently the transmission coefficient going to zero. One condition for the appearance of antiresonances in the transmission is the presence of nonspanning nodes in the wave function. Subsequently, these analyses also prevailed some qualitative similarities in the transmission behavior of the four systems at the Fermi level, such as the spin-polarized electronic transmission, distinguish broad peak for the up-spin electrons, sharp kink for the down-spin electron, etc. This information develops a conceptual understanding of the effect of structural orientation on the electronic transport phenomena. Further, we can argue that the electronic transmission through the junction can be tuned by varying the position as well as the orientation of attachment between the two porphyrin units, which is crucial for the strategic development in the nanoscale device fabrication based on linked or fused porphyrin dimers.

\textbf{(c) The electronic structure of 2D sheets:}

In contemporary research, substantial efforts have been made to successfully synthesized a series of two-dimensional (2D) transition metalorganic materials (MOMs) via metal-directed surface reactions.\textsuperscript{83,84} As a consequence of extended systems, these 2D MOMs possess appealing features like better stability and conductivity than their molecule counterparts. The experimental realization of the tetrameric metalloporphyrin sheet has been achieved recently,\textsuperscript{85} indicating that
the 2D infinite metalloporphyrin sheet is experimentally feasible. From the application prospect, these materials are primarily investigated for catalytic purposes like oxygen reduction reaction (ORR) as a substitute for Pt containing complexes. Further, the success in the synthesis of porphyrin oligomers triggers future attempts of obtaining porphyrin-based molecular nanowires (PNWs) for their extraordinary electro-optical and nonlinear optical properties resulting from the π-conjugation systems.

Fig. 9: The relaxed unit cell of the systems considered for the periodic calculation. The 2D orientation of the structures is designed based on the different points of attachment for porphyrin units. (b) The corresponding spin-polarized band structures. The red and black lines represent the two different spin-channels and green dotted lines showing the Fermi level.

In the light of realistic application, the molecular design should be extended further to periodic models. The previous reports encourage us to explore the possibilities of viability and the
electronic structure of the 2D sheet-like orientation of fused porphyrin-based materials. Taking an analogy from the earlier results, intuitively we have designed three novel 2D structures for the porphyrin oligomers. The single unit cell of these three systems is reported in Fig. 9 (a). Here, we have considered the unit cell to be composed of four porphyrin molecules attached in a different fashion, which should be the minimal unit to account for the relative electronic modulations. The significant differences in the electronic environment of the systems are evident from their corresponding spin-polarized band structures reported in Fig. 9(b). As we have seen from the band diagrams, although four metal centers are present in the unit cell, the systems are slightly magnetic. This is due to the strong anti-ferromagnetic interaction between the metal centers. The electronic behavior of the three systems is entirely different from one another. A critical analysis of the band structure reveals that system 1 is semi-conducting in nature with a specific band-gap. Similarly, system 2 seemingly half-metallic with one spin-channel is in the metallic region and another one is insulating. These characteristic electronic properties of TM-Pc monolayers affirm the promising aspects of the material for spintronics. Eventually, system 3 shows typical metallic behavior with the accumulation of flat bands around the Fermi level. To obtain some better insights into the electronic levels and trace the contribution of Fe metal centers, we have mapped the total and partial density of states (TDOS and PDOS) for the systems, and plots are reported in Figure 10.

Fig. 10: The total and partial density of states (TODS and PDOS) plots for systems 1, 2 and 3 from left to right, respectively. Here, the black and red lines represent the TDOS for up and down spin electrons. Similarly, the green line indicates the contributions from iron d-electrons, while the filled curves with purple color designated the p-orbital contributions of nitrogen atoms. The Fermi level is set at zero.
The computed TDOS showing almost symmetric distributions with some distinct deviations around the Fermi level. This correlates well with the lower magnetic moment values of the system. The contribution of electronic states of the metal centers toward the TDOS around the Fermi level (the yellow and purple shades in the plots) leads to the existence of spin-polarity in the systems. Besides, the introduction of metal centers induced disturbance to the spin states of p orbitals and the plot became unsymmetrical. In the case of system 1, the electrons from iron and d and nitrogen p orbitals occupy the spin-down states just below the Fermi level and no occupied state can be found across the Fermi level which makes system 1 a semiconductor. Subsequently, system 2 shows half-metallic nature as the p-electrons from nitrogen in the up-spin channel spread across the Fermi level and the iron d-electrons in the down-spin channel located just below the Fermi level creating a gap for the down-spin channel. Whereas, system 3 exhibits metallic nature with the significant contribution from iron d-electrons in the up-spin channel in the occupied states, and the down-spin channel is mostly occupied by the p-electrons from nitrogen.
Fig. 11: Comparison between experimental and simulated STM images of the three systems generated based on the Tersoff–Hamann method\textsuperscript{92} within the DFT framework. (a) the relaxed structure of the three different systems, (b) relevant experimental STM images reported in previous studies and (c) simulated STM maps, the purple box represents the molecular zone that appeared in the graphics.

The most efficient approach to obtaining a direct correlation between theoretical atomistic models to experimental systems is Scanning Tunneling Microscopy (STM). With the rapid progress in modern ab initio methods now it is possible to handle ever-larger structures. Subsequently, the constant improvement of experimental STM leading to higher resolution images (i.e. smaller structures). Due to its simplicity, the Tersoff–Hamann (TS) method has been incorporated into most existing DFT codes. Although the TH method cannot explain the origin of atomic resolution in STM measurements, it often provides a reasonably good qualitative prediction of the experimental observations.\textsuperscript{93} On the other hand, there are certain complications with the implementation of the NEGF approach for the theoretical analysis of STM.\textsuperscript{94} The main obstacle is positioning the STM tip at an arbitrary offset with respect to the surface plane. This together with the fact that tip and sample materials are highly inhomogeneous, makes it highly problematic to represent the combined substrate-tip interface within the same supercell.\textsuperscript{95} So, now we are in a position to make some sensible comparison between experimental and calculated STM images based on Tersoff–Hamann (TS) method. The experimental STM map has many advantages, however, it is blind to the atomic species observed in the STM images. This weak point can be covered-up, by comparison to calculated STM images. If calculated and experimentally observed STM images are showing close similarities, one can very reasonably assume that the underlying geometry is the same. To account for the relevance of our simulated STM images to the experimental reality, we have obtained sophisticated experimental results from some of the recent reports.

Zhang and co-workers studied the Sonogashira cross-coupling reactions on an Au(111) surface with three different metal-coordination structures and used scanning tunneling microscopy to resolve the products formed at the successive reaction steps.\textsuperscript{96} The observed STM images of the butadiene bridge Cu-porphyrin oligomers showing reasonable agreement to our simulated map.
Further, the STM images reported by Nakamura et al.\textsuperscript{86} and Grill et al.\textsuperscript{97} in their respective studies manifested excellent correlation with our calculated STM surfaces for similar systems. The comprehensive electronic structure calculations in combination with the extensive analytical simulations strongly suggest the experimental feasibility of linked metalloporphyrin two dimensional (2D) arrays and assumed to be the porphyrin analogs of graphene.

4. Conclusions:

In the present study, we have systematically analyzed the electronic properties of the smallest building block of a metalloporphyrin based covalent metal-organic framework. Subsequently, two iron-porphyrin units are linked together in four different patterns and constitute a homologous series of molecular wire or porphyrin tap. The one-dimensional array encompasses tunable electronic coupling between its ends, and often provides an interface to the electronic conjugation extends over a significant part of the molecule. Our theoretical calculations exquisitely crafted the correlation between the type of linker and the porphyrin linkage topology (\(\beta\) or meso) that govern the inter-porphyrin electronic coupling in these arrays, hence their photophysical properties. Apparently, the present theoretical strategies on diporphyrine linkage can be analogous to the “Rubik’s Cube”. The single metalloporphyrin unit could be considered as the blocks of a particular color and you can fix a different colored block between two adjacent metalloporphyrin units by shuffling the cube. This spontaneously triggers a series of changes in the arrangement of colored patterns within the cube. It is the symbolic representation of the modulations in the electronic properties of the diporphyrin systems due to the different modes of attachment between two metalloporphyrin units. A critical analysis of the electronic modulations reveals that the \(\alpha\)-\(\beta\) fused diporphyrins supposed to exert the strongest electronic interactions and the smallest optical HOMO-LUMO gaps (0.31 eV) among the fused diporphyrins studied so far. Similarly, the triply linked diporphyrins have a highly symmetric structure and are likely to be free from acute structural distortion. On the other hand benzo-fused, diporphyrin system exhibits a modest blue shift in the Q-band relative to that of the other systems is the consequence of a strong interporphyrin interaction mediated through the benzenoid unit. Additionally, the manifestation of spin-polarized electronic transmission is an appealing content of these model systems for future spintronics. Moreover, the higher probability of existence for two dimensional (2D)
metalloporphyrin arrays under experimental condition could be the graphene analog of the covalent metal-organic framework. Therefore, the extension of this simulation strategy for the experimental realization of higher oligomeric and polymeric porphyrin arrays is expected to be a fascinating project for next-generation molecular electronics.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement:

This work was supported by research project RVO 61388963 of the Czech Academy of Sciences. We acknowledge the financial support of the Czech Science Foundation (AS, PH: P208/12/G016 and 19-27454X). This work was supported by the Ministry of Education, Youth and Sports from the Large Infrastructures for Research, Experimental Development and Innovations project “IT4Innovations National Supercomputing Center – LM2015070” as well as from project LO1305 (PH).

Footnote

† Electronic supplementary information (ESI) available.
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Graphical Abstracts

Directly linked metalloporphyrins: A quest for the bio-inspired materials

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- Extended metalloporphyrin array could potentially mimic the biological design of an energy harvesting material.
- The electronic environment of diporphyrin systems could be tuned according to their topological changes.
- The spin-polarized electronic transmission is an interesting aspect of these hybrid systems.
- 2D metalloporphyrin arrays are the graphene analogues of a covalent metal-organic framework.