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Electronic Communication across Porphyrin-Hexabenzocoronene Isomers

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Abstract: Single-molecule electronic components (SMECs) are envisioned as next generation building blocks in quantum circuit systems. However, challenges such as the reproducibility of the electrode attachment to the individual molecules hamper their fundamental investigation. For our purpose, we introduce quasi optoelectronic electrodes (QOEs) that allow for rapid investigations of the properties and suitability of compounds for molecular electronic devices. In particular, we probe hexa-peri-hexabenzocoronene (HBC) as a model system for D_{6h} symmetrical nanographenes, with porphyrins as QOEs attached to the periphery. We prepared selectively bis-porphyrin functionalized HBCs with an ortho-, metaand para-substitution geometry and studied their communication properties, in correlation to the geometrical alignment and size of the system, by electrochemistry and optical spectroscopy. Further insights into structure-property relationships were gained by DFT calculations and X-ray diffraction analysis.

Since the invention of conventional electronic components in the 1950s, the growths in technological advancement, as described by Moore's Law,^[1] goes hand in hand with the subsequent downsizing of the electronic elements. In that respect, the terminus of nano-sized electronics, can be envisioned in the fabrication of electronic circuits based on single-molecule electronic components (SMECs).^[2] Unlike conventional, macroscopic systems, at the transition to the molecular level (<100 nm) quantum mechanical effects, such as the Coulomb blockade^[3] and rectification,^[4] start to dominate the performance of electronic devices. Subsequently, it is crucial to gain full control over the shape and size and therefore about the characteristics of molecules used for SMECs. Nanographenes, which are small fragments of the periodic 2D-material graphene, and related structures received considerable attention amongst the physical sciences in recent years.^[5] Due to their unique (opto)electronic properties,[6] intensive investigations towards efficient and

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atomically precise bottom-up syntheses and functionalization,[7] on the one hand, but also towards applications on the other hand, such as in molecular electronic devices,^[8] were conducted. Aside from difficulties in the selective preparation of suitable compounds, another obstacle preventing SMECs to enter the field of commercialization, is based on the poor control over the connection of the molecules to the electrodes.^[9] Break junction experiments, which rely on e.g., strong interactions between gold electrodes and sulfur containing anchor groups, reveal to be quite efficient in binding the molecules. However, they often fail in controlling the specific coordination site at the electrodes, which leads to fluctuations in each device performance.^[2] Recently, a variety of molecules, including e.g., porphyrins,^[9,10] oligothiophenes,[11] and hydrocarbons,[12] were investigated in single-molecule conductance studies in correlation to their length and conformational state.

Herein, our interest is focused on the relative effect of the position of the electrodes within the nanographene and how it relates to the size of the π -system. For that purpose, we decided not to build actual molecular electronic devices, but rather to prepare model compounds that enable predictions about the potential characteristics of a SMEC in dependence of the angular alignment of the electrodes. We use D_{6h} symmetrical hexa-perihexabenzocoronene (HBC), a hexagonal fragment of graphene, which allows for the geometrically precise functionalization in the periphery. We prepared selectively a logical series of bisfunctionalized HBCs, containing an ortho-, meta- and parasubstitution pattern (Figure 1). To overcome the difficulty of the electrode attachment at an HBC-based electronic component, we introduced peripherally attached porphyrins as duasi





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optoelectronic electrodes (QOEs).^[12d] This enables to study the electronic communication between the porphyrins across the nanographene's π -system, probed by optical spectroscopic methods.^[13] Finally, we target to understand if fluctuations in device performances, due to a different electrode alignment, are size-dependent and how they can be utilized in nanographene based integrated circuits.^[14]

A general strategy to the desired *ortho-*, *meta-* and *para*conjugates **7Zn**, **8Zn** and **9Zn**, is depicted in Scheme 1. We followed a post-functionalization approach, relying on Suzukicoupling reactions of appropriately halogenated HBCs with borylated porphyrin **10**. Therefore, *ortho-* and *para-*unsubstituted hexaphenylbenzenes (HPBs) **1** and **3** were prepared via the common Diels-Alder strategy, reacting tetracyclones with tolans. On the other hand, the uncommon *meta-*unsubstituted HPB **2** is not available via standard techniques. Typically, tris-substituted systems with an 1,3,5- substitution pattern, obtained from [2+2+2] cyclotrimerization reactions of unsymmetrical tolans, are used as a *meta-*equivalents.^[15] However, we synthesized *meta-*HPB **2** selectively by the recently developed F*p*NA (functionalization of *para-*nitroaniline) method.^[16] The syntheses of **1**, **2**, **3**, **10** and the respective precursors are described in the supporting information. With unsubstituted HPBs 1, 2 and 3 in hand, we carried out a selective bis-iodination at the respective vacant peripheral positions, utilizing [bis(trifluoroacetoxy)iodo]benzene and I2, yielding the bis-iodo HPBs in good yields.[16,17] The oxidation reactions to the planar bis-iodo-HBCs 4, 5 and 6 were carried out under standard Scholl conditions, using FeCl₃ as an oxidant.^[16] Finally, Suzuki coupling reactions of 4, 5 and 6 with boronic ester porphyrin 10, Pd(PPh₃)₄ and Cs₂CO₃ were conducted, yielding the ortho-, meta- and para- conjugates 7Zn, 8Zn, and 9Zn in moderate yields around 50%. Typical side-products were monocoupled, mono-dehalogenated conjugates. However, attempts changing the labile iodide to the more robust bromide via a postbromination of 1, 2 and 3, which is known for e.g., the preparation of hexa-bromo-HPB,^[18] resulted in unselective over-bromination of the HPBs. Since the yields for isomers 7Zn, 8Zn and 9Zn were virtually equivalent, an influence of steric repulsion on the reaction efficiency can be ruled out.



Scheme 1. Synthesis of *ortho-*, *meta-* and *para-bis-porphyrinato-zinc(II)* HBCs **7Zn**, **8Zn**, and **9Zn**; a) bis(trifluoroacetoxy)iodo]benzene, I₂, CH₂CI₂; b) FeCI₃, CH₃NO₂, CH₂CI₂; c) **10**, Pd(PPh₃)₄, Cs₂CO₃, toluene, DMF; full synthetic details can be extracted from the supporting information; single-crystal X-ray structure of *meta-*HPB **2** is depicted as an ORTEP model with thermal ellipsoids drawn at 50 % probability; hydrogen atoms are omitted for clarity.^[24]

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Alternatively, ortho substituted systems like **7** can be prepared via a Diels-Alder route^[19] (see supporting information) or by a mixed cyclotrimerization approach.^[20]

The electronic interaction between the two porphyrins via the HBC unit was investigated by UV/Vis absorption and steady state emission spectroscopy as depicted in Figure 2 and summarized in Table 1. Depending on the substitution geometry, different spectral features are observed. The most distinct indicator is the shape of the porphyrins Bband (Soret-band), which changes clearly with respect to the angular alignment of the porphyrins to each other.[21] The Bband is, compared to reference porphyrin tetra(3,5-di-tert-

butylphenyl)-porphyrinatozinc(II) (Figure 2, black line in insert), red-shifted and



Figure 2. Absorption and emission spectra of **7Zn**, **8Zn**, and **9Zn**, measured in CH₂Cl₂ at rt; a) absorption spectra; inserts show magnifications of the B-band (left) and Q-bands (right); spectrum of reference compound tetra(3,5-di-*tert*-butylphenyl)-porphyrinato-zinc(II) (black, dashed) is added to the magnification of the B-bands; b), c), d) steady state fluorescence emission spectra of zinc-porphyrin-HBCs **7Zn**, **8Zn** and **9Zn**.

significantly broadened. Ortho-conjugate 7Zn shows an absorption maximum at 424 nm with a small at 435 nm, whereas in the case of meta-porphyrin-HBC 8Zn a rising split in the B-band with one maximum at 425 nm and a shoulder peak at 433 nm emerges. Even stronger, para-conjugate 9Zn shows a distinct split of the B-band with two maxima at 426 nm and 435 nm, respectively. The B-band shows a distinct correlation between substitution geometry and electronic properties. The left maximum of the B-band decreases in intensity and gets red shifted in the order of ortho- to meta- to para-geometry. The intensity of the right maximum, however, shows the opposite trend. Noteworthy, HBCs functionalized with only one porphyrin show no split in the B-band absorption.[13a,g] Therefore, the relative distortions of the B-band can be understood as qualitative measure for the electronic communication ability across nanographene based SMECs. Interestingly, the HOMO-LUMO optical transitions, reflected in the porphyrins Q-bands, remain unaffected by the substitution pattern and appear at 550 and 590 nm for all three isomers. Also, the absorption of the HBC's βband is uninfluenced by the substitution geometry and appears at 357 nm for all three isomers 7Zn, 8Zn, and 9Zn.

Steady state fluorescence spectra (Figure 2b-d) show upon excitation of the HBC's β -band at 357 nm, similar to earlier reported HBC–porphyrin conjugates,^[13a,d-g] an efficient energy transfer from the central HBC core to the porphyrins. Therefore, only fluorescence of the porphyrins' Q-bands at 600 and 648 nm

is visible. Direct excitation of the porphyrins' B-band results in the same fluorescence signals, though at a higher intensity. With respect to substitution geometry, the emission intensity at 648 nm is slightly higher than at 600 nm for the ortho-conjugate 7Zn, whereas for meta- and para-systems 8Zn, 9Zn the opposite is true. Spectroscopic details are listed in Table 1. The same absorption/emission behavior can be observed for the respective free-base conjugates 7FB, 8FB, 9FB (see supporting information Figure S5). Electrochemical information of 7Zn, 8Zn and 9Zn were gained by cyclic and differential pulse voltammetry in CH₂Cl₂ with Fc/Fc⁺ used as a reference and 0.1 M TBAPF₆ as supporting electrolyte. They all contain three reduction and oxidation steps. (Table 1 and Figure S7-S9). The HOMO-LUMO gaps of 7Zn, 8Zn and 9Zn, determined by the difference of the first reduction at -1.5 V and the first oxidation at 0.7 V, are 2.2 eV, which are in good agreement with the optical bandgaps (Table 1). In cyclic voltammetry, the oxidations unveil reversibility, while the reduction steps show quasi-reversible behavior. However, the optoelectronic details are not resolved in the electrochemcial measurements.

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Figure 3. Single crystal X-ray structure of **7FB**;^{124]} a) depicted as ORTEP model with thermal ellipsoids drawn at 50% probability; hydrogen atoms and solvent molecules are omitted for clarity; b) depicted as stick model; aryl moieties omitted for clarity; c) geometry optimized structures of free-base *ortho*, *meta*, *para* bis-porphyrin-HBC conjugates **7FB**, **8FB** and **9FB** and depiction of the highest occupied molecular orbitals (HOMOs) at the DFT B3LYP 6-31G* level of theory; *t*Bu groups were replaced by H-atoms; orbitals are visualized at an *iso*-value = 0.015.

The porphyrins of ortho system 7Zn experience a sterically more stressed situation compared to meta and para conjugates 8Zn and 9Zn. However, lack in communication, due to an orthogonal alignment of the porphyrin and HBC plane, can be excluded. As shown in Figure 3a and b, the single crystal X-ray structure of 7FB clearly demonstrates dihedral angles <90°.[24] In order to shed light on the spectroscopic outcome observed for bis-porphyrin-HBCs, we conducted DFT calculations at the B3LYP 6-31G* level of theory (Figure 3c). We replaced the tBu groups and the central Zn-ion by hydrogens to reduce computational cost. With an increasing core-to-core distance of the porphyrins from 10.7 Å to 18.3 Å and 21.3 Å for the ortho-, meta- and para-conjugates, respectively, through-space communication has only minor impact on the spectral features. However, the situation clarifies upon inspecting the distribution of the molecular orbitals. Although the majority of the highest occupied molecular orbital (HOMO) is located on the porphyrins, part of it is also based on the HBC core. Hereby, the conjugation pathway is found to go always across the middle ring of the HBC core. In the ortho-case, rather than communicating directly through the biphenyl fragment, the communication takes an angular pathway through the HBC's central ring.^[23] Less pronounced, this indirect pathway is also true for the meta-conjugate. On the other hand, para-structures find their most direct communication through the middle of the HBC.

In order to estimate a size-correlated angle-dependency^[22] of nanographenes, we compared spectroscopic data on benzenespaced ortho, meta, para bis-porphyrin conjugates, published by Joo, Osuka, Kim and co-workers.^[21a] We noticed that the left maximum of the B-band undergoes an angle dependent shift (Table S3), as it is true for herein presented conjugates. The right maximum (if existent), however, is always located at ~ 434 nm, no matter if the porphyrins are linked via a benzene or HBC spacer. Therefore, based on the position of the left maximum, we defined angular response parameter from an the ratio $\lambda_{\text{left-max}}(o, m, p) / \lambda_{\text{left-max}}(o)$ and plotted it against the substitution angle. As shown in Figure 4a, a quadratic fit describes well the angle dependency, which is significantly stronger for the small benzene fragment (blue line) than compared to the larger hexabenzocoronene (red line). From the second derivative of the parabolic dependency, the angular response coefficient car is plotted against the diameter of the nanographene (Figure 4b).^[11a] From the linear fit, we estimate a threshold diameter of \approx 14 Å for D_{6h} Thus, symmetric peri-condensed nanographenes. considering the next larger nanographene with armchair periphery (C114), the diameter of 19.8 Å suggests that the substitution geometry will have only a minor influence on the (opto)electronic characteristics.



Figure 4. Angular and size dependent communication correlation: a) quadratic fitting ($y = ax^2 + bx + c$) of the angular response as function of the attachment angle in benzene (blue) and HBC (red) spaced bis-porphyrin conjugates; dotted black line corresponds to electronically isotropic graphene; b) diameter correlation for D_{6n} symmetrical armchair nanographenes; green rim with 14 Å diameter.

Summarized, the successful preparation and characterization of a logical series of ortho-, meta- and para-bis-porphyrin functionalized hexabenzocoronenes was achieved. Depending on the substitution pattern a distortion of the porphyrins' B-band, which reflect the strength of the electronic interaction between the two optical electrodes in the ground state, were observed. Hereby, the porphyrins' interaction via the HBC's π -surface increases from ortho-, to meta-, and para-alignment, respectively. Hence, depending on the geometrical arrangement, specific electric resistances can be addressed. However, extrapolation of the herein found dependency with respective benzene-spaced conjugates suggest that this effect becomes neglectable for nanographenes with diameters >14 Å. In order to verify this hypothesis, we are working on the preparation of larger bisporphyrin substituted nanographenes. While the observed photophysical phenomena require further investigations, the first experimental insights are important steps towards understanding and engineering novel nanographene based electronics. Timeresolved photophysical experiments as well as in-depth timedependent DFT calculations are currently in progress.

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Table 1. Spectroscopic and electrochemical data for 7Zn, 8Zn and 9Zn, recorded at rt in CH_2Cl_2.

	ortho-7Zn	meta- 8Zn	para- 9Zn
Abs: λ _{Soret} / nm (ε / 10 ⁴ M ⁻¹ cm ⁻¹)	423.8 (53.1) 435 (28.3) ^[a]	425.4 (50.0) 433 (40.7) ^[a]	425.8 (45.9) 434.6 (46.5)
Abs: λ _{Q-bands} / nm (ε / 10 ⁴ M ⁻¹ cm ⁻¹)	550 (3.50) 589 (0.92)	551(3.60) 589 (1.00)	551(3.80) 589 (1.10)
FWHM _{Soret} / nm	21.7	23.1	24.9
Fluo: λ _{exc} : β-band λ _{emi} / nm (rel. int.)	600 (0.25) 648 (0.27)	600 (0.28) 647 (0.27)	600 (0.30) 647 (0.29)
Fluo: λ _{exc} : Soret _{max} λ _{emi} / nm (rel. int.)	599 (0.99) 648 (1.00)	600 (1.00) 649 (0.95)	600 (1.00) 650 (0.92)
E _{red1} , E _{red2} , E _{red3} / V	-1.8, -1.7, -1.5	-1.8, -1.7, -1.5	-1.8, -1.7, -1.5
E _{ox1} , E _{ox2} , E _{ox3} / V	0.7, 1.0, 1.3	0.7, 1.0, 1.3	0.7, 1.0, 1.3
E _g / eV	2.2	2.2	2.2

[a] Shoulder.

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Conflict of interest

The authors declare no conflict of interest.

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[24] CCDC 1892714 (2), 1892716 (7FB) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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COMMUNICATION

Hexabenzocoronene was utilized as a model system for nanographenes and probed spectroscopically by peripherally attached porphyrins as quasi optical electrodes. A selective functionalization of the nanographene in *ortho-*, *meta-*, and *para-*position revealed alternation in communication properties between the porphyrins. These insights help to understand the role of electrode alignments in next generation singlemolecule nanoscale electronics.



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