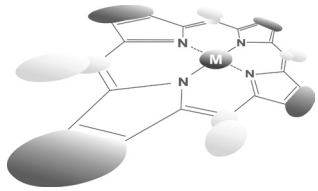
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2018; **22**: 454–460
DOI: 10.1142/S1088424618500451

Published at http://www.worldscinet.com/jpp/



Synthesis of a porphyrin-hexaarylbenzene-hexabenzocoronene triad

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Received 5 March 2018
Accepted 21 March 2018

ABSTRACT: The synthesis of a triad consisting of porphyrin and hexabenzocoronene (HBC) units, which are connected *via* a central hexaarylbenzene (HAB) core, is presented. The *ortho* substitution pattern at the core results in a close proximity of the two chromophores, which influences their properties such as the intensity ratio of UV-vis absorption bands.

KEYWORDS: porphyrin, hexabenzocoronene, hexaarylbenzene.

INTRODUCTION

Porphyrins are, due to their light harvesting properties, widely used as organic building blocks and investigated intensively. Since the first synthesis of *meso* substituted porphyrins by Rothemund in 1935 [1–4], improved synthetic protocols by Adler, Longo and co-workers [5, 6] as well as by Lindsey *et al*. [7, 8] were developed, which allow the production of porphyrins under mild conditions in high yields. Complex multi–porphyrin architectures have been synthesized such as linear *meso*-connected porphyrin strings with up to 24 units [9–14] as well as cyclic porphyrin arrangements [15–21]. Furthermore, porphyrins have also been combined with other chromophores, either indirectly or directly. For example, hexaarylbenzenes (HABs) have been used as an indirect linker between porphyrin and coumarin units [22]. Previously, we have worked with similar systems, in which porphyrins were connected to HABs [23–25], but in a final reaction they were transformed to the respective hexabenzocoronenes (HBCs), therefore forming a chromophore. The reaction towards porphyrin-HBCs has a significant impact on the properties of the porphyrins. Due to the large π–system of the HBC, strong electronic communication with the porphyrin as well as strong intermolecular interactions in the solid state and gas phase were observed [23–25]. So far, porphyrins attached either to HABs or to HBCs separately are known. However, a combination of porphyrin, HAB and HBC within one molecule has not been reported yet and therefore, we decided to synthesize a porphyrin-HAB-HBC triad, in which the HAB serves as a bridge between the porphyrin and HBC.

RESULTS AND DISCUSSION

For the synthesis of a porphyrin-HAB-HBC triad **10**, the two building blocks **4** and **8** were needed. Porphyrin **4** was prepared by a known statistical porphyrin synthesis but using microwave radiation as a heating source (Scheme 1) [26, 27]. The AB_3 TMS-ethynylporphyrin was obtained in 10% yield and subsequently metallated by stirring the free-base porphyrin with an excess of $Zn(OAc)_2$ in a CH_2Cl_2/MeOH solution in quantitative yield. Finally, the TMS protection group was removed by using TBAF as a fluorine source which yielded the ethynylporphyrin **4** in 90% yield.

The second building block, HBC **8**, was synthesized according to modified literature procedures (Scheme 2) [28]. Iodotolan **5** [28] and *tert*-butyl substituted tetracyclone **6** [24] were reacted in a Diels–Alder reaction at 260 °C in the microwave reactor. Iodo-HPB **7** was obtained in 78% yield and converted to the corresponding HBC **8** under oxidative Scholl conditions in 98% yield.

Both building blocks **4** and **8** were reacted in a Sonogashira coupling reaction in which the

◊ SPP full member in good standing

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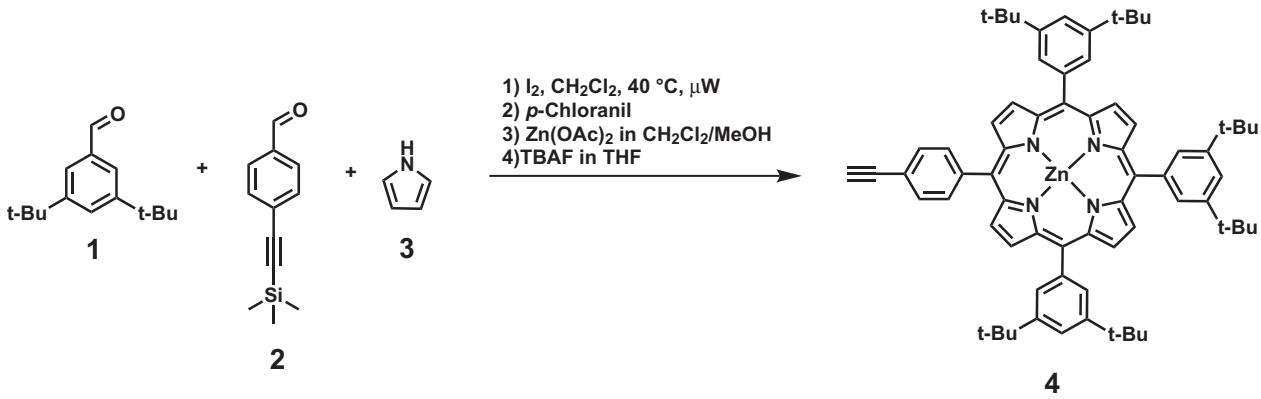
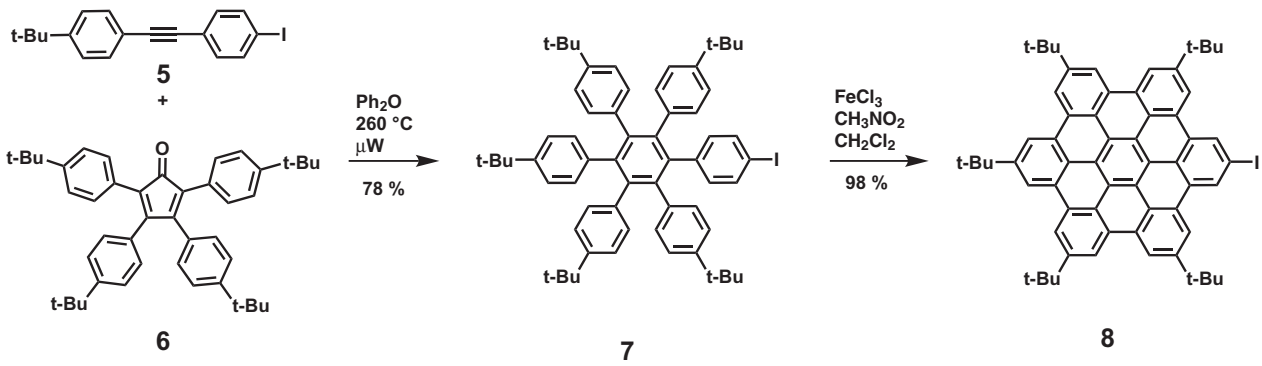
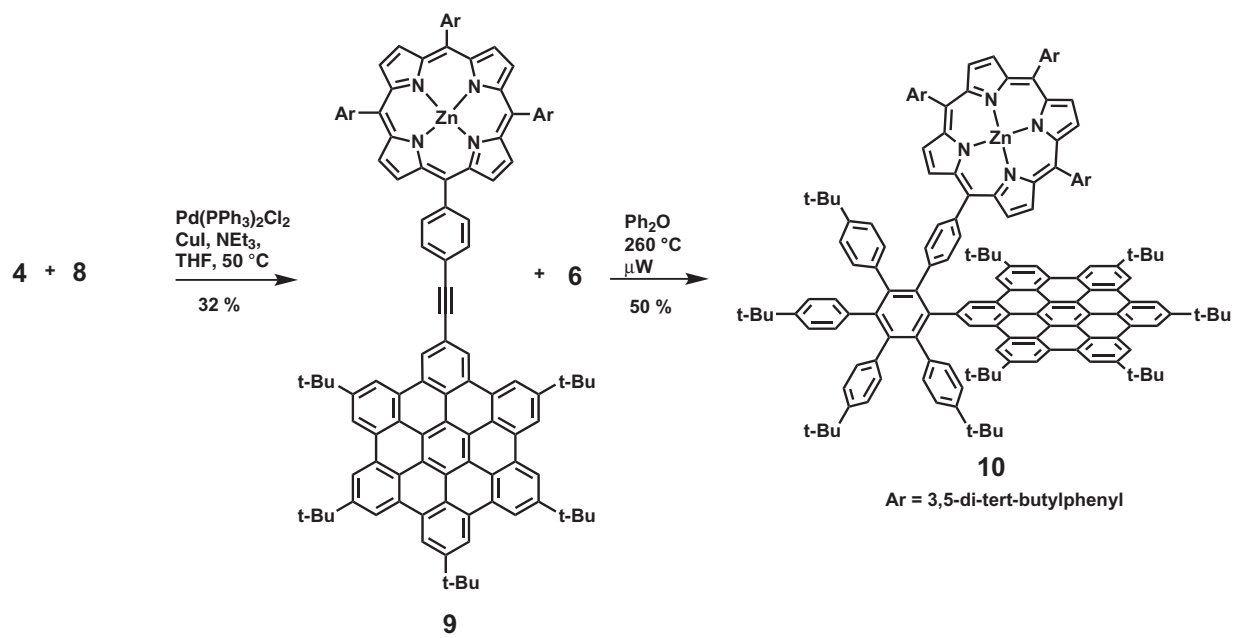


Scheme 1. Synthesis of zinc-ethynylporphyrin **4**



Scheme 2. Synthesis of iodo-HBC **8**



Scheme 3. Synthesis of porphyrin-HAB-HBC triad **10**

acetylene-bridged porphyrin-HBC system **9** was formed in 32% yield (Scheme 3). In addition to the desired product, a homocoupling product between two porphyrins was obtained, which explains the relatively low yield of **9**. Nevertheless, **9** and **6** were successfully reacted in a final Diels–Alder reaction in the microwave reactor and the porphyrin-HAB-HBC triad **10** was obtained in 50% yield.

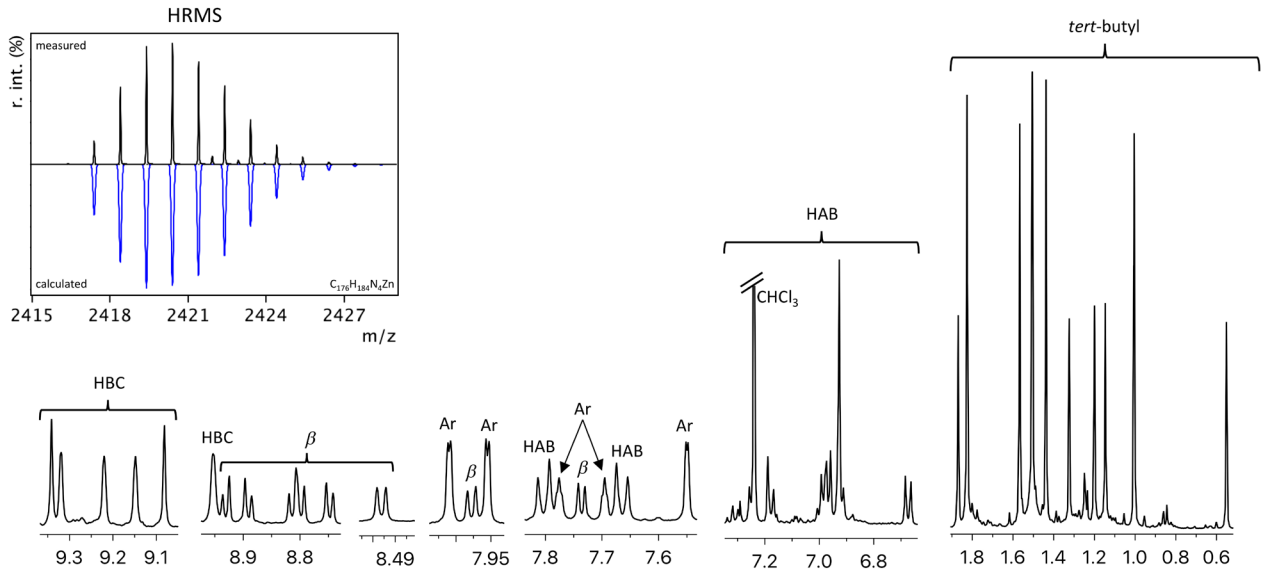


Fig. 1. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$, rt) and HRMS (APPI-ToF)

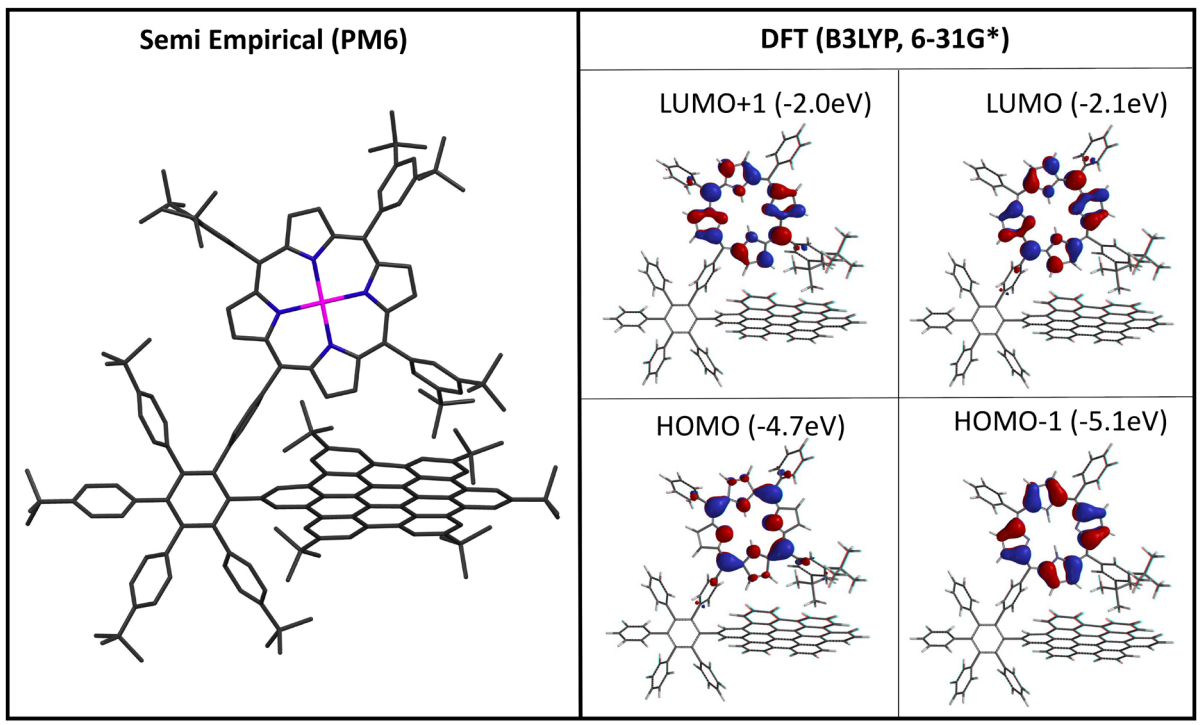


Fig. 2. Left: Calculated structure of complete molecule (semi empirical, PM6). Hydrogens are omitted for clarity. Right: DFT (B3LYP, 6-31G*) calculated molecular orbitals of a simplified molecular structure. *Tert*-butyl groups and the central zinc atom were omitted for calculation time saving reasons

The ^{1}H NMR (Fig. 1) shows the successful formation of the product. The most downfield shifted signals from 9.34–8.95 ppm originate from the protons attached to the HBC and appear as six separate singlets. Further upfield, the resonances of the β-pyrrolic protons generate six doublets (^3J = 4.7 Hz) found at 8.89–8.51 ppm with only two of them overlapping. Due to the low symmetry of the porphyrin, eight signals for the β-pyrrolic protons were expected, and the remaining two protons come to resonance at 7.98 ppm and 7.74 ppm. This is a significant upfield shift compared to normal β-pyrrolic protons, which are usually in the range of ~9 ppm [29, 30]. This shift is due to the close proximity of the two β-pyrrolic protons to the aromatic HBC core (see calculated structure in Fig. 2). The protons of the aryl substituents show up at 8.01–7.55 ppm as three doublets (^4J = 1.7 Hz)

and two triplets (^4J = 1.7 Hz). The resonances of the hydrogen atoms corresponding to the HAB part of the molecule are shown from 7.32–6.67 ppm with the exception of two signals, which appear more downfield shifted at 7.90 ppm and 7.66 ppm as two doublets (^3J = 7.9 Hz). These signals can be ascribed to the four protons of the benzene ring which is connected to the porphyrin. The aliphatic region shows 10 singlets from which three originate from the HBC part of the molecule, four from the HAB scaffold and three from the porphyrin's aryl substituents. Furthermore, HRMS (APPI-ToF) confirms the presence of the product in which the measured spectrum perfectly matches the calculated isotope pattern (Fig. 1).

The relative orientation of the porphyrin and HBC towards the central HAB core is shown in Fig. 2. The porphyrin is almost in the same plane as the inner HAB benzene ring, whereas the HBC is twisted by ~60°. This arrangement leads to a close proximity of the porphyrin to the HBC plane, especially for the two β-pyrrolic positions as well as for the *tert*-butyl groups of the aryl substituent. Frontier molecular orbitals (HOMO, LUMO) as well as HOMO-1 and LUMO+1 were calculated using DFT and are located exclusively on the porphyrins, whereas HOMO-2 and HOMO-3 are found on the HBC unit.

The UV-vis absorption spectrum (Fig. 3) shows strong absorption features for the HBC at 347, 363 and 394 nm as well as for the porphyrin at 423, 549 and 588 nm. These absorption features are in the same spectral region as reference compounds hexa-*tert*-butyl-HBC [31] and tetra(3,5-di-*tert*-butylphenyl)zinc-porphyrin [32, 33] but the intensity ratio is unambiguously different. Although the porphyrin's Soret band at 423 nm is still the strongest absorption (ε = 450 000), the HBC band at 363 nm (ε = 220 000) reaches almost 50% of the porphyrin's Soret-band absorption. The molar absorption coefficient of **10** at 363 nm is significantly higher compared to the reference hexa-*tert*-butyl-HBC (ε = 150 000) [31]. Additionally, a broad absorption band from ~630–850 nm is shown, which is not present in the spectra of the reference compounds.

CONCLUSION

We have shown the successful synthesis of a porphyrin-HAB-HBC triad. Due to the *ortho* substitution at the central HAB core, both chromophores are in close proximity to each other and therefore strongly interact with each other. Although UV-vis absorption spectra were recorded, further investigations of the photophysical characteristics are needed in order to understand the optoelectronic properties in more detail.

EXPERIMENTAL

***Zinc-TMS-ethynyl-porphyrin* 11.** Four microwave vials were prepared: each vial was charged with a magnetic stir bar, CH_2Cl_2 (20 mL), 3,5-di-*tert*-butylbenzaldehyde (327 mg, 1.50 mmol), 4-(trimethylsilyl-ethynyl) benzaldehyde (101 mg, 0.50 mmol) and pyrrole (140 µl, 2.00 mmol). Just before the reaction started, I_2 (50 mg, 0.20 mmol) was added to the particular vial and it was sealed with a septum. The mixture was heated in the microwave (20 s pre-stirring, 5 min at 40 °C, max, power 100 W, cooling off — for exact conditions, see supporting information). A flask charged with *para*-chloranil (1.47 g, 6.00 mmol) in 30 mL CH_2Cl_2 was prepared and heated to reflux. After each reaction the septum was removed and the reaction mixture poured into the *para*-chloranil solution flask. After the content of the last vial was added to the

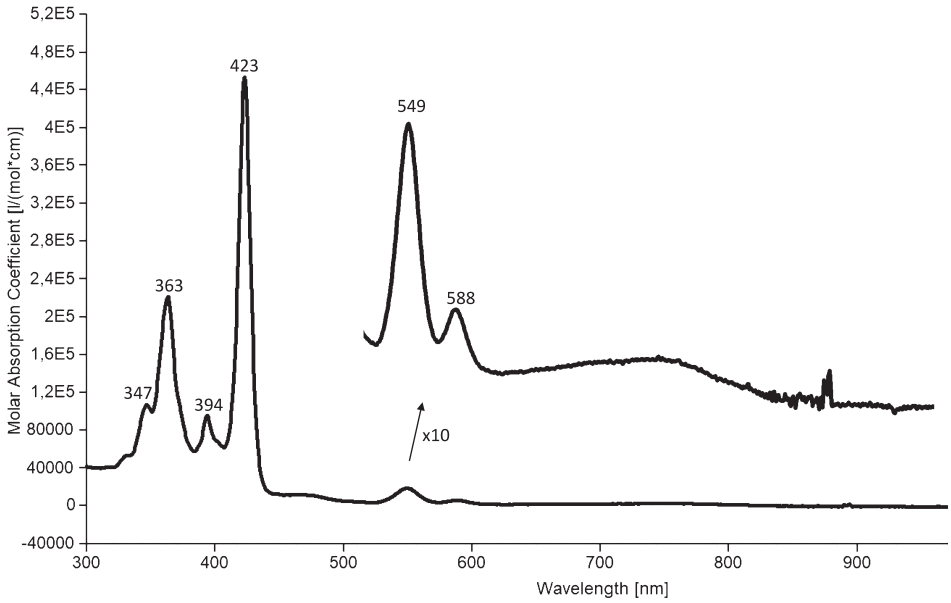


Fig. 3. UV-vis absorption spectrum of **10** in CH_2Cl_2.

flask, the reaction mixture was stirred for 30 min at 40 °C. The solvent was removed; the residue pre-purified by silica plug filtration (CH_2Cl_2) and the red porphyrin fraction was collected. The solvent was removed, 3–4 drops of NEt_3 were added and the crude product was purified by column chromatography (SiO_2, hexanes/CH_2Cl_2, 3:1). The second fraction was identified as the product. The product was obtained as a red solid in 10.1% yield (212 mg, 0.202 mmol). Free-base porphyrin (212 mg, 0.202 mmol) was dissolved in 50 mL $CHCl_3$, a saturated solution of $Zn(OAc)_2 \cdot 2\ H_2O$ in MeOH (15 mL) was added and the mixture was stirred under light exclusion for 18 h at rt. The solvent was removed under reduced pressure and the residue purified by silica plug filtration (hexanes/CH_2Cl_2, 1:1). The pure product was obtained in 99% yield (222 mg, 0.200 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ [ppm] = 9.01–8.99 (m, 6H), 8.91 (d, J = 5.0 Hz, 2H), 818 (d, J = 6.5 Hz, 2H), 8.08–8.07 (m, 6H), 7.86 (d, J = 6.5 Hz, 2H), 7.79–7.77 (m, 3H), 1.50 (s, 36H), 1.50 (s, 18H), 0.39 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, rt): δ [ppm] = 150.54, 150.52, 150.50, 150.45, 150.43, 150.40, 150.37, 149.75, 149.73, 149.70, 148.55, 143.43, 141.78, 141.75, 134.37, 134.03, 132.66, 132.52, 132.42, 132.20, 132.06, 131.96, 131.59, 131.14, 130.34, 130.02, 129.77, 129.43, 122.75, 122.55, 122.22, 122.20, 120.98, 120.68, 119.69, 105.25, 95.20, 35.05, 32.20, 31.91, 31.62, 31.33, 0.28, -0.07. UV-vis (THF): λ [nm] (ε [$M^{-1}cm^{-1}$]) = 405 (46800), 426 (561000), 557 (23100), 597 (11600). MS (LDI) m/z (rel. int.) = 1110 (M^+, 100%). HRMS (APPI, toluene) for $C_{73}H_{84}N_4SiZn$ (M^+) calc.: 1110.5726, found: 1110.5757. mp > 350 °C (decomp.).

***Zinc-ethynyl-porphyrin* 4.** Zinc-porphyrin **11** (378 mg, 0.34 mmol) was dissolved in 50 mL THF and a 1 M TBAF solution in THF (1 mL, 1.00 mmol) was added. The mixture was stirred for 90 min under light exclusion at rt, the solvent was removed and the residue was purified by silica plug filtration (hexanes/CH_2Cl_2, 2:1). The product was obtained as a red solid in 89.7% yield (317 mg, 0.305 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm] = 9.00–8.99 (m, 6H), 8.91 (d, J = 4.7 Hz, 2H), 8.20 (d, J = 8.3 Hz, 2H), 8.08–8.06 (m, 6H), 7.88 (d, J = 8.1 Hz, 2H), 7.79–7.76 (m, 3H), 3.29 (s, 1H), 1.51 (s, 36H), 1.51 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, rt): δ [ppm] = 150.61, 150.51, 150.48, 149.76, 148.65, 148.62, 143.84, 141.80, 134.32, 132.53, 132.40, 132.28, 131.43, 131.29, 131.09, 130.41, 130.23, 129.72, 129.64, 127.25, 122.85, 122.63, 121.27, 120.87, 119.57, 83.85, 77.99, 34.98, 31.69. UV-vis (THF): λ [nm] (ε [$M^{-1}cm^{-1}$]) = 405 (39900), 425 (512000), 557 (18400), 597 (8000). MS (LDI): m/z (rel. int.) = 1037 (M^+, 100%). HRMS (APPI, toluene) for $C_{70}H_{76}N_4Zn$ (M^+) calc.: 1036.5356, found: 1036.5342. mp > 350 °C (decomp.).

***Iodo-HPB* 7.** Iodo tolan **5** [28] (296 mg, 0.82 mmol, 1 eq) and *tert*-butyl substituted tetracyclone **6** [24] (500 mg, 0.82 mmol, 1 eq) were dissolved in Ph_2O (2.0 mL), purged with argon and heated to 260 °C in the microwave reactor for 12 h. The reaction mixture was diluted with a small amount of CH_2Cl_2 and the product was precipitated *via* the addition of MeOH. The product was filtered off and recrystallized from CH_2Cl_2/MeOH. After drying *in vacuo*, the product was obtained as a white solid in 78.4% yield (606 mg, 0.644 mmol).^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm] 7.14 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 4H), 6.81–6.75 (m, 6H), 6.69–6.60 (m, 10H), 6.57 (d, J = 8.4 Hz, 2H), 1.11 (s, 18H), 1.07 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$, rt): δ [ppm] = 147.92, 147.57, 147.53, 140.91, 140.86, 140.78, 140.08, 138.62, 137.80, 137.76, 137.57, 135.54, 133.65, 131.09, 131.03, 129.10, 128.28, 123.42, 123.09, 90.63, 34.06, 33.97, 31.14, 31.11. HRMS (MALDI) for $C_{62}H_{69}I$ (M^+) calc.: 940.4444, found: 940.4439. mp > 350 °C.

***Iodo-HBC* 8.** Iodo-HPB **7** (200 mg, 0.213 mmol, 1 eq) was dissolved in CH_2Cl_2 (200 mL) and degassed *via* bubbling N_2 through the solution for 15 min. A solution of dry $FeCl_3$ (1.03 g, 6.38 mmol, 30 eq) in CH_3NO_2 (6.0 mL) was added *via* syringe and the reaction was stirred for further 2 h at rt under slight bubbling of N_2. The reaction was quenched *via* the addition of MeOH (50 mL). The solvent was removed under reduced pressure and the product was purified by a silica plug filtration (CH_2Cl_2, ∅3.5 cm · 9 cm). Final purification was achieved by recrystallization from $CHCl_3$/MeOH. The product was obtained as a yellow solid in 98.5% yield (195 mg, 0.210 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm] = 9.13 (s, 2H), 9.06 (s, 2H), 8.97 (s, 2H), 8.83 (s, 2H), 8.67 (s, 2H), 8.53 (s, 2H), 1.94 (s, 9H), 1.89 (s, 18H), 1.78 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, rt): δ [ppm] = 148.36, 148.17, 148.04, 131.70, 130.18, 129.83, 129.48, 129.38, 128.16, 123.73, 123.18, 123.10, 122.87, 119.99, 119.61, 119.51, 118.96, 118.61, 118.54, 118.36, 93.62, 35.77, 35.66, 35.53, 32.20, 32.14, 32.05. HRMS (APPI, toluene) for $C_{62}H_{57}I$ (M^+) calc.: 928.3500, found: 928.3512. mp > 350 °C.

***Acetylene bridged porphyrin-HBC dimer* 9.** Iodo-HBC **8** (20.0 mg, 21.5 μmol, 1 eq), zinc-ethynyl-porphyrin **4** (24.6 mg, 23.7 μmol, 1.1 eq), $Pd(PPh_3)_2Cl_2$ (0.8 mg, 1.1 μmol, 0.05 eq) and CuI (0.4 mg, 2.2 μmol, 0.1 eq) were dissolved in 2 mL THF and 1 mL NEt_3 and degassed immediately (three times: sonication for 1 min under vacuum, followed by a purge with N_2 gas). The reaction was heated to 50 °C in an oil bath for 22 h. The reaction mixture was separated by column chromatography (SiO_2, hexanes/CH_2Cl_2, 2:1, ∅2.5 cm · 40 cm). The desired product was obtained in 32.4% yield (12.8 mg, 6.96 μmol). As a byproduct, significant amounts of homocoupling product of two porphyrins were obtained (13.7 mg, 6.60 μmol). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ [ppm] = 9.24 (s, 2H), 9.20–9.12 (m, 6H), 9.10 (bs, 2H), 9.06 (s, 4H), 8.98 (bs, 2H), 8.90 (bs, 4H), 8.48 (d, J = 8.2 Hz, 2H), 8.34 (d, J = 8.1 Hz, 2H), 8.16 (d, J = 1.8 Hz, 4H), 8.12 (d, J = 1.8 Hz, 2H), 7.83 (t, J = 1.9 Hz, 2H), 7.81 (t, J = 1.8 Hz, 1H), 2.01 (s, 9H), 1.96 (s, 18H), 1.89 (s, 18H), 1.56 (s, 36H), 1.55 (s, 18H). HRMS (MALDI, dctb) for $C_{132}H_{132}N_4Zn$ (M^+) calc.: 1838.9811, found: 1838.9748. mp > 350 °C (decomp.).

***Porphyrin-HPB-HBC triad* 10.** Porphyrin-HBC dimer **9** (12.8 mg, 6.96 µmol, 1 eq) and *tert*-butyl substituted tetracyclone **6** [24] (8.5 mg, 13.9 µmol, 2 eq) were dissolved in Ph_2O (0.25 mL) and heated to 260 °C in the microwave reactor for 12 h. The reaction mixture was diluted with little CH_2Cl_2 and the product precipitated *via* the addition of MeOH. The product was filtered off, dried and obtained in 50% yield (8.5 mg, 3.5 µmol). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm] = 9.34 (s, 2H), 9.32 (s, 2H), 9.22 (s, 2H), 9.15 (s, 2H), 9.08 (s, 2H), 8.95 (s, 2H), 8.93 (d, *J* = 4.6 Hz, 1H), 8.89 (d, *J* = 4.7 Hz, 1H), 8.81 (t, *J* = 5.4 Hz, 2H), 8.75 (d, *J* = 4.7 Hz, 1H), 8.51 (d, *J* = 4.7 Hz, 1H), 8.01 (d, *J* = 1.7 Hz, 2H), 7.98 (d, *J* = 4.7 Hz, 1H), 7.96 (d, *J* = 1.9 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.77 (t, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 4.7 Hz, 1H), 7.69 (t, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 1.7 Hz, 2H), 7.35–7.25 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.06–6.87 (m, 10H), 6.67 (d, *J* = 7.9 Hz, 2H), 1.87 (s, 9H), 1.83 (s, 18H), 1.57 (s, 18H), 1.51 (s, 18H), 1.44 (s, 18H), 1.32 (s, 9H), 1.20 (s, 9H), 1.15 (s, 9H), 1.00 (s, 18H), 0.55 (s, 9H). UV-vis (CH_2Cl_2): λ [nm] (ε [$M^{-1}cm^{-1}$]) = 347 (107 000), 363 (221 000), 394 (95 400), 423 (454 000), 549 (18 700), 588 (5870). MS (MALDI): m/z (rel. int.) = 2419.57 (M^+, 100%). HRMS (APPI, toluene/CH_2Cl_2) for $C_{176}H_{184}N_4Zn$ (M^+) calc.: 2419.3851, found: 2419.3907. mp > 350 °C (decomp.).

Acknowledgments

We gratefully acknowledge the funding by the German Research Council (DFG) through the Collaborative Research Centre SFB 953 (Synthetic Carbon Allotropes) as well as by the German Fond der Chemischen Industrie (FCI). M. M. thanks the Graduate School of Molecular Science (GSMS) for financial support.

Supporting information

^{1}H NMR, MS and HRMS spectra as well as detailed conditions for microwave reactions are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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