Supporting Information for:

Synthesis and characterization of a benzene-centered, phthalocyanine hexamer

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**General Methods**: Melting points (m.p.) were determined in a Büchi 504392-S equipment and are uncorrected. UV/vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. MALDI-TOF MS spectra and MALDI-TOF MS-MS spectra were obtained from an Applied Biosystem 4700 instrument equipped with a Nd:YAG laser operating at 355 nm. Elemental analysis were performed with a Perkin-Elmer 2400 CHN equipment. Column chromatography was carried out on silica gel Merck-60 (230-400 mesh, 60 Å). Analytical thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel 60 F-254 from Merck. Size-exclusion chromatography was carried out using Bio-Beads® S-X1 Beads (200-400 mesh) from BIO-RAD. Chemicals and solvents were purchased from commercial suppliers (Aldrich, Fluka, Strem, Acros, Fischer) and used without further purification. Iodo-substituted ZnPc 2, tri-tert-butylethynylphthalocyaninatozinc(II) and ZnPc dimer 3 were prepared following a reported procedure.\(^1\) ZnPc-containing hexasubstituted benzene 1 was obtained as a mixture of regioisomers and characterized as such.

Additional spectroscopic data for the **tri-tert-butyl-iodophthalocyaninatozinc(II)** (2):

\[
\text{UV/vis (THF): } \lambda_{\text{max}} (\log \varepsilon) = 673 \text{ nm (5.17), 607 nm (4.41), 350 nm (4.80).}
\]

Additional data for the **bis[(tri-tert-butylphthalocyaninato)zinc(II)-zinc(II)]ethyne** (3):

\[
\text{UV/vis (THF): } \lambda_{\text{max}} (\log \varepsilon) = 705 \text{ nm (5.29), 670 nm (5.29), 642 nm (4.79), 609 nm (4.64), 352 nm (5.03); MALDI-TOF MS (dithranol): } m/z \text{ (% intensity) 1511-1522 (isotopic pattern) (100) } [M]^+, 3021-3040 \text{ (isotopic pattern) (15) } [M_2]^+, 4534-4554 \text{ (isotopic pattern) (2) } [M_3]^+ \text{ (see Figure S1).}
\]
Figure S1 MALDI-TOF MS spectrum (dithranol) of the ZnPc dimer 3. Besides the peak corresponding to the molecular ion \([3]^+\), the peaks of the supramolecular ions \([3_2]^+\) and \([3_3]^+\) due to intermolecular association are also present.

Hexa[tri-tert-butyl-phthalocyaninatozinc(II)]benzene (1):

Bis[(tri-tert-butylphthalocyaninato)zinc(II)-zinc(II)]ethyne (3) (30.3 mg, 0.02 mmol) was refluxed in dry dioxane (2 mL) under argon for 7 hrs in the presence of \(\text{Co}_2(\text{CO})_8\) (2 mg, 6 x 10\(^{-3}\) mmol). The solution was then reduced in volume and the resulting residue purified first by silica gel column chromatography (hexane/dioxane, 2/1) and then by BIO-BEADS\textsuperscript{®} size-exclusion column chromatography (THF). The blue solid obtained was washed with MeOH (15 mL) and dried under reduced pressure to afford the desired product (1) as a dark-blue powder.

Yield: 4.8 mg (16%); RF = 0.71; m.p. >300 °C; \(^1\)H NMR (200 MHz, CDCl\(_3\), 25 °C, TMS) (not reported due to the broadness of the peaks); FT-IR (KBr) \(\nu\) (cm\(^{-1}\)) = 3416,
2951, 1616, 1481, 1090, 1049; UV/vis (THF): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 676 nm (5.10), 620 nm (4.64), 347 nm (4.97); MALDI-TOF MS (dithranol): \( m/z \) (% intensity) 4532-4557 (isotopic pattern) (100) \([M]^+\); elemental analysis for C_{270}H_{234}N_{48}Zn_{6} (FW = 4543.4): Calcd.: C 71.38, H 5.19, N 14.80; Found: C 71.52, H 5.32, N 15.30.

**Figure S2** MALDI-TOF MS-MS spectrum (dithranol) of the peak at \( m/z \) = 4543 corresponding to the ZnPc-containing hexasubstituted benzene 1. No fragmentation of the molecular ion \([1]^+\) was observed.

**Figure S3** Top view (left hand-side) and side view (right hand-side) of the computer-simulated three-dimensional structure of one of the regioisomers of the ZnPc-containing persubstituted benzene 1 obtained by using the Hyperchem program with the MM+ force field (for clarity tert-butyl groups as well as hydrogen atoms have been omitted after the energy minimization). In the minimized structure each of the six tightly packed ZnPc units adopt a tilted arrangement with respect to the central benzene ring plane in order to minimize the steric congestion of the system. The resulting structure resembles a six-blade “molecular propeller”. Carbon atoms are in light blue, nitrogen atoms are in dark blue and zinc atoms are in red.