

**Supporting Information for:**  
**Synthesis and characterization of a benzene-centered, phthalocyanine  
hexamer**

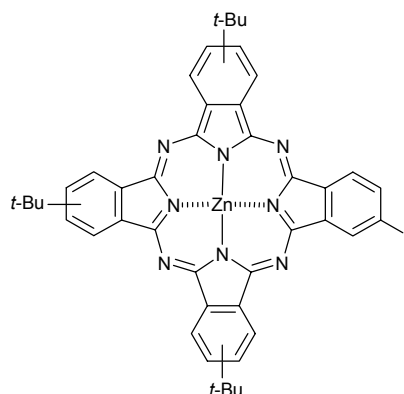
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**General Methods:** Melting points (m.p.) were determined in a Büchi 504392-S equipment and are uncorrected. UV/vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. MALDI-TOF MS spectra and MALDI-TOF MS-MS spectra were obtained from a 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, 60Å). 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<sup>®</sup> 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.<sup>1</sup> ZnPc-containing hexasubstituted benzene **1** was obtained as a mixture of regioisomers and characterized as such.

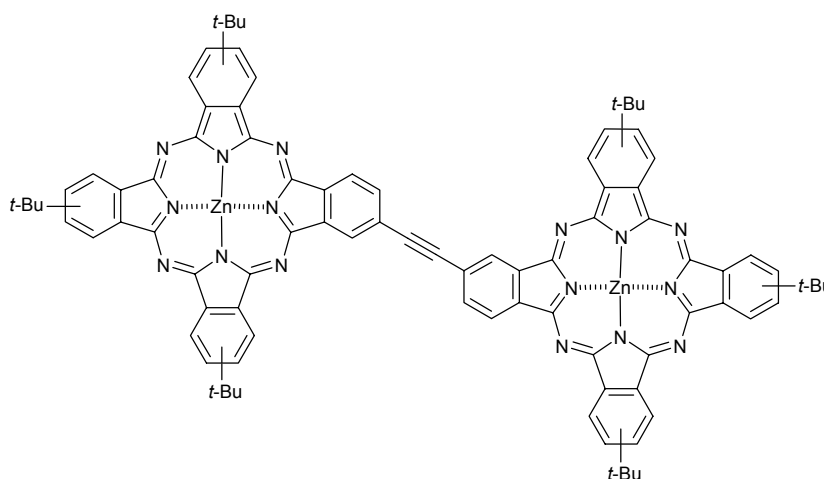
<sup>1</sup> E. M. Maya, P. Vázquez and T. Torres, *Chem. Eur. J.*, 1999, **5**, 2004.

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

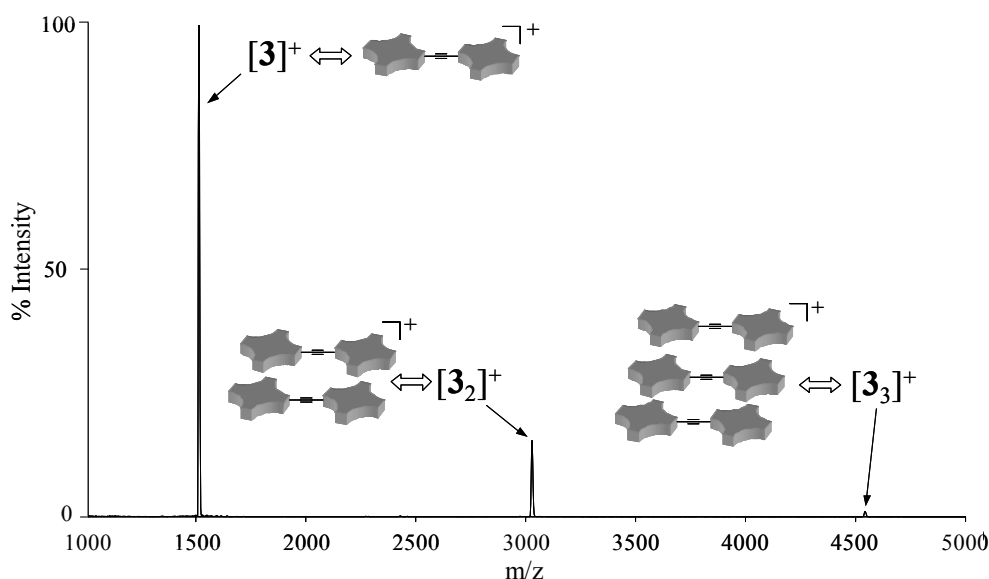


UV/vis (THF):  $\lambda_{\max}$  ( $\log \epsilon$ ) = 673 nm (5.17), 607 nm (4.41), 350 nm (4.80).

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

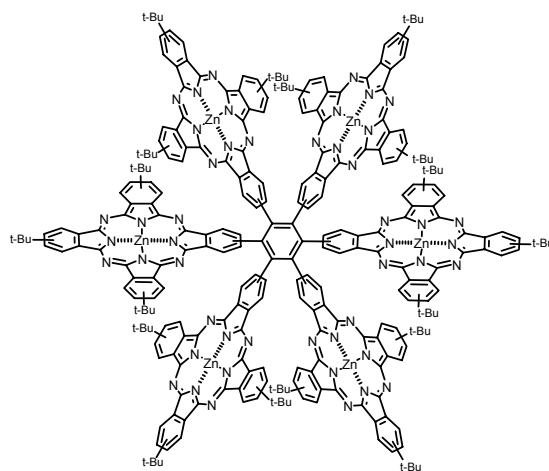


UV/vis (THF):  $\lambda_{\max}$  ( $\log \epsilon$ ) = 705 nm (5.29), 670 nm (5.29), 642 nm (4.79), 609 nm (4.64), 352 nm (5.03); MALDI-TOF MS (dithranol):  $m/z$  (% intensity) 1511-1522 (isotopic pattern) (100)  $[M]^+$ , 3021-3040 (isotopic pattern) (15)  $[M_2]^+$ , 4534-4554 (isotopic pattern) (2)  $[M_3]^+$  (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.

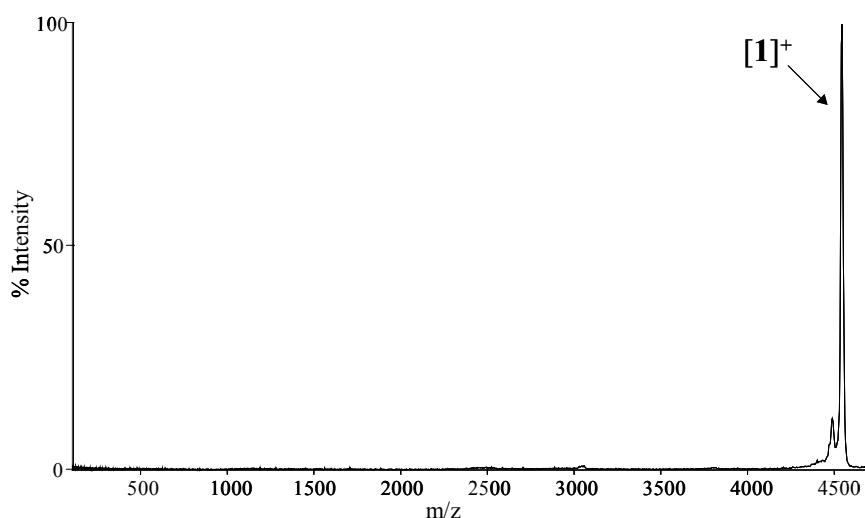
### Hexa[tri-*tert*-butyl-phthalocyaninatozinc(II)]benzene (**1**):



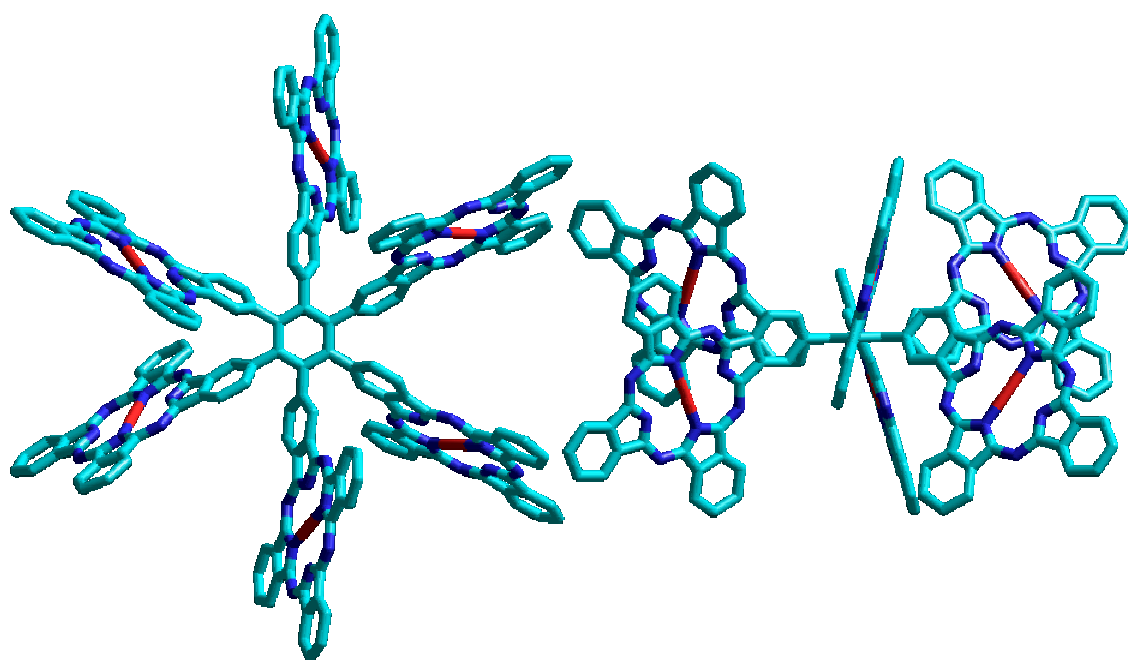
Bis[(tri-*tert*-butylphthalocyaninato)zinc(II)-zinc(II)]ethyne (**3**) (30.3 mg, 0.02 mmol) was refluxed in dry dioxane (2 mL) under argon for 7 hrs in the presence of  $\text{Co}_2(\text{CO})_8$  (2 mg,  $6 \times 10^{-3}$  mmol). The solution was then reduced in volume and the resulting residue purified first by silica gel column chromatography (hexane/dioxane, 2/1) and then by BIO-BEADS<sup>®</sup> 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;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS) (not reported due to the broadness of the peaks); FT-IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) = 3416,

2951, 1616, 1481, 1090, 1049; UV/vis (THF):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 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<sup>+</sup> 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.