Supplementary Material (ESI) for Chemical Communications
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Supporting Information

A Carbazole-containing Porphyrinoid: Synthesis and Oxidation to the Porphyrin-state

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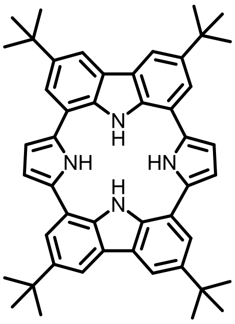
General Information

Commercially available reagents and solvents were used without further purification unless otherwise stated. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AMX700 in THF-d_8, using a 5 mm broadband probe. The experiments were conducted at 298 K and the temperature was regulated by standard ^{1}H methanol or glycol NMR samples using the topspin 2.1 software (Bruker). MALDI-TOF spectrometry was conducted on a Bruker Reflex IITOF spectrometer, utilizing a 337 nm nitrogen laser. Tetracyanoquinodimethane (TCNQ) was used as the matrix substance for solid state prepared samples. HRESI mass spectrometry was measured on a QTof Ultima 3 Fa. Micromass/Waters. Solution UV-vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 100 spectrophotometer. Solution photoluminescence spectra were recorded on a SPEX-Fluorolog II(212) spectrometer. Cyclic voltammetry was measured on a Princeton Applied Research Parstat 2273 instrument with anhydrous solvents under argon atmosphere. Melting points were determined on a Büchi hot stage apparatus and are uncorrected.

3,6-Di-*tert*-butyl-1,8-diiodo-9*H*-carbazole[1] (**4**) and 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole[2] (**5**) were synthesized following the literature procedures.

Synthesis of macrocycle 3



3

396.4 mg (0.74 mmol, 1 eq) of 3,6-di-*tert*-butyl-1,8-diiodo-9*H*-carbazole (**4**), 239.3 mg (0.81 mmol, 1 eq) of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (**5**) and 9 mg (5 µmol, 0.01 eq) of $Pd(PPh_3)_4$ were dissolved in toluene (1000 ml). EtOH (400 ml) and 2M K_2CO_3 (60 ml, excess) were added to the solution and the reaction mixture was degassed 3 times. The reaction mixture was stirred at 85°C for 17h. The solvents were removed *in vacuo*, the crude was redissolved in EtOAc and filtered over 1 cm silica. The crude product was purified by column chromatography using hexane : EtOAc (3:1) as eluent. Additionally, the crude was suspended in hexane and the precipitated was filtered off to yield 46 mg (0.04 mmol, 10%) of macrocycle **3** as a colourless solid.

^{1}H-NMR (THF-d_8, 700 MHz, 298 K): δ = 1.53 (s, 36H), 6.73 (d, ^{3}J*=2.22 Hz,* 4H), 7.72 (d, ^{4}J*=1.80 Hz,* 4H), 8.07 (t, ^{4}J*=1.80 Hz,* 4H), 10.53 (s, 2H), 11.13 (s, 2H) ppm. ^{13}C-NMR (THF-d_8, 176 MHz, 298 K): δ = 32.4, 35.4, 109.1, 115.4, 118.6, 122.8, 126.3, 133.8, 136.9, 143.7 ppm. ^{1}H^{15}N-NMR (THF-d_8, 700 MHz, 298 K): δ = -231.35 (pyrrole), -271.68 (carbazole) ppm. Mp > 400°C. MALDI TOF (TCNQ as matrix) m/z = 684.36 g/mol - calculated: 684.42 g/mol for $C_{48}H_{52}N_4$. HRESI MS (THF 1:1 MeCN): $[C_{50}H_{52}N_4+H]^+$ m/z = 685.4290 g/mol - calculated 685.4270 g/mol.

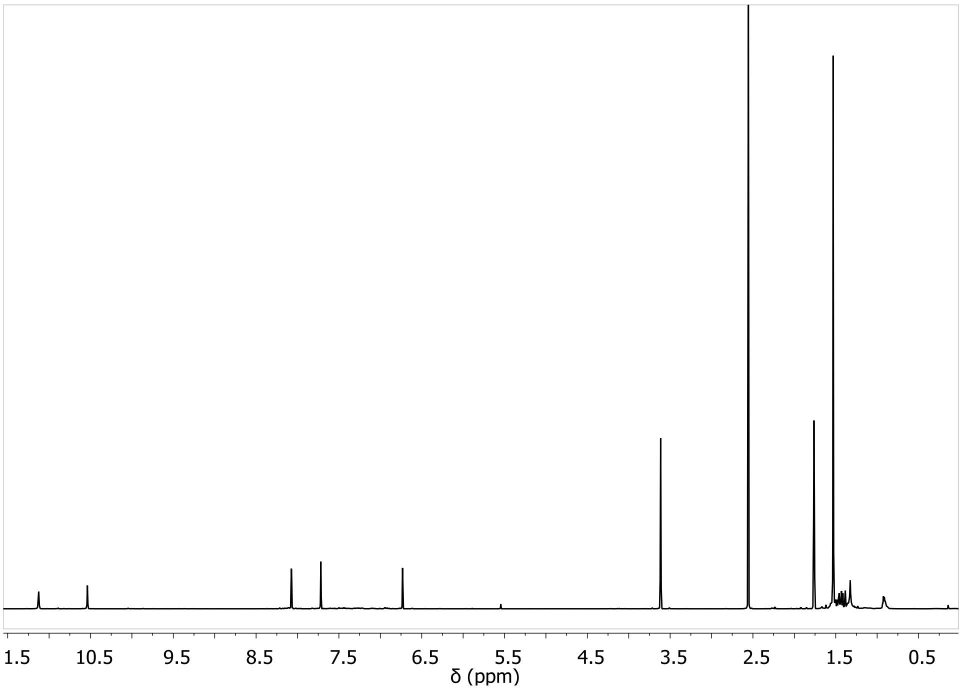


Fig. S1: ^{1}H NMR spectrum of macrocycle **3** recorded in THF-d_8 at 298 K, 700 MHz.

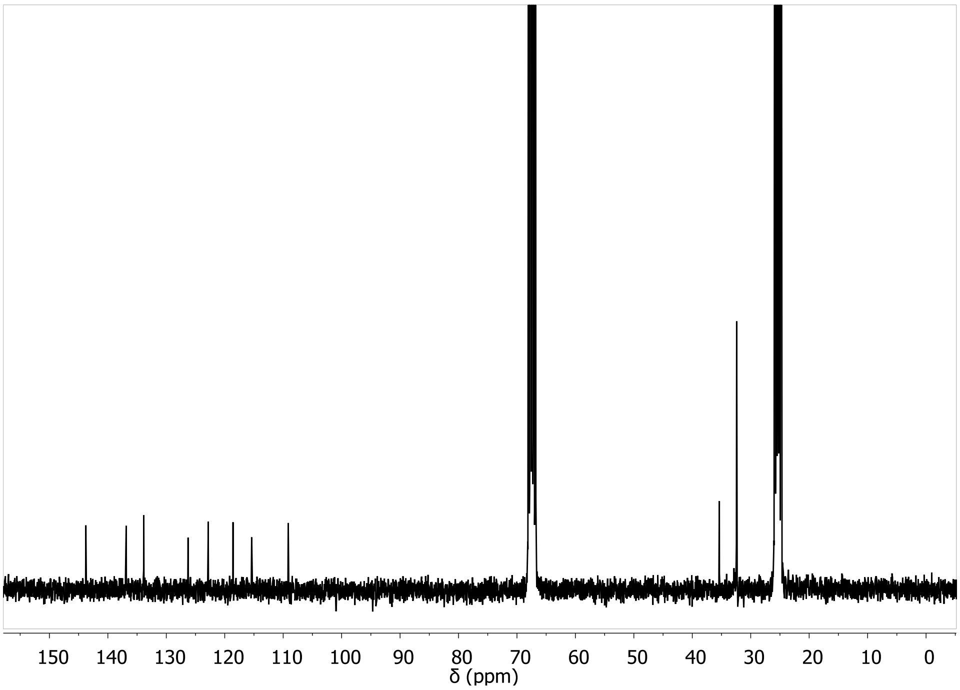
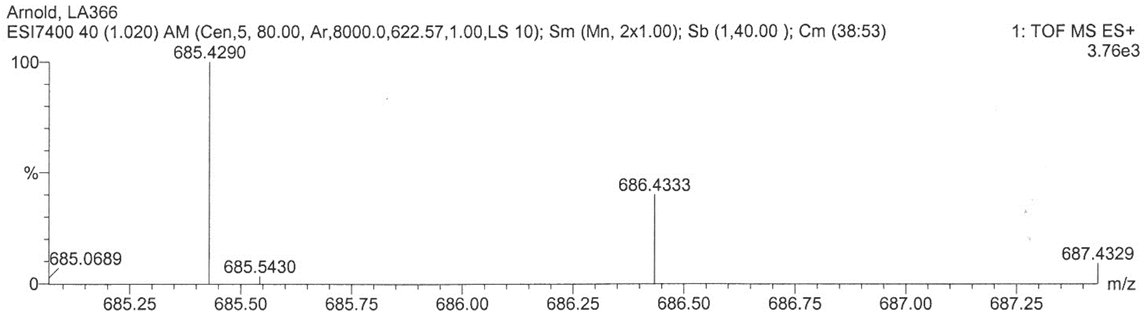


Fig. S2: ^{13}C NMR spectrum of macrocycle **3** recorded in THF-d_8 at 298 K, 176 MHz.



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Minimum:                                    -1.5
Maximum:                  200.0     10.0    100.0

Mass        Calc. Mass    mDa       PPM     DBE       Score       Formula

685.4290    685.4270      2.0       2.9     24.5      1           C48  H53  N4
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Fig. S3: HRESI mass spectrometry macrocycle **3**.

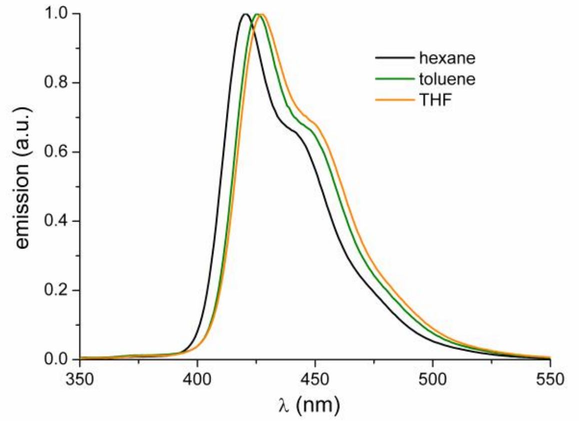

Fig. S4: Emission spectra of macrocycle **3** recorded in different solvents.

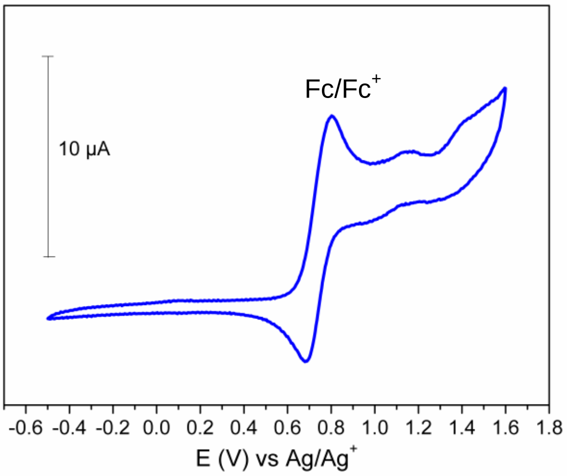

Fig. S5: Cyclic voltammogram of macrocycle **3**; 10^{-3} M sample solution in DMF, 10^{-1} M solution of *n*-Bu_4NPF_6 as electrolyte; working and counter electrode: Pt, reference electrode: Ag; ferrocene reference (Fc/Fc^+).

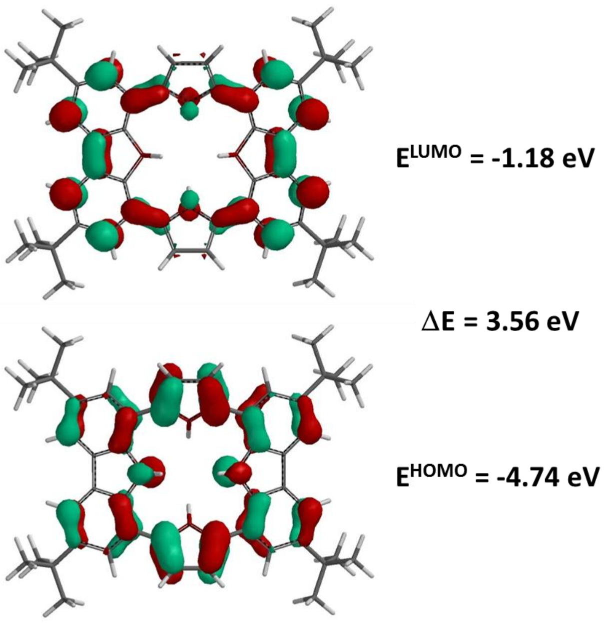

Fig. S6: Calculated HOMO, LUMO and LUMO+1 orbital energies of macrocycle **3** at B3LYP/6-31G(d) level of theory using Spartan 4.0 program.[3]

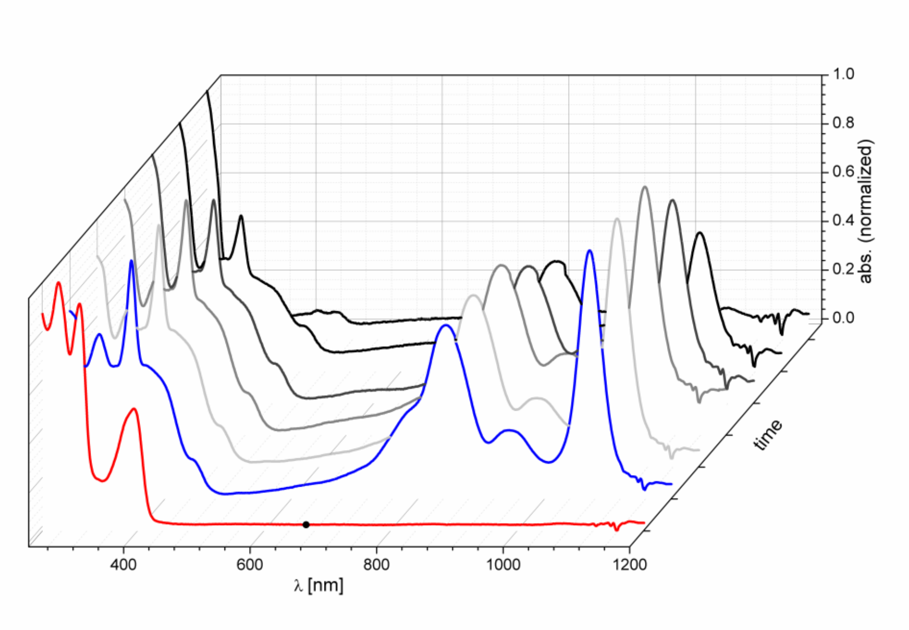

Fig. S7: Electronic absorption spectra porphyrinoid **3** (red), porphyrin **2** (blue) in CH_2Cl_2 at rt and the stepwise decomposition of the porphyrin species.

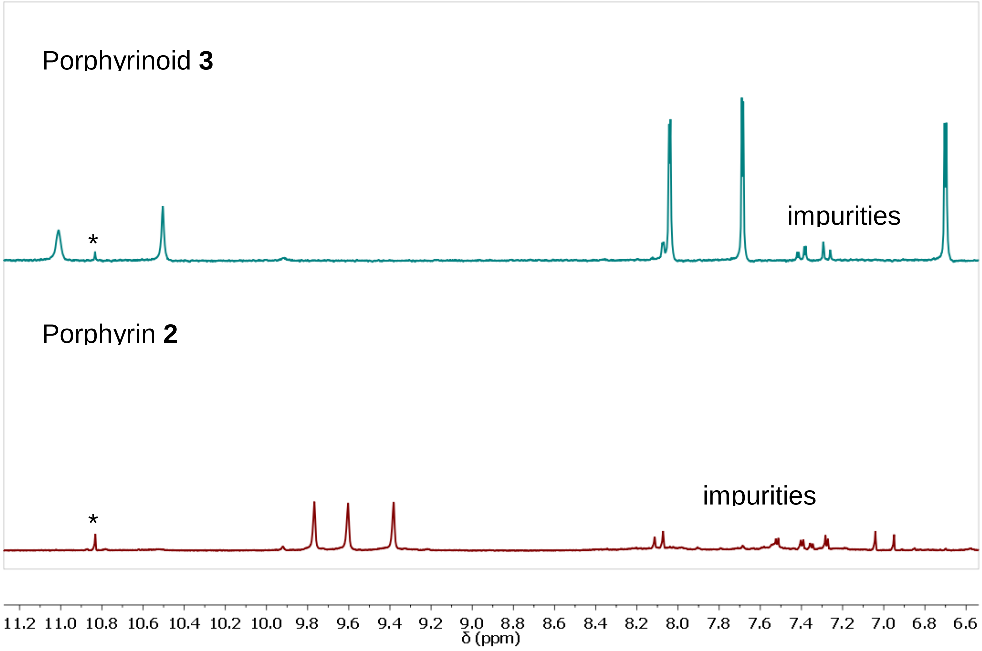

Fig. S8: Aromatic region of the ^{1}H NMR spectra of porphyrinoid **3** (blue) and porphyrin **2** (in THF-d_8, 700 MHz, 298 K, *from solvent).

References

1. M. Inoue, T. Suzuki and M. Nakada, *J. Am. Chem. Soc.*, 2003, **125**, 1140-1141.
2. J. Takagi, K. Sato, J. F. Hartwig, T. Ishiyama and N. Miyaura, *Tetrahedron Lett.*, 2002, **43**, 5649-5651.
3. Karman Ave. Suite 370, Irvine, CA 92612 USA, Spartan version 4.0, Wavefunction, Inc., 18401 edn.