Supporting Information

Utilization of $Sc_3N@C_{80}$ in Long-Range Charge Transfer Reactions

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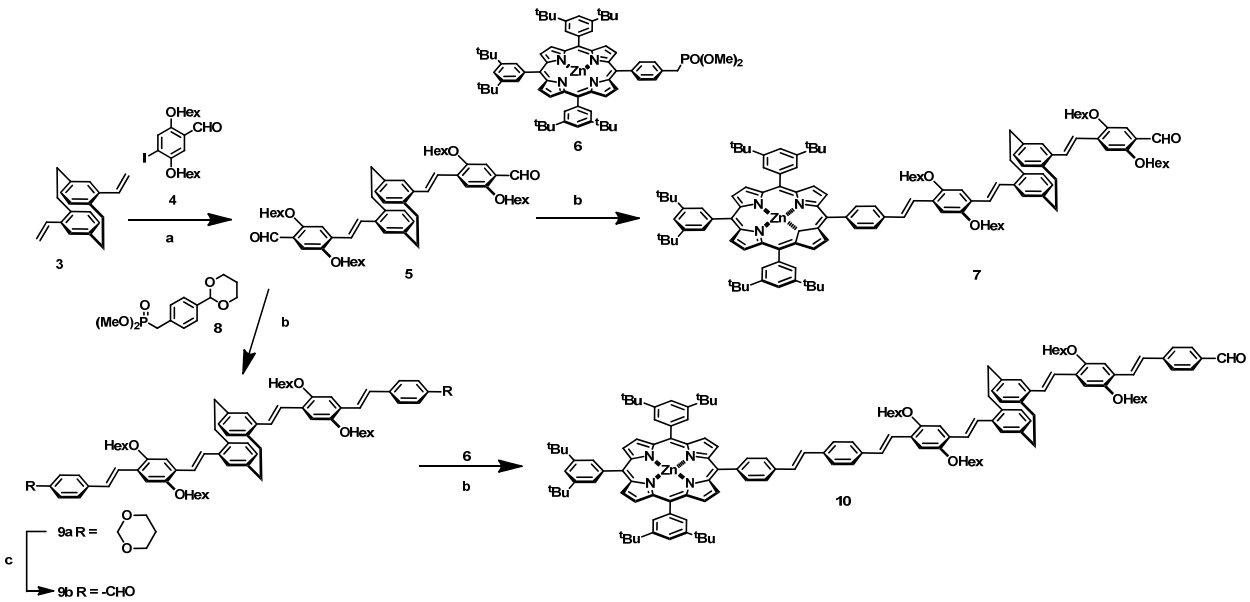
2. General methods

Anhydrous solvents were purchased from Aldrich and used as received. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. For precursor, NMR spectra were recorded on a Bruker Avance 300 and 500 (^{1}H: 300 MHz; ^{13}C: 75 MHz and/or ^{1}H: 500 MHz; ^{13}C: 125 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. For the compounds **1** and **2**, NMR spectra were recorded using a Bruker Avance 500 spectrometer. MALDI-TOF mass spectra were obtained in a Voyager-DE STR mass spectrometer. HPLC was performed using a Varian Prostar 210 equipped with a Cosmosil - pentabromobenzyl (PBB) (4.6 x 250 mm) column and a UV detector. UV-Vis spectra were recorded in a Varian Cary 50 spectrophotometer using $CHCl_3$ as solvent. All the electrochemical measurements were made in a 0.050 M solution of tetrabutylamonium hexafluorophosphate (*n*BuNPF$_6$) in *o*-dichlorobenzene as supporting electrolyte using a 1 mm ϕ glassy carbon electrode as working electrode, a platinum wire as counter electrode and a silver wire as a pseudo reference electrode. The redox potentials were calibrated using ferrocene as internal standard.

$Sc_3N@I_h$-C_{80} was prepared by arc discharge of graphite rods packed with graphite/Sc_2O_3/Cu in 7:2:1 ratio (see: S. Stevenson, M. A. Mackey, M. C. Thompson, H. L. Coumbe, P. K. Madasu, C. E. Coumbe and J. P. Phillips *Chem. Commun.* **2007**, 4263-426). The packed rods were annealed at 1000°C for 12 hours and arced using the reactive atmosphere method (200 Torr He/10 Torr NH_3) (see: L. Dunsch, M. Krause, J. Noack and P. Georgi *J. Phys. Chem. Solids* **2004**, *65*, 309-315). The obtained soot was extracted with CS_2 and filtered using a short silica plug in order to remove the polyaromatic hydrocarbons. The crude fullerene mixture was then eluted with CS_2 through a silica column containing a layer of tris(4-bromophenyl)aminium hexachloro antimonate in order to remove the $Sc_3N@D_{5h}$-C_{80}, $Sc_3N@D_{3h}$-C_{78} and $Sc_3N@D_3$-C_{68} present in

the crude fullerene mixture leaving only $Sc_3N@I_h$-C_{80} (see: B. Elliott, L. Yu and L. Echegoyen *J. Am. Chem. Soc.* **2005**, *127*, 10885-10888). Once the solution was dried the black solid was washed with diethyl ether and dichloromethane to remove soluble contaminants and residual empty cage fullerenes. Finally the solid was dissolved in ortho-dichlorobenzene (*o*-DCB) and the solvent evaporated slowly overnight under a stream of nitrogen to yield microcrystalline $Sc_3N@I_h$-C_{80}.

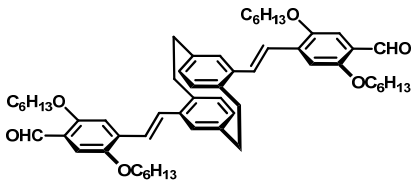


Scheme S1. *Reagents and conditions for the synthesis of the precursors: a) $Pd(OAc)_2$, K_2CO_3, Bu_4NBr, DMF, 100 °C, 79 %; b) ^{t}BuOK, THF, CH_2Cl_2; c) TFA, CH_2Cl_2:H_2O (1:1), 99 %.*

3. Synthetic details and characterization

Compounds **3**, **4**, **6** and **8** were prepared according to previously reported synthetic procedures **[**see: a) G. de la Torre, F. Giacalone, J. L Segura, N. Martín, D. M Guldi, *Chem. Eur. J.* **2005**, *11*, 1267 b) A. de la Escosura, M. V. Martinez-Diaz, P. Thordarson, A. E. Rowan, R. J. M. Nolte, T. Torres, *J. Am. Chem. Soc.* **2003**, *125*, 12300; c) J. F. Nierengarten, Tao Gu, *Helv. Chim. Acta,* **2004**, *87*, 2948; d) L. Rigamonti, B. Babgi, M. P. Cifuentes, R. L. Roberts, S. Petrie, R. Stranger, S. Righetto, A. Teshome, I. Asselberghs, K. Clays, M. G. Humphrey, *Inorg. Chem.* **2009**, *48*, 3562**]** and showed identical spectroscopic properties to those reported therein.

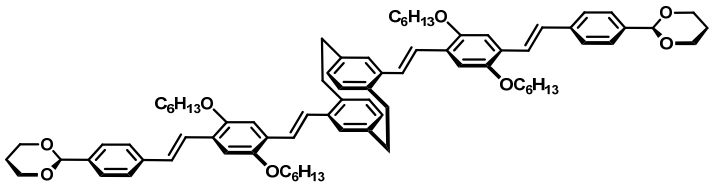
Compound 5.



To a dry round bottom flask equipped with a stirrer bar, compound **3** (150 mg, 0.57 mmol), compound **4** (747.2 mg, 1.73 mmol), $Pd(OAc)_2$ (15%), Bu_4NBr (185.7 mg, 0.57 mmol) and K_2CO_3 (238.8 mg, 1.73 mmol) were dissolved in anhydrous DMF. The resulting mixture was refluxing overnight. The reaction evolution was monitored by TLC and after the total consuming of the terminal alkene, the resulting mixture was allowed to reach room temperature. The solvent was then removed under vacuum and the mixture was quenched with a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The organic extracts were washed with water and dried over $MgSO_4$. The removal under vacuum of the organic solvent led to the crude product which was purified by column chromatography (silica gel, hexane/CH_2Cl_2 1:2) The solid was washed with a mixture of hexane / diethyl ether (7:3) to afford **5** as a yellow solid, in 79 % yield (395.5 mg, 0.45 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ 10.49, (s, 2H, -CHO), 7.40 (d, *J* = 16.40 Hz, 2H, Vinyl), 7.39 (s, 2H, ArH), 7.22 (d, *J* = 16.40 Hz, 2H, Vinyl), 7.17 (s, 2H, ArH), 6.77-6.71 (m, 4H, ArH-[2,2]paracyclophane), 6.45 (d, *J* = 7.71 Hz, 2H, ArH-[2,2]paracyclophane), 4.20-4.10 (m, 8H, α-CH_2), 3.65-3.55 (m, 2H, [2,2]paracyclophane), 3.20-2.90 (m, 6H, [2,2]paracyclophane), 2.00-1.85 (m, 8H, β-CH_2), 1.60-1.35 (m,24H, γ-, δ-, ε-CH_2), 0.95-0.90 (m, 12H, -CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) δ 189.2, 156.3, 151.0, 139.5, 138.8, 137.6,

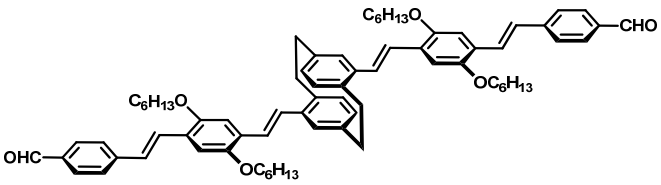
134.9, 133.5, 131.2, 130.4, 129.9, 124.8, 124.2, 111.4, 109.9, 69.4, 69.0, 34.5, 33.5, 31.7, 31.6, 29.5, 29.3, 26.0, 25.8, 22.7, 22.6, 14.1, 14.0; FTIR (neat): 2930, 2860, 1673, 1598, 1491, 1466, 1421, 1387, 1324, 1267, 1204, 1123, 1022, 965, 877, 836, 769, 733, 654 cm^{-1}; UV-vis (CH_2Cl_2), λ_{max} (ε): 394 (50000), 340 (38000) nm; MALDI-TOF m/z: 869.5 $[M]^+$.

Compound 9a.



Potassium *tert*-butoxide (39 mg, 0.345 mmol) was added portionwise to a solution of the phosphonate **8** (100 mg, 0.345 mmol) and compound **5** (100 mg, 0.115 mmol) in dry THF, under argon. The mixture was stirred at room temperature for 90 min and then methanol (10 mL) was added. The mixture was extracted twice with CH_2Cl_2, the combined organic layers were dried over $MgSO_4$ and the solvent was removed under vacuum to yield a residue which was purified by flash column chromatography (silica gel, CH_2Cl_2) to afford **9a** as a yellow solid (127.2, 0.107mmol) 93% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ 7.56 (d, *J* = 8.3 Hz, 4H, ArH), 7.50-7.48 (m, 5H, ArH), 7.31-7.14 (m, 11H, ArH), 6.75 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2H, ArH-[2,2]paracyclophane), 6.70 (d, *J* = 1.6 Hz, 2H, ArH-[2,2]paracyclophane), 6.44 (d, *J* = 7.6 Hz, 2H, ArH-[2,2]paracyclophane), 5.54 (s, 2H), 4.33-4.28 (m, 4H), 4.15-3.98 (m, 12H, α-CH_2), 3.65-3.57 (m, 2H, [2,2]paracyclophane), 3.16-2.87 (m, 6H, [2,2]paracyclophane), 2.34-2.18 (m, 2H), 1.99-1.85 (m, 8H, β-CH_2), 1.65-1.25 (m, 26H, γ-, δ-, ε-CH_2), 0.96-0.92 (m, 12H, -CH_3); ^{13}C RMN ($CDCl_3$, 75 MHz, 298 K) δ 151.3, 151.1, 139.4, 138.5, 138.2, 138.1, 137.8, 133.5, 130.2, 129.3, 128.4, 127.9, 127.6, 126.7, 126.4, 126.3, 125.0, 123.9, 111.5, 110.3, 101.6, 69.8, 69.3, 67.4, 34.5, 33.6, 31.8, 31.7, 29.7, 29.5, 26.1, 26.0, 25.8, 22.8, 22.7, 14.2, 14.1; FTIR (neat): 2926, 2858, 1730, 1694, 1594, 1562, 1496, 1464, 1421, 1386, 1338, 1307, 1257, 1206, 1164, 1025, 965, 859, 805, 732, 660 cm^{-1}; MALDI-TOF m/z (%): 1189.5 $[M+H]^+$.

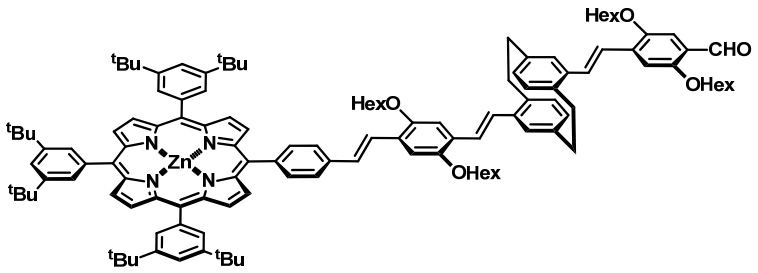
Compound 9b.



TFA (0.100 mL) was added to a bifasic mixture of compound **9a** (150 mg, 0.126 mmol) in CH_2Cl_2:H_2O (1:1) and was stirred at room temperature for 3 h. To the reaction mixture was added water (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic phase was washed with $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed under vacuum to obtain **9b** as an orange solid (132 mg, 0.123 mmol), 98% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ 10.01 (s, 2H, -CHO), 7.90 (d, *J* = 8.1 Hz, 4H, ArH), 7.75-7.65 (m, 5H, ArH and/or Vinyl), 7.35-7.15 (m, 11H, ArH and/or Vinyl), 6.80-6.70 (m, 4H, ArH-[2,2]paracyclophane), 6.45 (d, *J* = 7.7 Hz, 2H, ArH-[2,2]paracyclophane), 4.15-4.10 (m, 8H, α-CH_2), 3.65-3.55 (m, 2H, [2,2]paracyclophane), 3.20-2.90 (m, 6H, [2,2]paracyclophane), 2.00-1.85 (m, 8H, β-CH_2), 1.70-1.30 (m, 24H, γ-, δ-, ε-CH_2), 1.00-0.90 (m, 12H, -CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) δ 192.0, 151.9, 151.6, 144.6, 139.8, 138.7, 138.4, 135.5, 133.4, 130.7, 130.6, 129.0, 128.8, 127.6, 127.5, 127.2, 126.1, 125.3, 111.7, 110.9, 70.0, 69.8, 32.1, 32.0, 30.1, 30.0, 29.9, 26.5, 26.4, 23.1, 23.0, 14.5, 14.5; FTIR (neat): 2956, 2862, 1677, 1594, 1467, 1421, 1387, 1336, 1253, 1204, 1119, 1003, 963, 886, 823, 798, 767, 718, 651 cm^{-1}; UV-vis (CH_2Cl_2), λ_{max} (ε): 421 (82000), 333 (52000) nm; MALDI-TOF m/z: 1073.5 $[M+H]^+$.

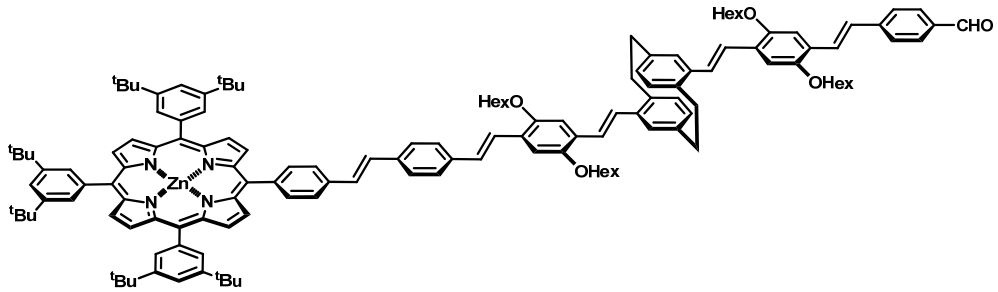
General procedure for the preparation of aldehydes 7 and 10. Potassium *tert*-butoxide (1.5 mmol) was slowly added to a refluxing solution of porphyrin **6** (1 mmol) and the corresponding oligomer (2 mmol) in dry THF under argon. After 16h, the mixture was cooled to room temperature, then, water and $CHCl_3$ were added. The combined organic phases were washed with water and dried over $MgSO_4$. After evaporation of the solvent the mixture was purified by flash column chromatography (silica gel, hexane / CH_2Cl_2 (1/1) affording the corresponding aldehyde. Unconverted oligomer was recovered in both cases.

Compound 7.



Yield: 40 % (30 mg, 0.016 mmol). ^{1}H NMR ($CDCl_3$, 300MHz, 298 K) δ 10.04 (s, 1H, -CHO), 9,09-9.06 (m, 8H, pyrrolic β-protons), 8.30 (d, *J* = 8.1 Hz, 2H, ArH porphyrin), 8.15-8.13 (m, 6H, ArH porphyrin), 7.98 (d, *J* = 8.1 Hz, 2H, ArH, porphyrin), 7.90-7.80 (m, 3H, ArH porphyrin), 7.55-7.15 (m, 10H, ArH and/or Vinyl), 6.87 (dd, *J* = 8.1 Hz, J = *1*.6 Hz, 1H, ArH-[2,2]paracyclophane), 6.80-6.75 (m, 3H, ArH-[2,2]paracyclophane), 6.53 (d, *J* = 8.1 Hz, 1H, ArH-[2,2]paracyclophane), 6.49 (d, *J* = 8.1 Hz, 1H, ArH-[2,2]paracyclophane), 4.25-4.10 (m, 8H, α-CH_2), 3.75-3.65 (m, 2H, [2,2]paracyclophane), 3.25-2.95 (m, 6H, [2,2]paracyclophane), 2.10-1.85 (m, 8H, β-CH_2), 1.75-1.25 (m, 78H, *t*Bu groups and γ-, δ-, ε-CH_2), 1.00-0.90 (m, 12H, -CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) δ 189.5, 156.7, 151.8, 151.6, 151.3, 150.9, 150.8, 150.5, 148.9, 142.7, 142.3, 140.0, 139.7, 139.2, 138.7, 138.6, 137.9, 137.4, 135.3, 135.2, 134.0, 133.9, 132.7, 132.6, 132.0, 131.7, 130.8, 130.6, 130.1, 130.0, 129.0, 128.2, 128.0, 127.4, 125.7, 125.1, 125.0, 124.4, 123.0, 122.9, 121.2, 112.0, 111.8, 110.8, 110.2, 70.3, 69.8, 69.7, 69.4, 35.3, 34.9, 34.0, 32.2, 32.1, 32.0, 31.9, 30.1, 30.0, 29.9, 29.7, 26.6, 26.5, 26.4, 26.2, 23.2, 23.1(2), 23.0, 14.6, 14.5, 14.4; FTIR (neat): 2955, 2861, 1696, 1591, 1494, 1466, 1421, 1366, 1290, 1251, 1196, 1118, 1004, 962, 888, 825, 797, 769, 717, 651 cm^{-1}; UV-VIS (CH_2Cl_2), λ_{max} (ε): 404 (81000), 424 (444000), 550 (23000), 591 (9200) nm; MALDI-TOF m/z: 1879.1 $[M+H]^+$.

Compound 10.

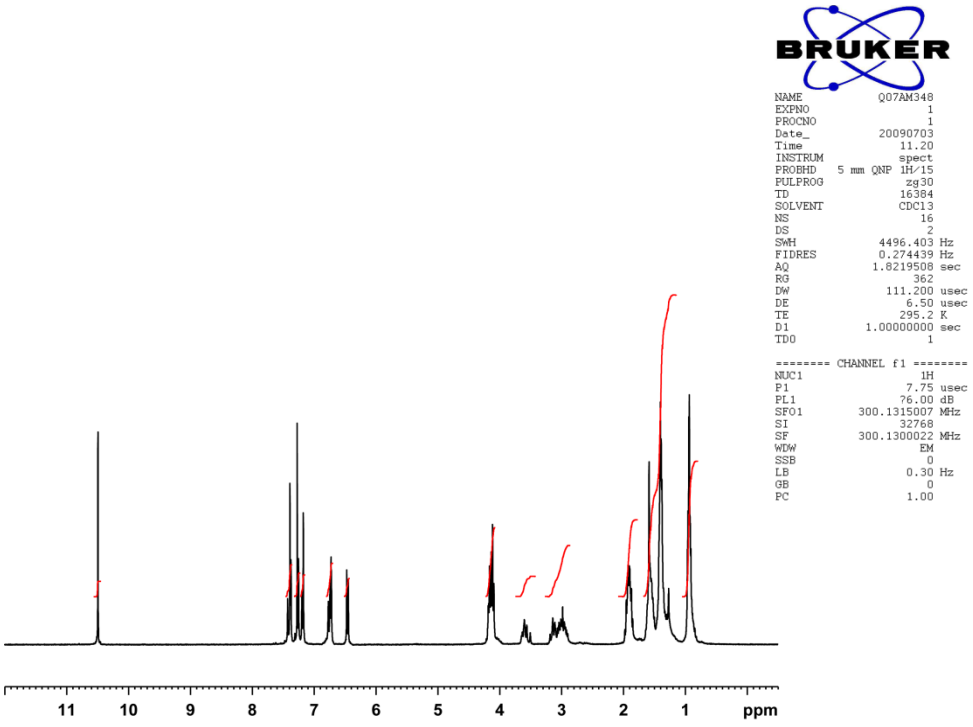


Yield: 43 % (31.4 mg, 0.015 mmol). ^{1}H NMR ($CDCl_3$, 300MHz, 298 K) δ 10.01 (s, 1H, -CHO), 9.10-9.00 (m, 8H, pyrrolic β-protons), 8.28 (d, *J* = 8.1 Hz, 2H, ArH porphyrin), 8.15-8.10

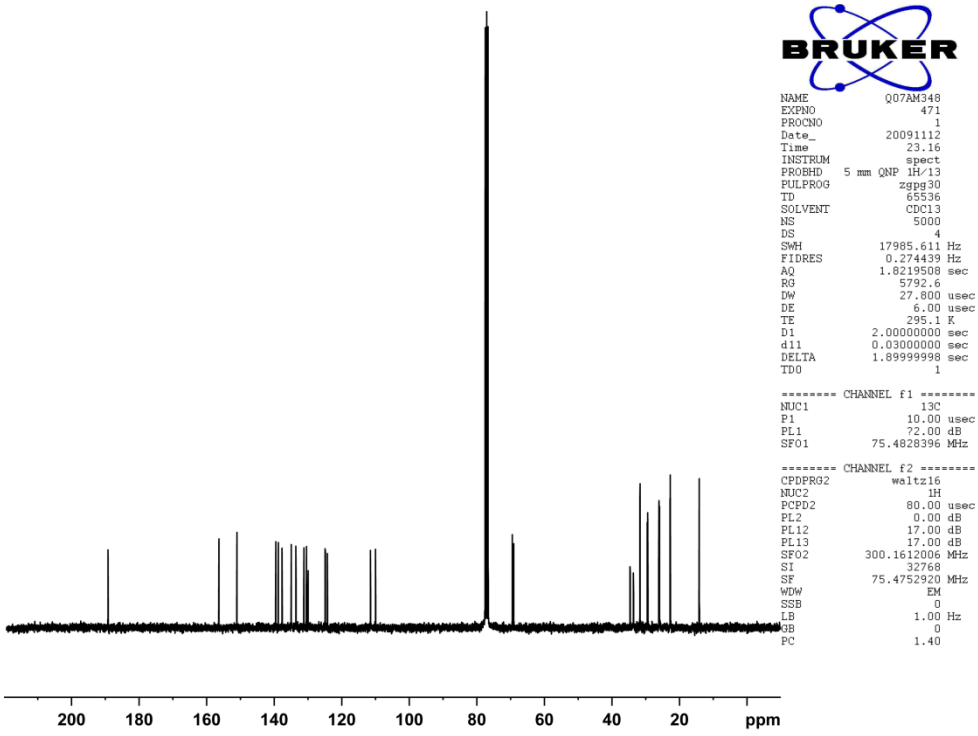
(m, 6H, ArH porphyrin), 7.95 (d, J = 8.1 Hz, 2H, ArH porphyrin), 7.85-7.80 (m, 3H, ArH porphyrin), 7.70-7.20(m, 20H, ArH and Vinyl), 6.85-6.75 (m, 4H, ArH-[2,2]paracyclophane), 6.50-6.45 (m, 2H, ArH-[2,2]paracyclophane), 4.20-4.15 (m, 8H, α-CH_2), 3.70-3.60 (m, 2H, [2,2]paracyclophane), 3.20-2.95 (m, 6H, [2,2]paracyclophane), 2.05-1.90 (m, 8H, β-CH_2), 1.70-1.25 (m, 78H, *t*Bu groups and γ-, δ-, ε-CH_2), 1.03-0.97 (m, 12H, -CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) δ 192.0, 151.9, 151.6, 151.5, 150.9, 150.8, 150.4, 149.0, 148.9, 144.6, 142.9, 142.2, 139.9, 139.8, 138.9, 138.7, 138.6, 138.5, 138.4, 138.0, 137.0, 136.9, 135.5, 135.3, 133.9, 133.8, 132.7, 132.6, 132.5, 132.0, 130.7, 130.6, 130.1, 130.0, 129.8, 129.6, 129.3, 129.0, 128.9, 128.7, 128.3, 128.0, 127.6, 127.5, 127.4, 127.3, 127.2, 126.1, 125.5, 125.3, 125.1, 124.9, 124.5, 124.4, 123.9, 123.0, 122.9, 121.2, 120.8, 119.5, 112.0, 111.8, 110.9, 110.7, 70.3, 70.1, 69.8, 35.4, 35.3, 34.9, 34.1, 34.0, 32.3, 32.2, 32.1, 32.0, 31.9, 30.6, 30.1, 30.0, 29.9, 29.8, 26.6, 26.5, 26.4(2), 23.2, 23.1, 23.0(2), 14.5, 14.4; FTIR (neat): 2956, 2925, 2859,1696, 1594, 1465, 1422, 1337, 1250, 1207, 1000, 964, 870, 803, 771, 717, 648 cm^{-1}; UV-VIS (CH_2Cl_2), λ_{max} (ε): 405 (106000), 424 (444000), 550 (23000), 591 (9200) nm; MALDI-TOF m/z: 2083.2 $[M+H]^+$.

^{1}H NMR and ^{13}C NMR of precursors

Compound 5.

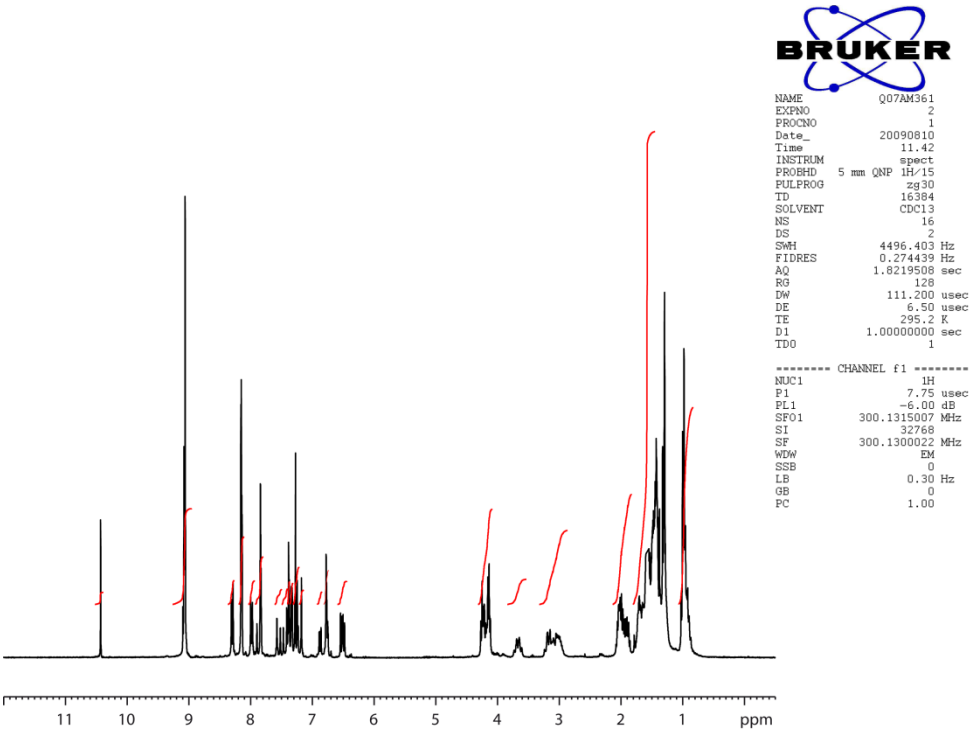


^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **5**.

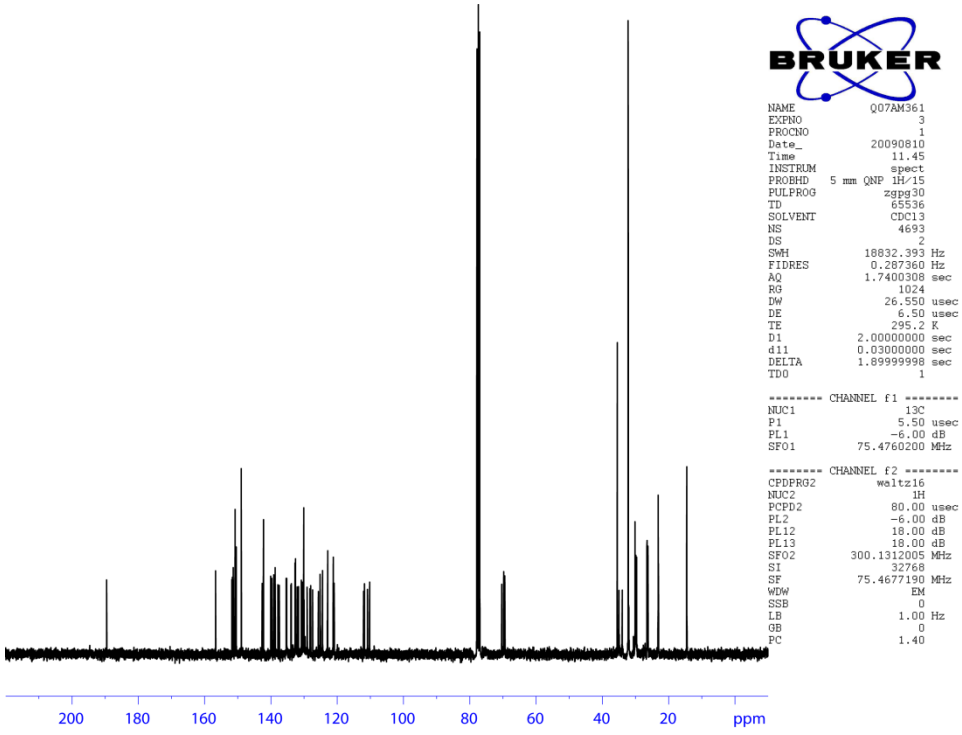


^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **5**.

Compound 7.

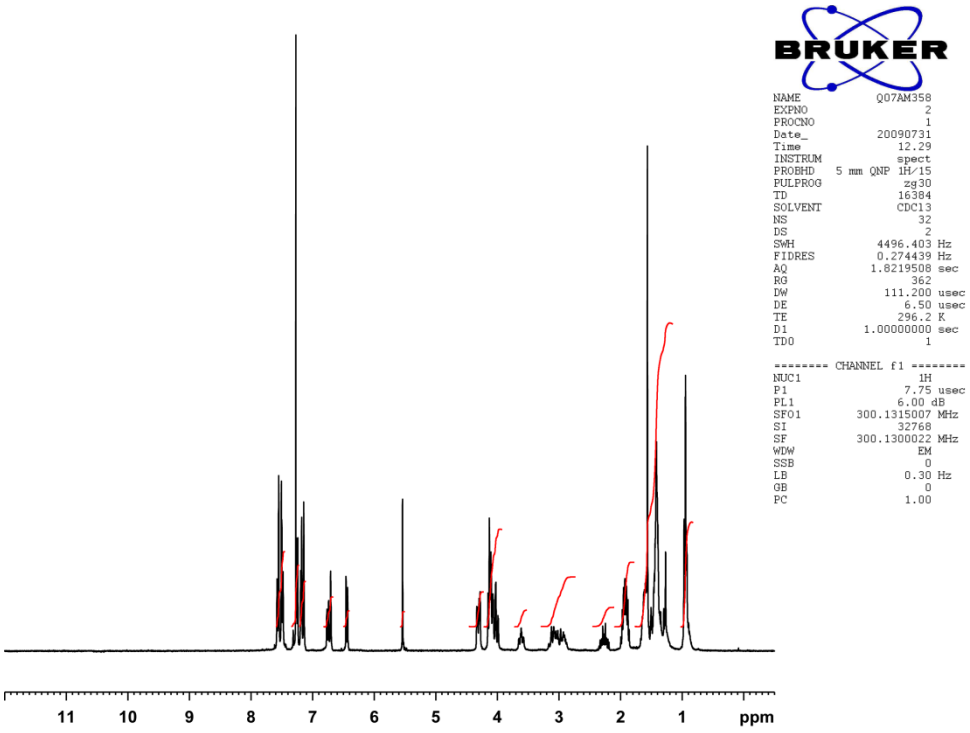


^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **7**.

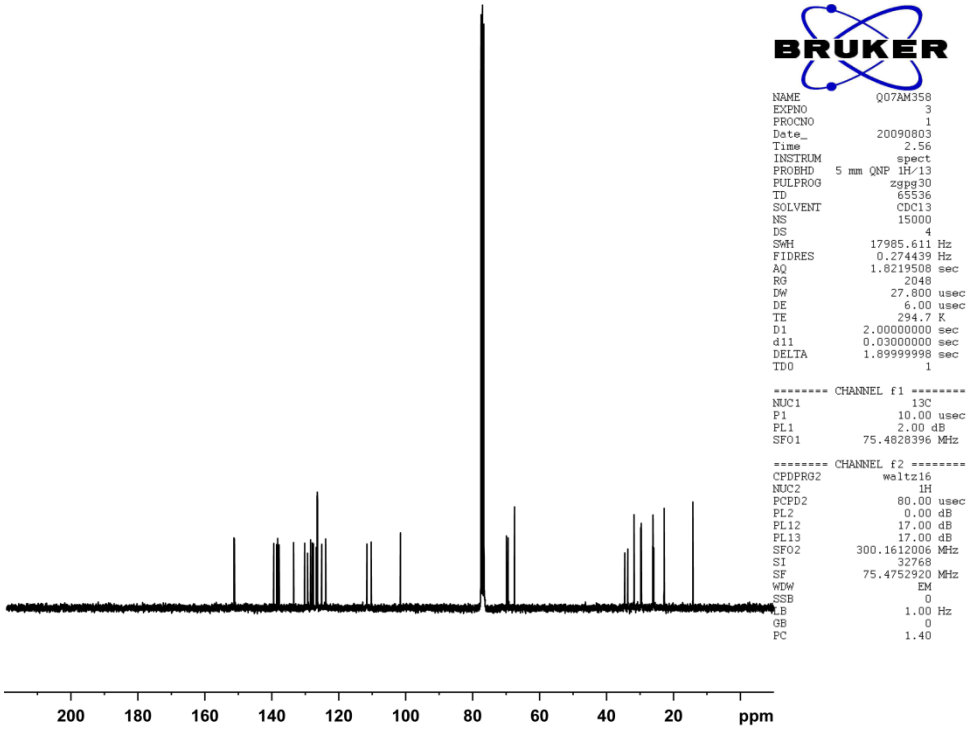


^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **7**.

Compound 9a.

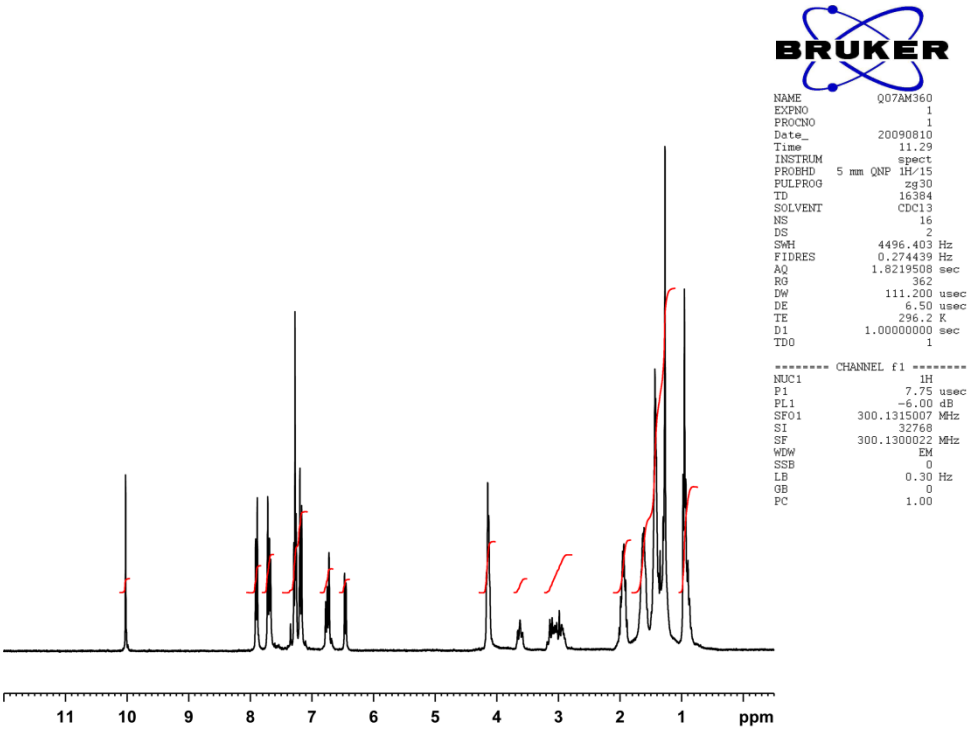


^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **9a**.

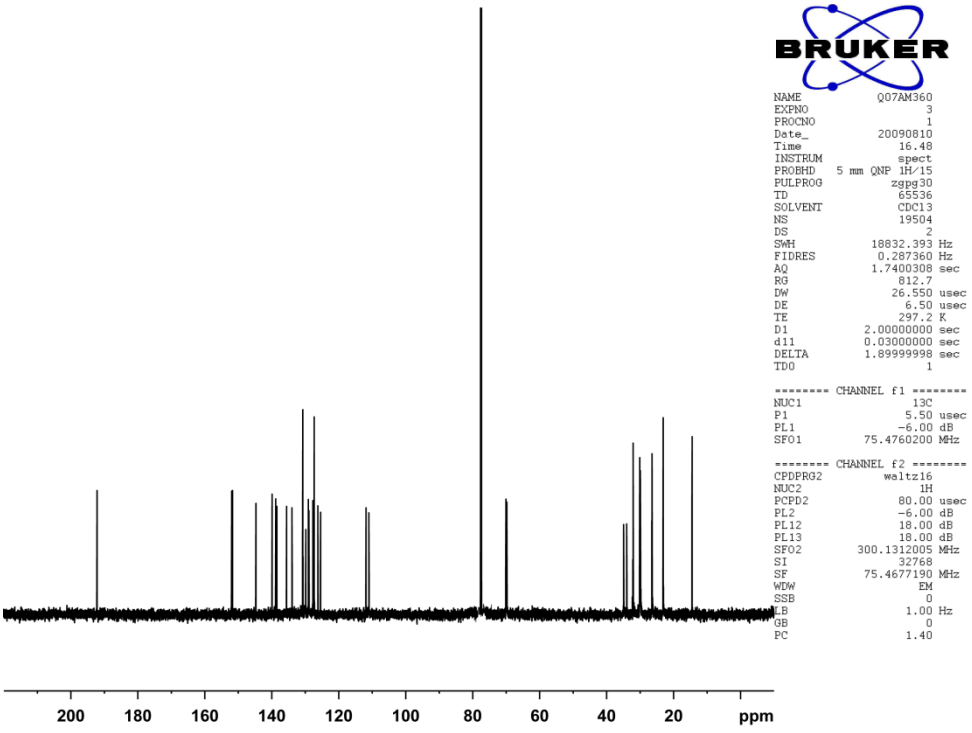


^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **9a**.

Compound 9b.

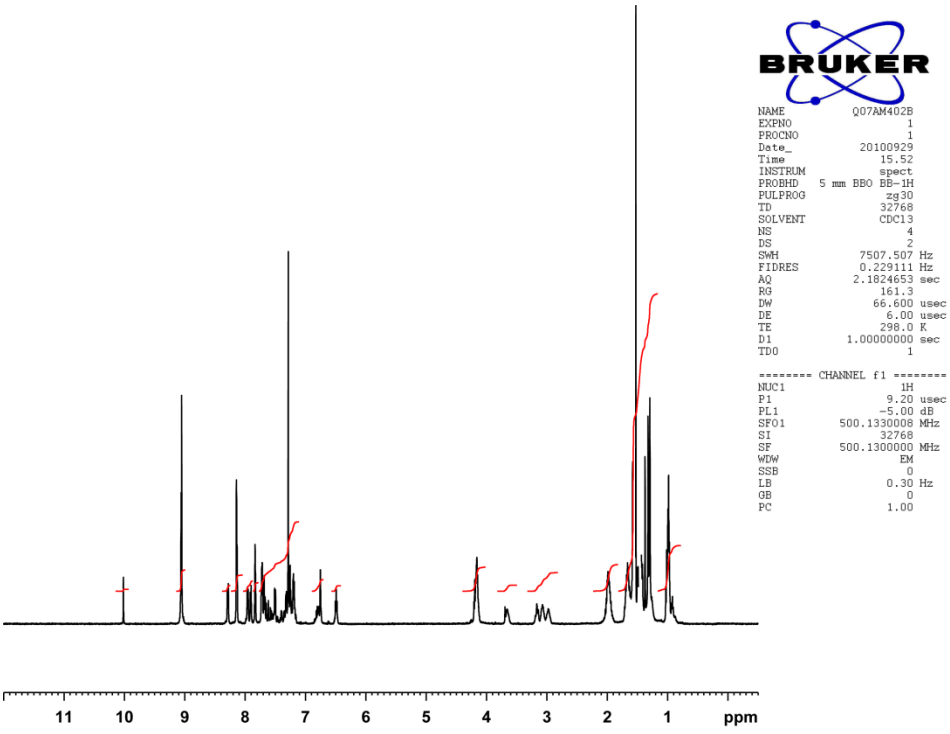


^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **9b**.

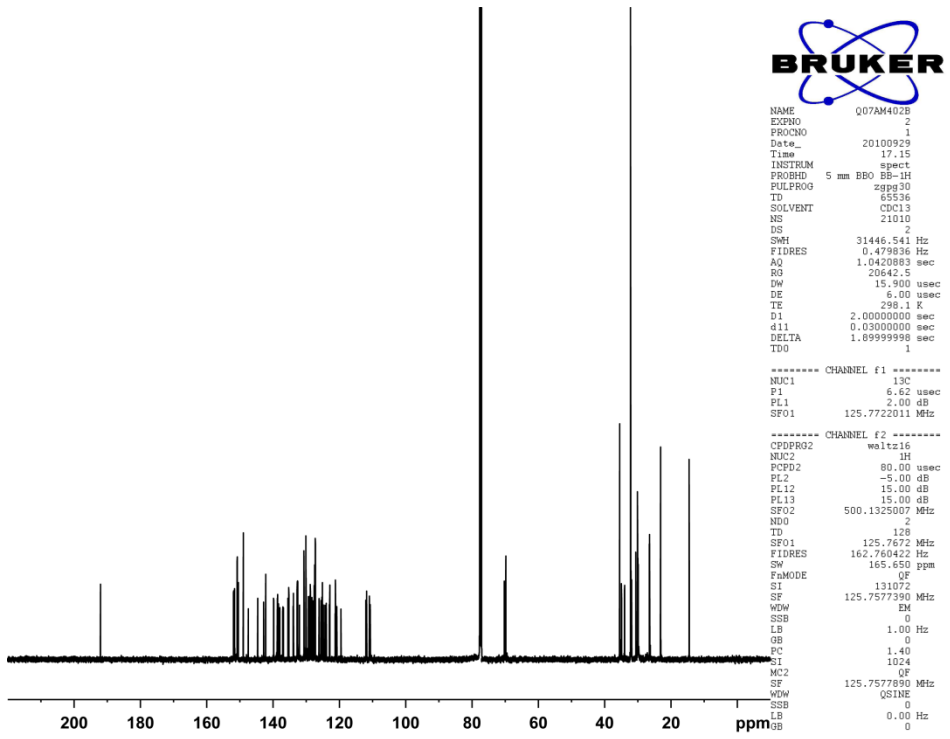


^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **9b**.

Compound 10.

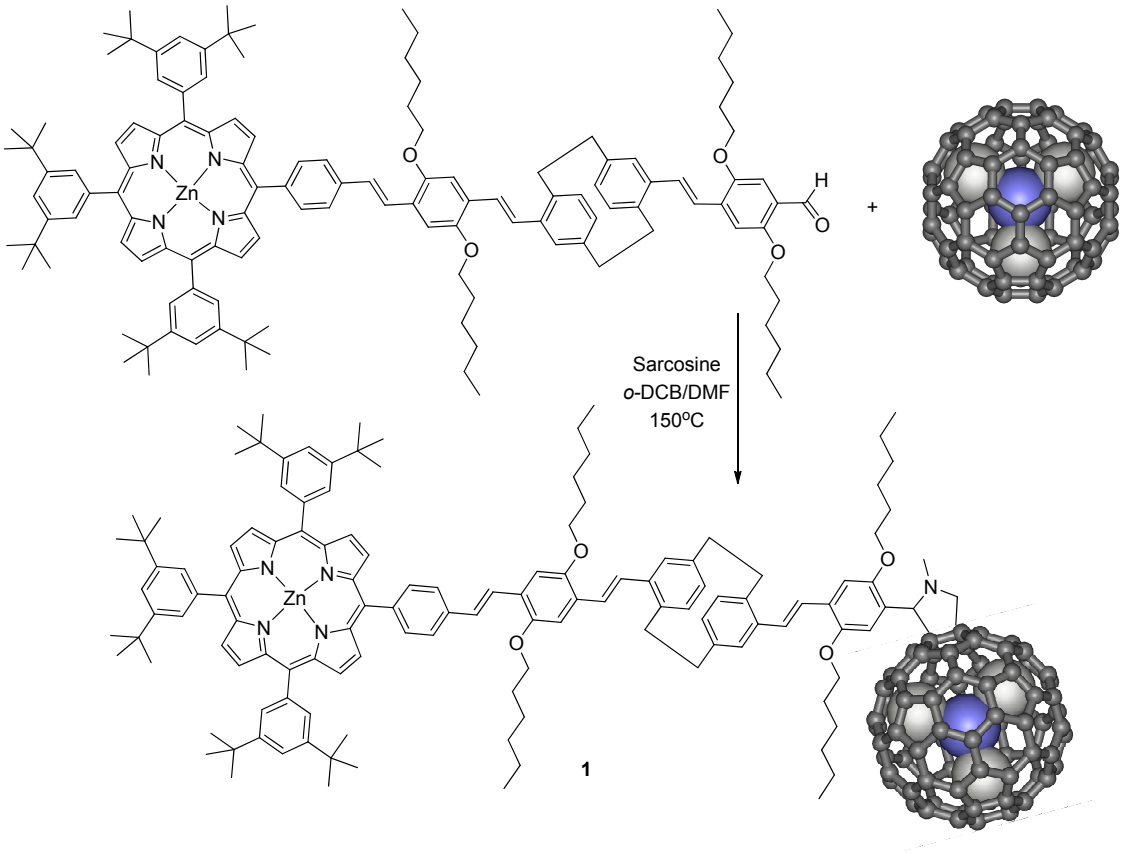


^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) of compound **10**.



^{13}C NMR ($CDCl_3$, 125 MHz, 298 K) of compound **10**.

4. Synthesis of 1.



Scheme S2. Synthesis of **1**.

10.0 mg of $Sc_3N@I_h$-C_{80} (9.01 μmol, 1 eq), 25.0 mg of aldehyde **7** (13.3 μmol, 1.5 eq) and 0.81 mg of sarcosine (9 μmol, 1 eq) was poured in a 100 mL Schlenk flask under argon. 50 mL of *o*-dichlorobenzene:DMF 4:1 solvent mixture was added. The reaction mixture was heated to 150°C while stirring for 15 minutes. The progress of the reaction was followed by TLC using silica plates eluting with CS_2 to remove the unreacted $Sc_3N@I_h$-C_{80} and a second elution with pure toluene in order to elute the product and part of the unreacted aldehyde **7**. The solvent was removed overnight under a stream of nitrogen. The remaining solid was then dissolved in CS_2 and purified on a silica gel column eluting first with CS_2 for removing the unreacted $Sc_3N@I_h$-C_{80} followed by increasing polarity mixtures of CS_2 and toluene for eluting the product and recover the unreacted aldehyde **7**. The fraction containing the product was further purified by HPLC using a PBB column (4.6 x 250 mm) eluting with toluene at 2.0 mL/min. Compound **1** has

a retention time of 9.6 min under those conditions. After evaporating the toluene and washing the remaining solid with diethyl ether, 3.2 mg of product was obtained. (11.8% yield).

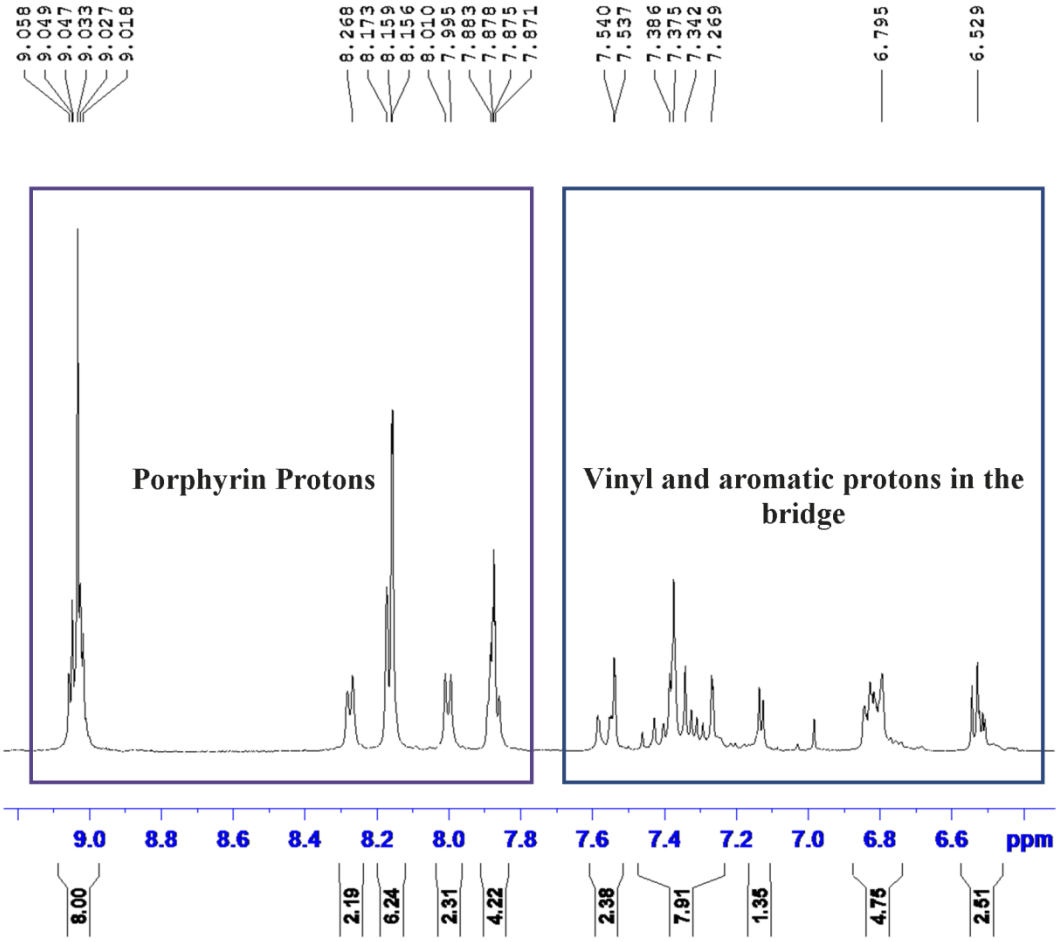


Figure S1. ^{1}H NMR spectrum of **1** (aromatic region).

^{1}H NMR (500 MHz, CS_2/Acetone-d6 external) δ: 9.1-8.95 (m, 8H, pyrrolic β-protons), 8.27 (d, 2H, J = 7.5 Hz, ArH porphyrin), 8.16 (m, 6H, ArH porphyrin), 8.00 (d, 2H, J = 7.5 Hz, ArH porphyrin), 7.88 (m, 3H, ArH porphyrin), 7.65–6.4 (m, 16H, Vinyl and/or ArH in the bridge), 4.40-4.20 (m, 9H, eight from O-CH_2 and one from the pyrrolidine ring), 4.00-3.00 (m, 10H, eight from [2,2]paracyclophane CH_2 groups a two from the pyrrolidine ring), 2.6 (s, 3H, N-CH_3), 2.03 (m, 8H, -CH_2-), 1.70 (m, 8H, -CH_2-), 1.60 (m, 54H, *t*Bu groups), 1.50 (m, 16H, -CH_2-), 1.10 (m, 12H, -CH_3). MALDI-TOF m/z: 3013.02 (negative ionization, 9-nitroanthracene as matrix).

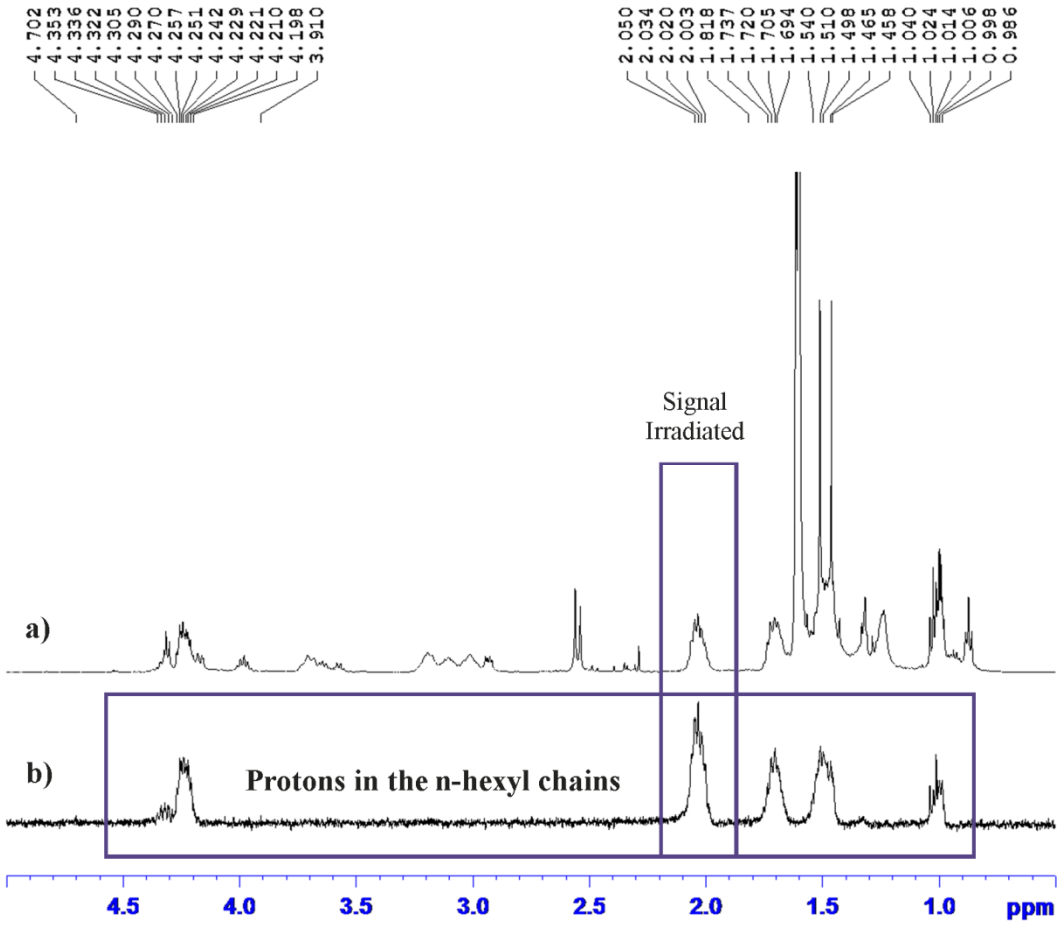


Figure S2. (a) ^{1}H NMR spectrum of **1** (aliphatic region) (b) Selective TOCSY experiment showing the signals of the n-hexyl aliphatic chains.

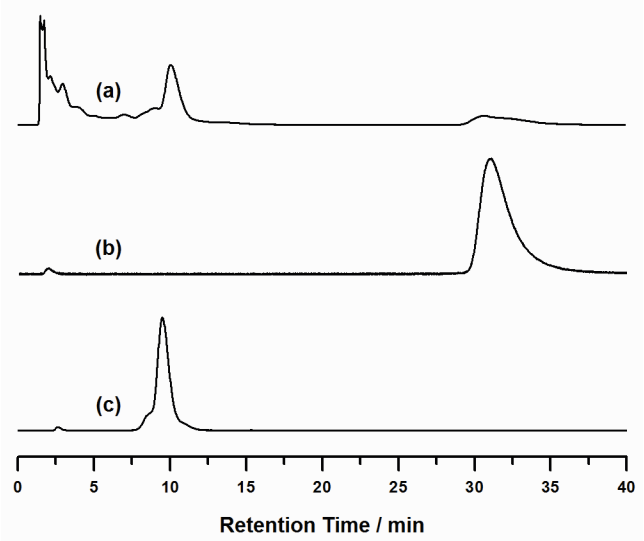


Figure S3. HPLC traces of (a) toluene fraction from the silica column (b) pure $Sc_3N@I_h$-C_{80} (c) pure **1**. PBB column (4.6 x 250 mm) – toluene 2 mL/min.

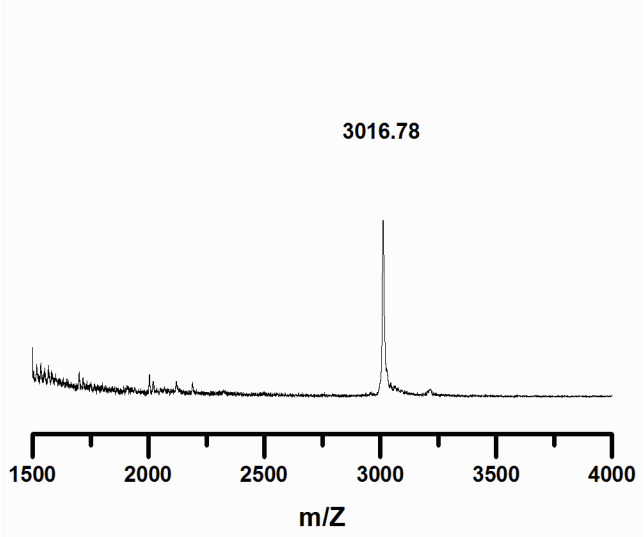


Figure S4. MALDI-TOF mass spectrum of **1**. (Negative ionization mode – 9-nitroanthracene as matrix).

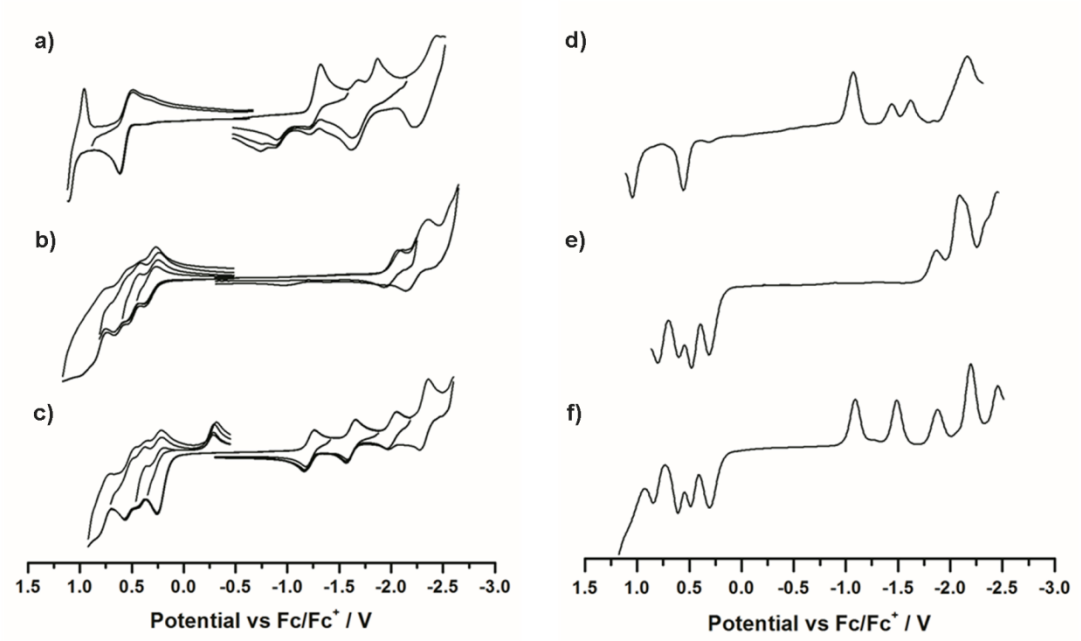
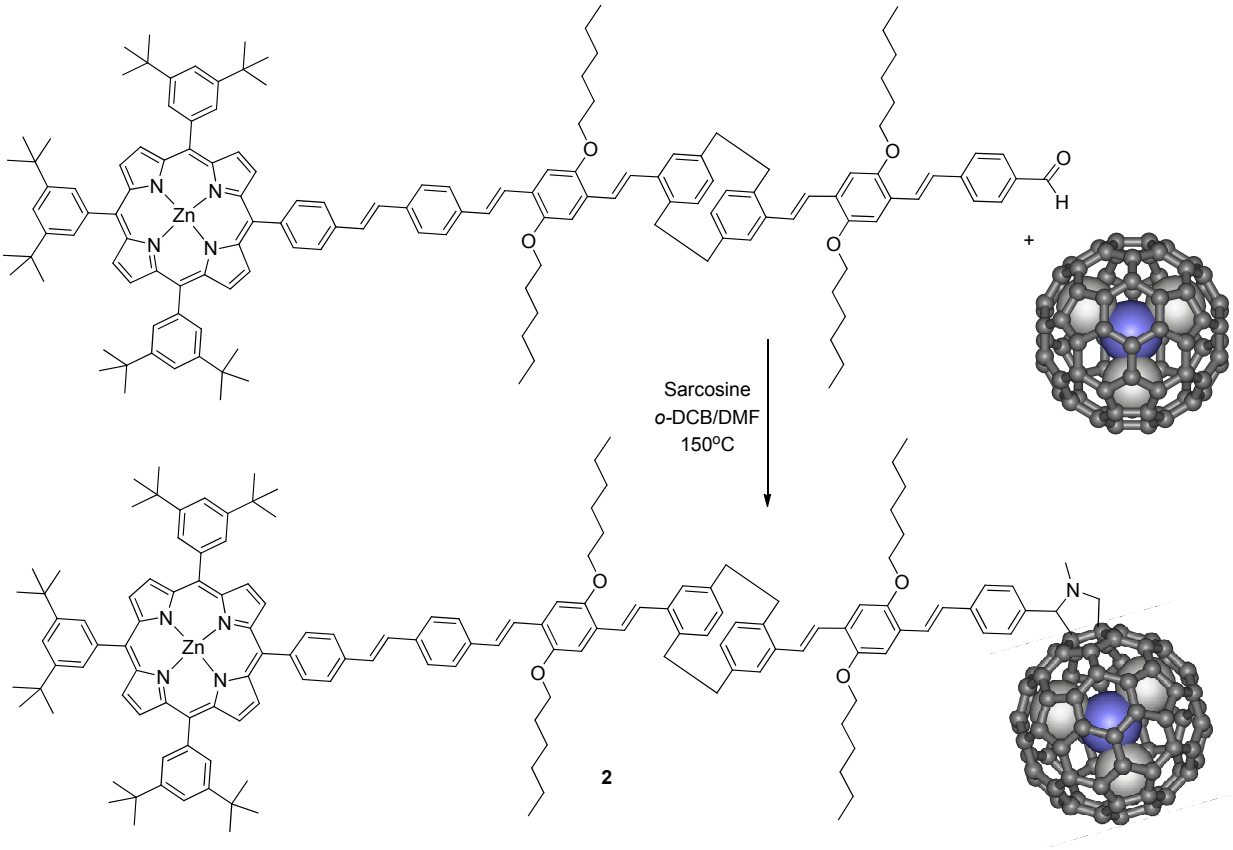


Figure S5. Left – Cyclic voltammograms of (a) $Sc_3N@I_h$-C_{80} (b) aldehyde **7** (c) pure **1**. Right - Osteryoung Square Wave Voltammetry (OSWV) of (d) $Sc_3N@I_h$-C_{80} (e) aldehyde **7** (f) pure **1**.

5. Synthesis of 2.



Scheme S3. Synthesis of **2**

8.6 mg of $Sc_3N@I_h$-C_{80} (7.75 µmol, 1 eq), 20.0 mg of aldehyde **10** (9.59 µmol, 1.23 eq) and 0.70 mg of sarcosine (7.8 µmol, 1 eq) was poured in a 50 mL Schlenk flask under argon. 25 mL of *o*-dichlorobenzene:DMF 4:1 solvent mixture was added. The reaction mixture was heated to 150°C while stirring for 3 hours. The progress of the reaction was followed by TLC using silica plates eluting with CS_2 to remove the unreacted $Sc_3N@I_h$-C_{80} and a second elution with pure toluene in order to elute the product and the unreacted **10**. After evaporating the solvent, the remaining solid was then dissolved in CS_2 and purified on a silica gel column eluting first with CS_2 for removing the unreacted $Sc_3N@I_h$-C_{80} followed by increasing polarity mixtures of CS_2 and toluene for eluting the product and recover the unreacted **10**. The fraction containing the product was further purified by HPLC using a PBB column (4.6 x 250 mm) eluting with toluene

at 2.0 mL/min. Compound **2** has a retention time of 11.4 min under those conditions. After evaporating the toluene and washing the remaining solid with diethyl ether, 2.5 mg of product was obtained. (10.0 % yield).

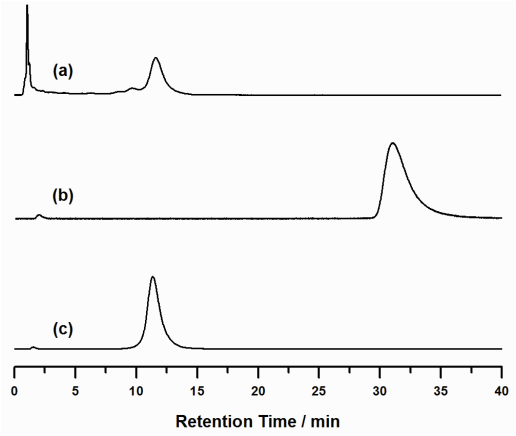


Figure S6. HPLC traces of (a) toluene fraction from the silica column (b) pure $Sc_3N@I_h$-C_{80} (c) pure **2**. PBB column (4.6 x 250 mm) – toluene 2 mL/min

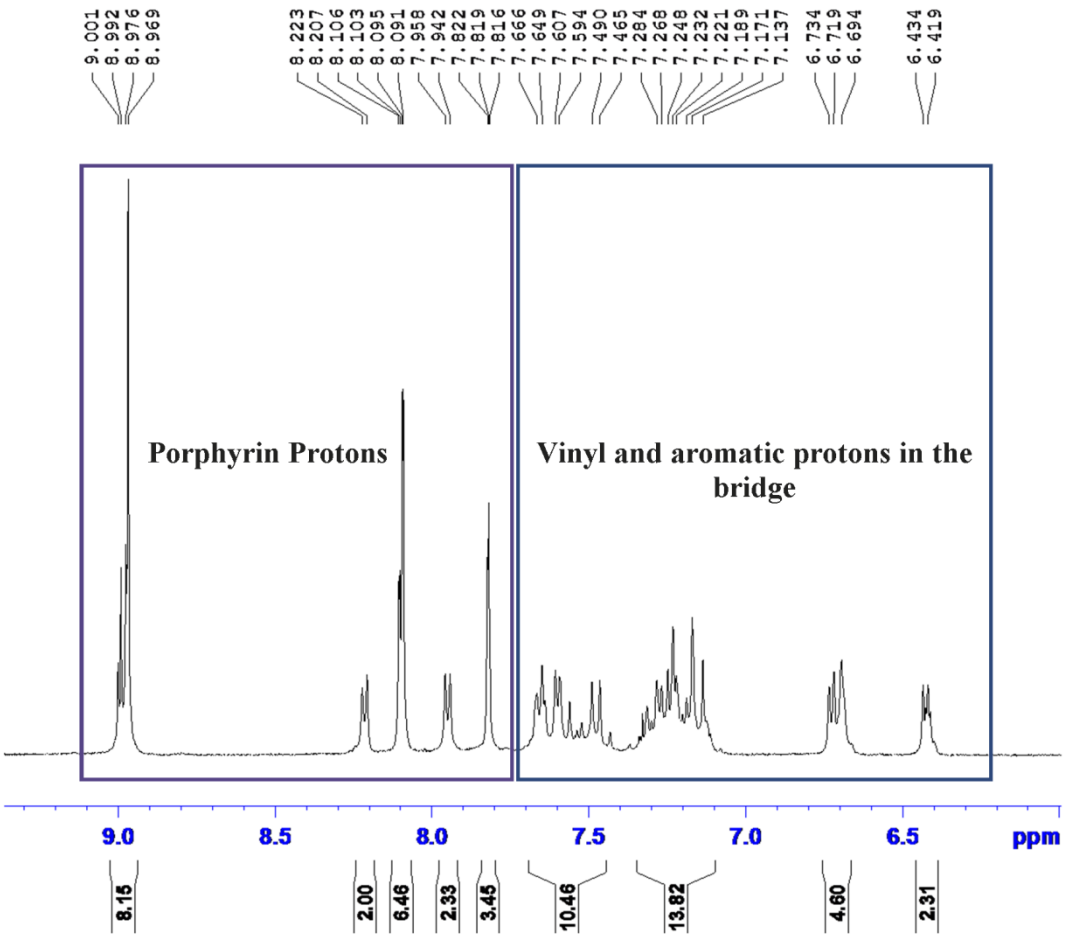


Figure S7. ^{1}H NMR spectrum of **2** (aromatic region)

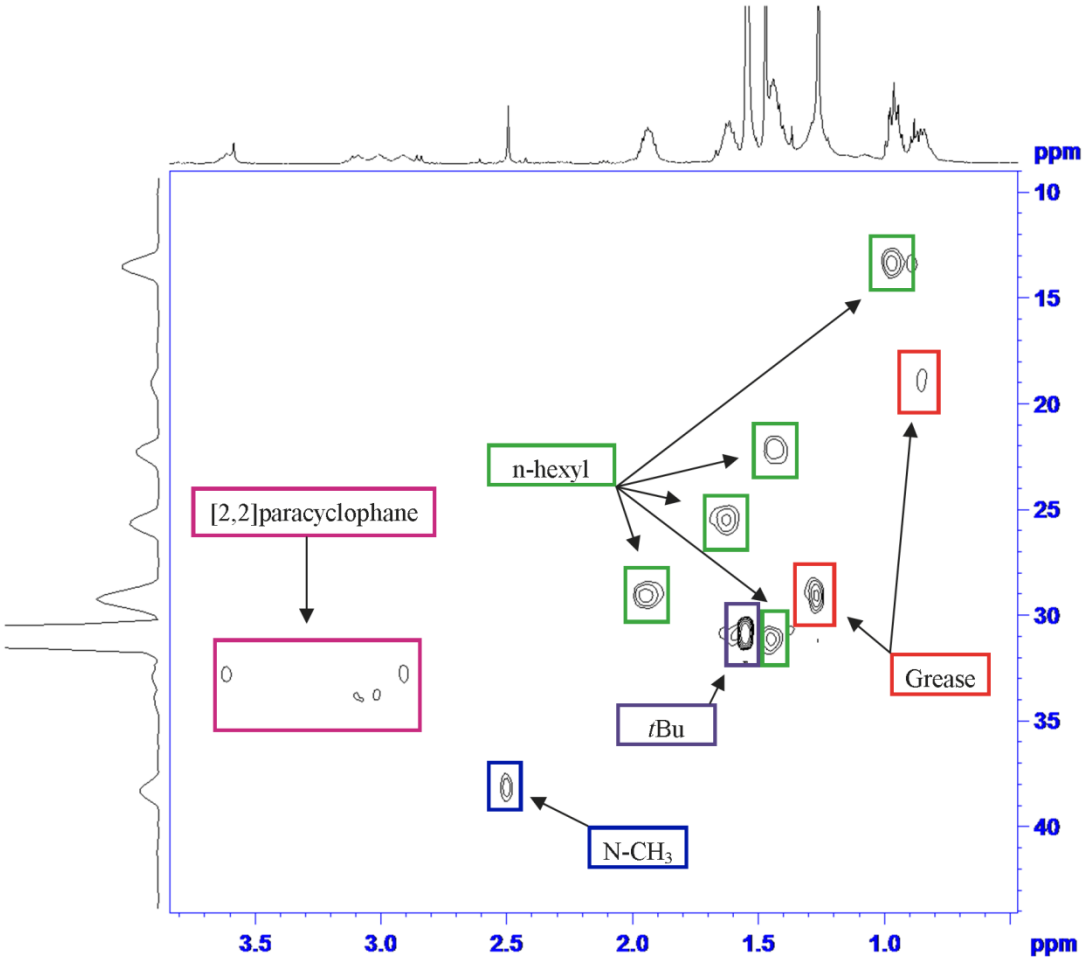


Figure S8. ^{1}H-^{13}C HSQC experiment of **2** (aliphatic region)

^{1}H NMR (500 MHz, CS_2/Acetone-d6 external) δ: 8.98 (m, 8H, pyrrolic β-protons), 8.21 (d, *J* = 7.5 Hz, 2HArH porphyrin), 8.10 (m, 6H, ArH porphyrin), 7.95 (d, *J* = 7.5 Hz, 2H, ArH porphyrin), 7.82 (m, 3H, ArH porphyrin), 7.70–7.40 (m, 10H, Vinyl and/or ArH in the bridge), 7.39–7.00 (m, 12H, Vinyl and/or ArH in the bridge), 6.8 (br, 4H, Vinyl and/or ArH in the bridge), 6.42 (m, 2H, Vinyl and/or ArH in the bridge), 4.20-4.00 (m, 9H, eight from O-CH_2 and one from the pyrrolidine ring), 3.70–2.80 (m, 10H, eight from [2,2]paracyclophane CH_2 groups a two from the pyrrolidine ring), 2.49 (s, 3H, N-CH_3), 1.93 (m, 8H, -CH_2-), 1.62 (m, 8H, -CH_2-), 1.54 (m, 54H, *t*Bu groups), 1.40 (m, 16H, -CH_2-), 1.07 (m, 12H, -CH_3). MALDI-TOF m/z: 3221.04 (negative ionization, 9-nitroanthracene as matrix).

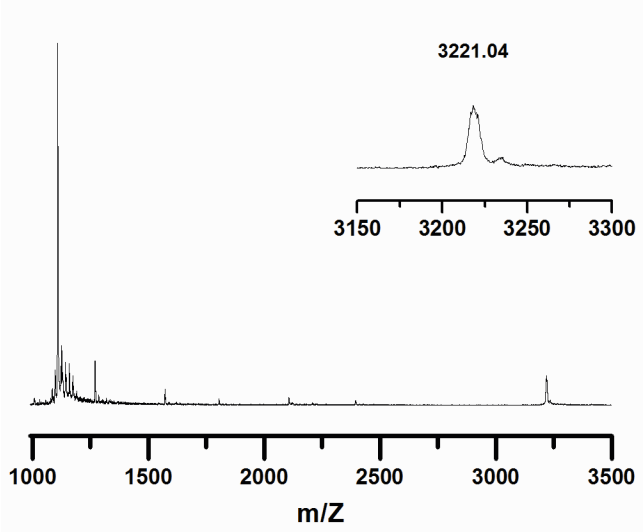


Figure S9. MALDI-TOF mass spectrum of **2** (Negative ionization mode – 9-nitroanthracene as matrix).

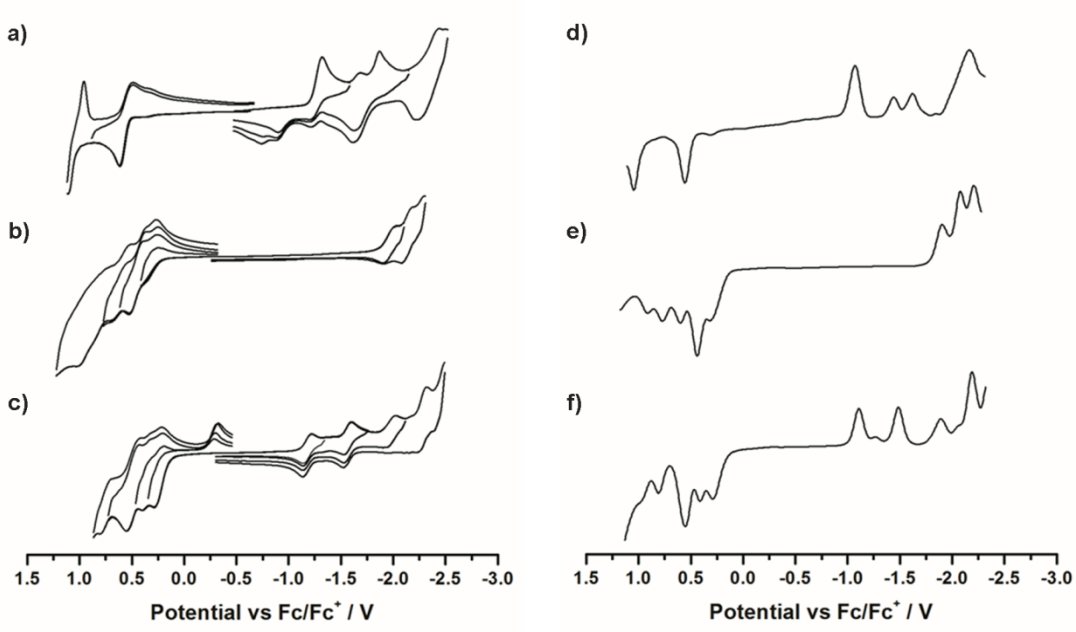


Figure S10. Left – Cyclic voltammograms of (a) $Sc_3N@I_h$-C_{80} (b) aldehyde **10** (c) pure **2**. Right - Osteryoung Square Wave Voltammetry (OSWV) of (d) $Sc_3N@I_h$-C_{80} (e) aldehyde **10** (f) pure **2**.

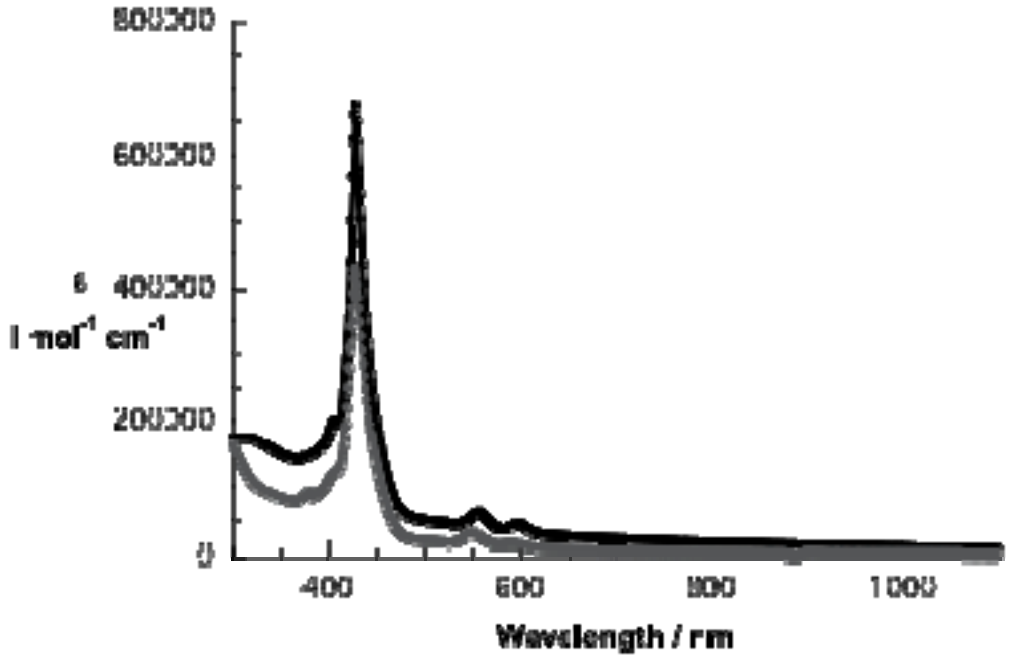


Figure S11 – Absorption spectra of **2** in THF (black spectrum) and **2** in toluene (grey spectrum).

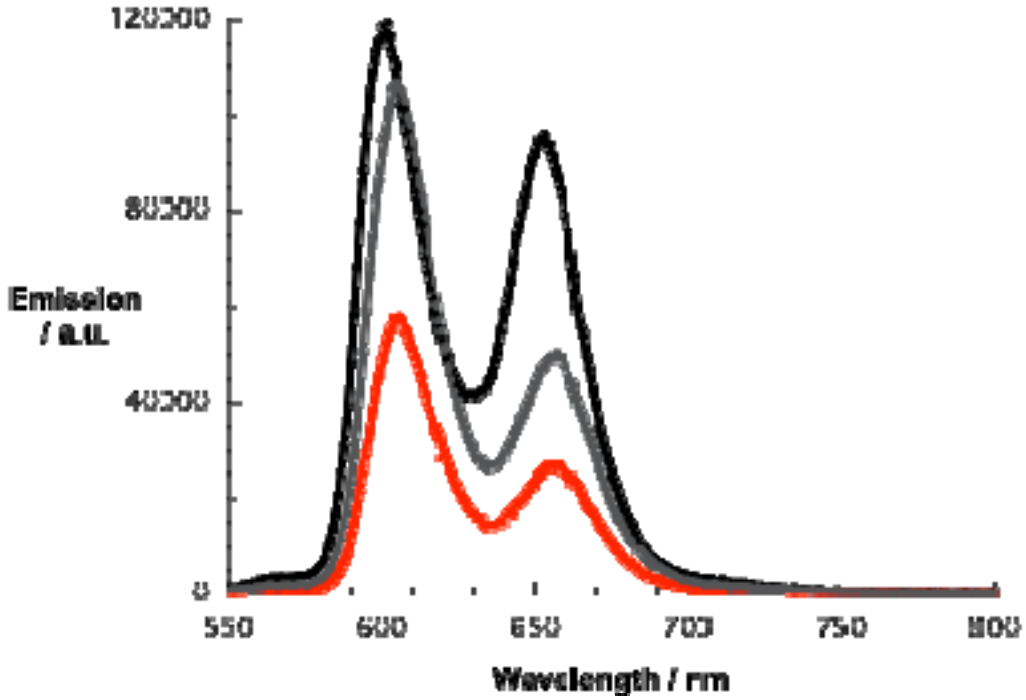


Figure S12 – Room temperature fluorescence spectra of ZnP (black spectrum), **2** (grey spectrum), and **1**(red spectrum) in THF exhibiting the same optical density of 0.05 at the 420 nm excitation wavelength.

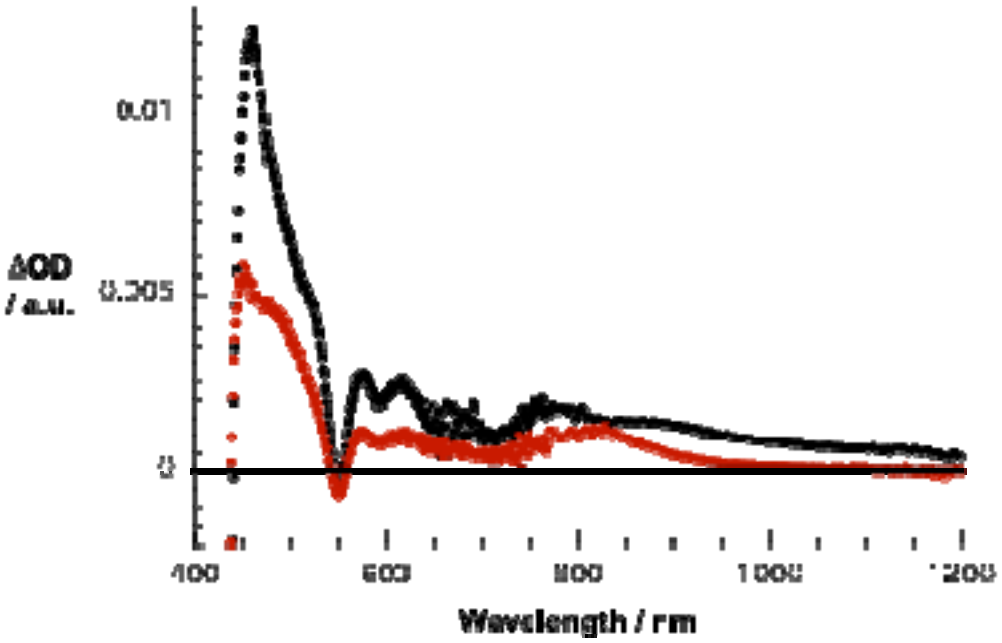


Figure S13 – Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm, 150 nJ) of ZnP in toluene with time delays of 5 ps (black spectrum) and 3000 ps (red spectrum) at room temperature.

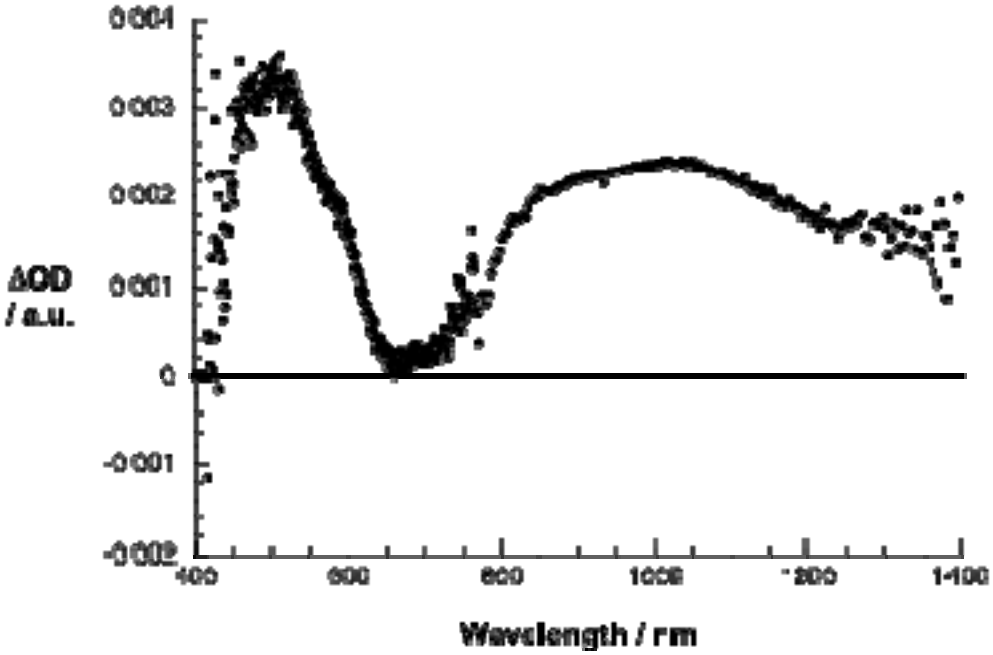


Figure S14 – Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm, 150 nJ) of $Sc_3N@C_{80}$ in toluene with a time delays of 5 ps at room temperature.