Supporting Information

Interfacing porphyrins and carbon nanotubes through mechanical links

Synthesis and characterization

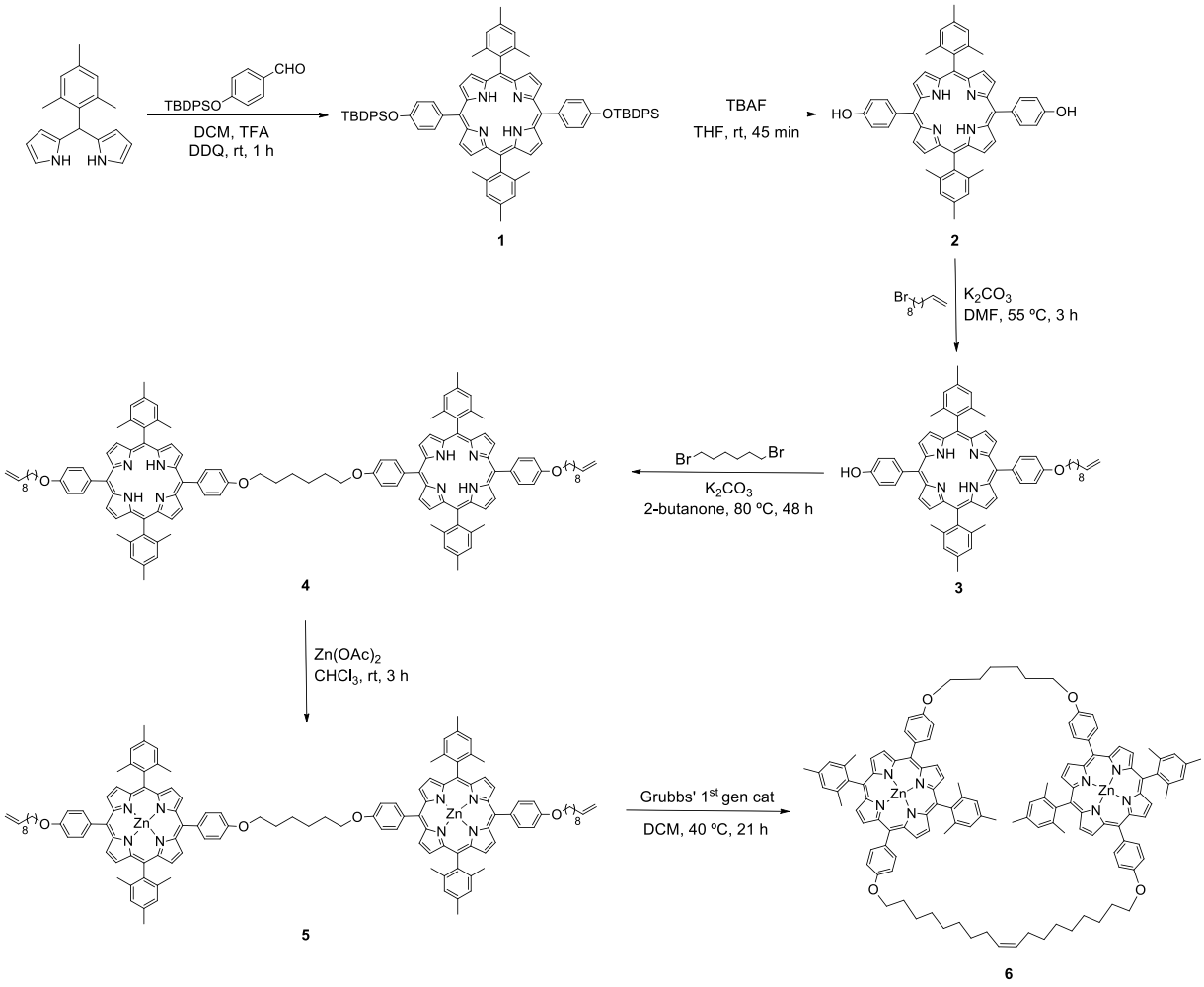
General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Column chromatography was performed using silica gel (Scharlau 60, 70-230 mesh) or aluminium oxide (Merck 90, standardized). Analytical thin layer chromatographies (TLC) were performed using aluminium-coated Macherey-Nagel silica gel 60 F254 plates or aluminium-coated Macherey-Nagel aluminium oxide F254 plates. NMR spectra were recorded on a BrukerAvance 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz) spectrometer at 298 K, unless otherwise stated, 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, b = broad. Fast atom bombardment (FAB) and matrix-assisted laser desorption ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a VG AutoSpec spectrometer and a Bruker REFLEX spectrometer, respectively. Thermogravimetric analyses (TGA) were performed using a TA Instruments TGAQ500 with a ramp of 10 °C/min under air from 100 to 1000 °C. UV-vis-NIR spectrums were performed using a Cary 5000 spectrometer (Varian) and 10x10 mm quarz cuvettes. Photoluminescence excitation intensity maps (PLE) were obtained with a FluoroLog 3 spectrometer from HORIBA Yobin Yvon using a 450 W Xenon lamp and a Symphony InGaAs array in combination with an iHR320 imaging spectrometer. For the visible range, a Fluoromax3 spectrometer from HORIBA Yobin

Yvon was used. Femtosecond transient absorption measurements were performed with the transient absorption pump probe system HELIOS from Ultrafast Systems. For the generation of laser pulses with a pulse width of 150 fs a CPA-2110 titanium:sapphire laser system from Clark-MXR Inc was used (output 775 nm, 1 kHz). The 420 nm excitation pulses were generated by using a noncollinear optical parametric amplifier (NOPA, Clark MXR). All pump probe measurements were carried out in 2 mm OS quarz cuvettes. Raman spectra were acquired with a WiTec alpha300r confocal Raman microscope. Samples were deposited onto silica wafers by drop casting. A HeNe Laser with an output of 633 nm was used for sample excitation. Atomic force microscopy (AFM) images were obtained with JPK NanoWizard II instrument, coupled to an inverted optical microscope Nikon Eclipse Ti-U. High resolution-transmission electron microscopy (HR-TEM) images were obtained in an imaging aberration corrected microscope JEM GRAND ARM300cF JEOL, operating at 60 kV in order to minimize the electron beam damage. Images were recorded on a slow-CCD camera GATAN Oneview. The optimized structure of **MINT-por** has been obtained using the Grimme's 3-corrected Hartree-Fock method (HF-3c). A quantum chemical method based on a Hartree-Fock calculation with a small Gaussian AO basis set present. This methodology has been developed to apply HF calculation to large systems. The main idea is to correct for some of the systematic deficiencies of a small basis Hartree-Fock calculation (instead of approximating HF) and use as a very fast QM method. It is also in many ways a better alternative to a minimal basis DFT method as there is no numerical integration involved. HF-3c has been defined for elements H-Xe with ECPs automatically used for the heavier elements.[1]

Experimental fine-tuning of the U-shape.

It should be noted that the chemical structure of the **U-por** is a bit different with respect to our previous U-shaped molecules used in the synthesis of MINTs. Specifically in the spacer between the two recognition units. In our previous samples, we linked the recognition units through a 1,4-xylylene spacer.[2] However, using these porphyrin units as recognition motifs for SWCNTs, we observed that the macrocycle cannot be formed, probably due to the unexpected rigid behavior for the aromatic spacer, since C_{10}, C_{14} and C_{18} alkenyl spacers were tested. For this reason, and in order to increase the flexibility of the ring, we used an alkyl spacer of similar size, 1,6-dibromohexane, to synthesize the **U-por**, succeeding in this way with the synthesis of the corresponding **mac-por**.

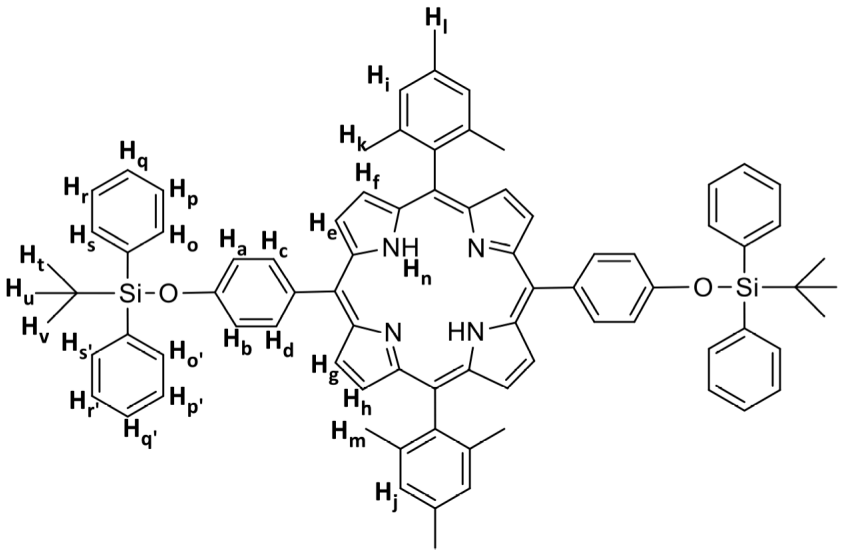
Also, it is important to note that the sterically demanding 2,4,6-trimethylphenyl moiety present as a substituent of the bis(1*H*-pyrrole)methane was deliberately chosen due to its ability to afford *meso* substituted porphyrins without scrambling, thus avoiding the formation of a complicated mixture of porphyrins.



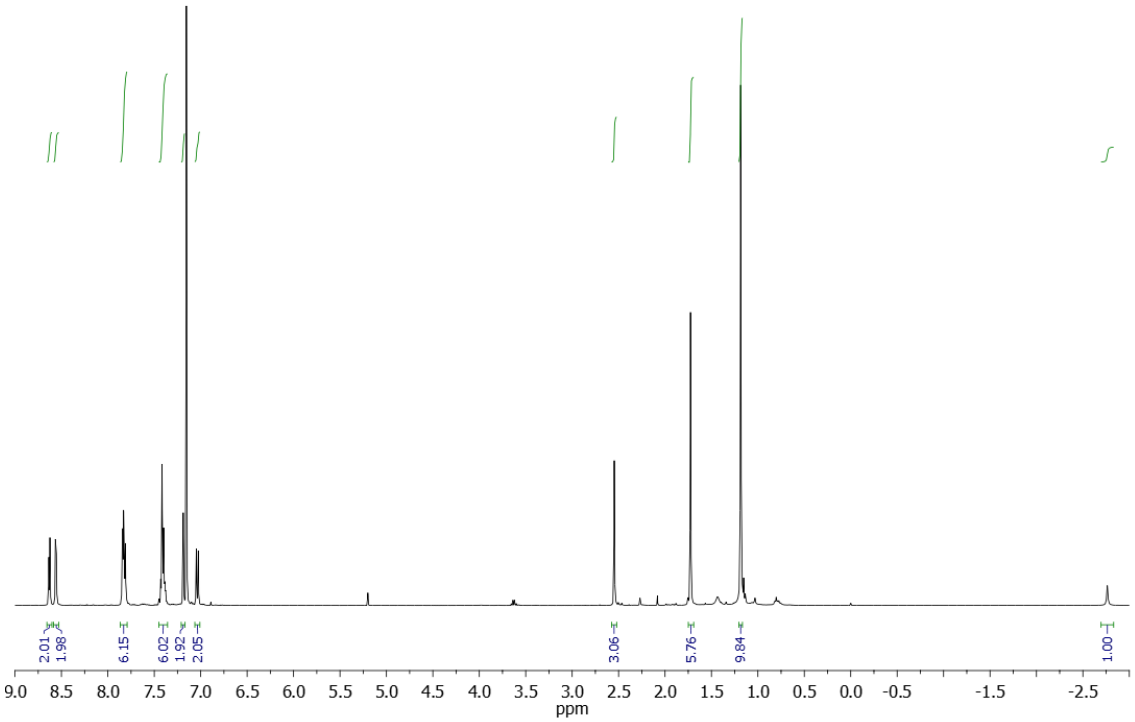
General scheme of synthesis of mac-por.

Synthesis of compound **1**. 5-mesityldipyrromethane (300 mg, 1.14 mmol) and 4-((tert-butyldiphenylsilyl)oxy)benzaldehyde (409 mg, 1.14 mmol) were dissolved in DCM (120 mL), and then TFA (163 μL, 2.12 mmol) was added slowly. The reaction was stirred at room temperature. After 30 min, DDQ (258 mg, 1.14 mmol) was added, and the reaction mixture was stirred at room temperature for a further 1 h. The complete reaction mixture was poured onto a pad of alumina and eluted with DCM until the eluting solution was pale brown. The solvent was removed under vacuum to give a dark solid which was dissolved in toluene (30 mL) and heated under reflux for 1 h in the

presence of DDQ (258 mg, 1.14 mmol) to oxidize any remaining chlorin. After cooling to room temperature, the solvent was removed under vacuum and the crude product was purified by column chromatography (aluminium oxide, hexane/toluene 7:3). Removal of the solvent under vacuum gave a purple solid. The compound **1** (296 mg, 43%) was characterized by ^{1}H, ^{13}C -NMR, MALDI and UV/vis.



Compound **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 4.7 Hz, 2H, $H_{e,f}$), 8.56 (d, J = 4.7 Hz, 2H, $H_{g,h}$), 7.88 – 7.78 (m, 6H, $H_{c,d,o,o',p,p'}$), 7.47 – 7.36 (m, 6H, $H_{q,q',r,r',s,s'}$), 7.19 (s, 2H, $H_{i,j}$), 7.04 (d, J = 8.5 Hz, 2H, $H_{a,b}$), 2.55 (s, 3H, H_l), 1.73 (s, 6H, $H_{k,m}$), 1.19 (s, 9H, $H_{t,u,v}$), -2.76 (s, 1H, H_n). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 139.5, 138.6, 137.7, 135.8, 135.3, 134.9, 133.1, 130.1, 127.9, 127.7, 119.1, 118.3, 118.0, 29.7, 26.7, 21.6, 19.7. MS m/z: calculated for $C_{82}H_{78}N_4O_2Si_2[M+H]^+$ 1207.6, found MALDI 1207.6. λ_{abs} ($CHCl_3$) 421, 518, 553, 593, 648 nm.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6.02
1.92
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5.76
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1.00
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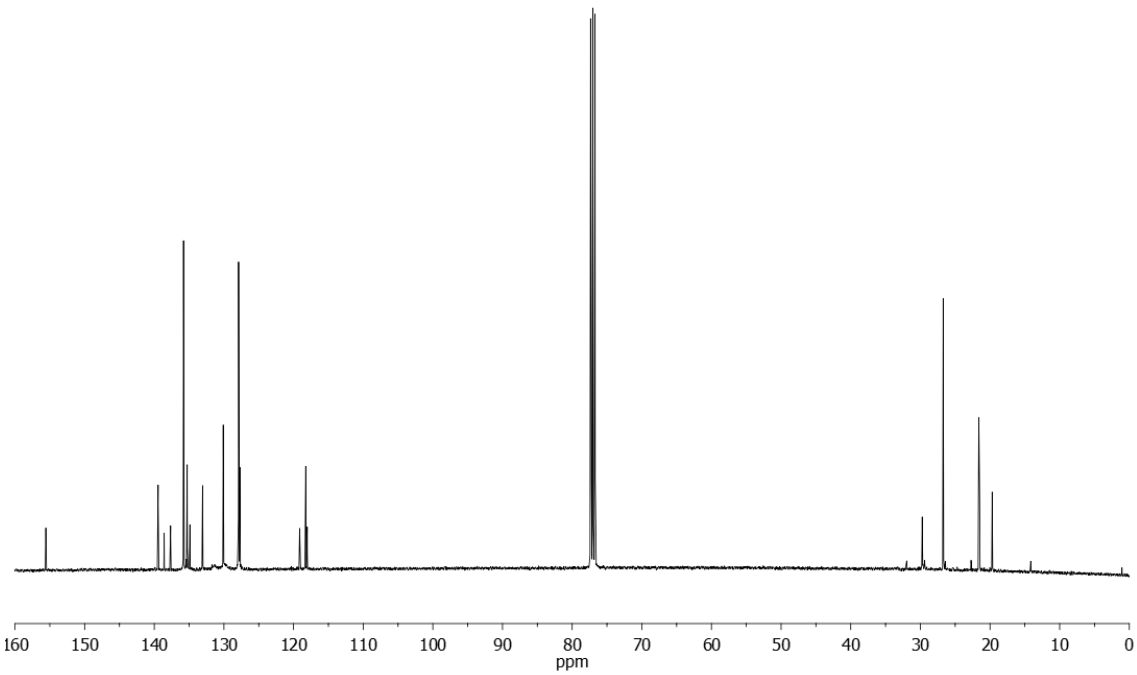
ppm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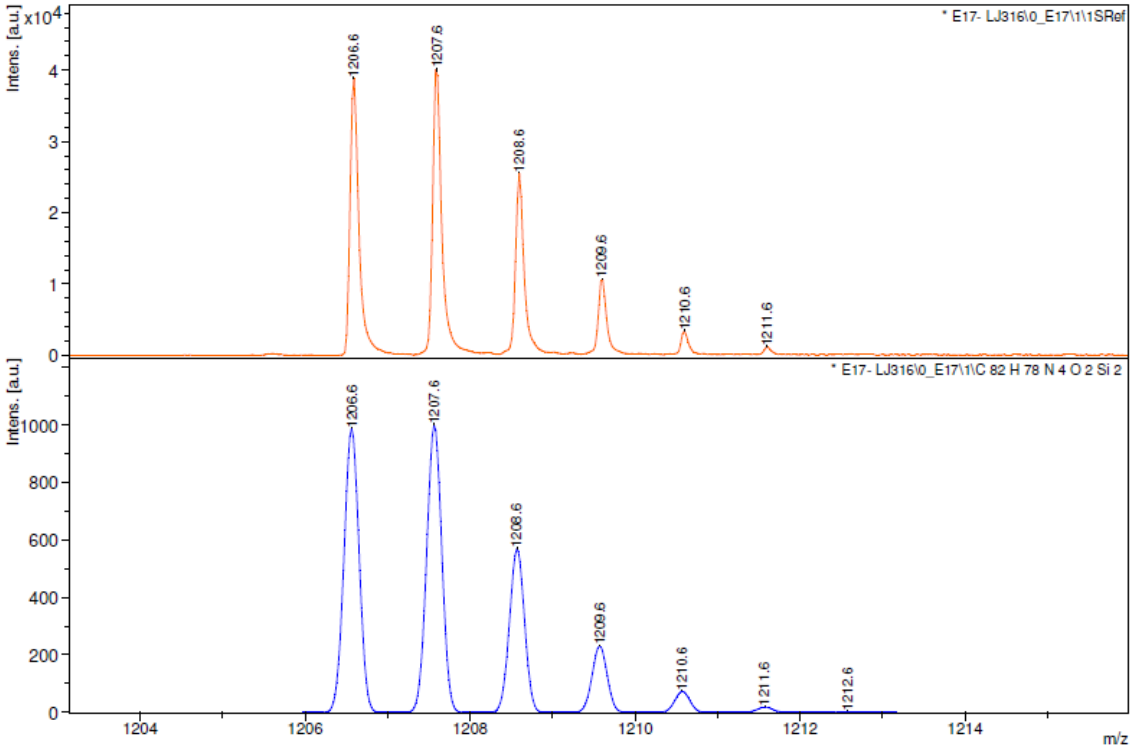
ppm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3
2
1
0
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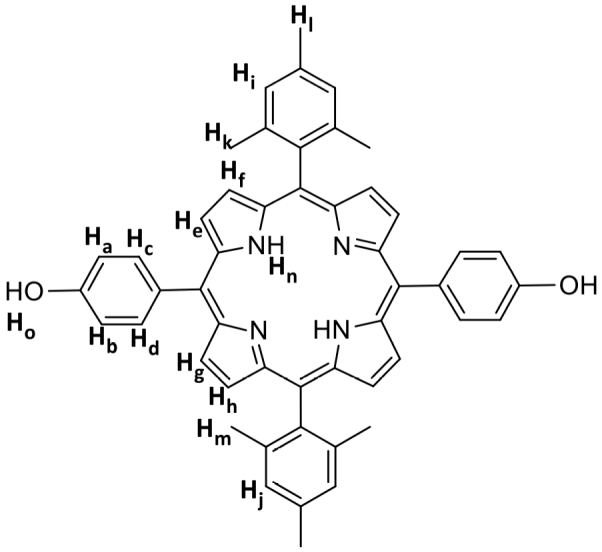
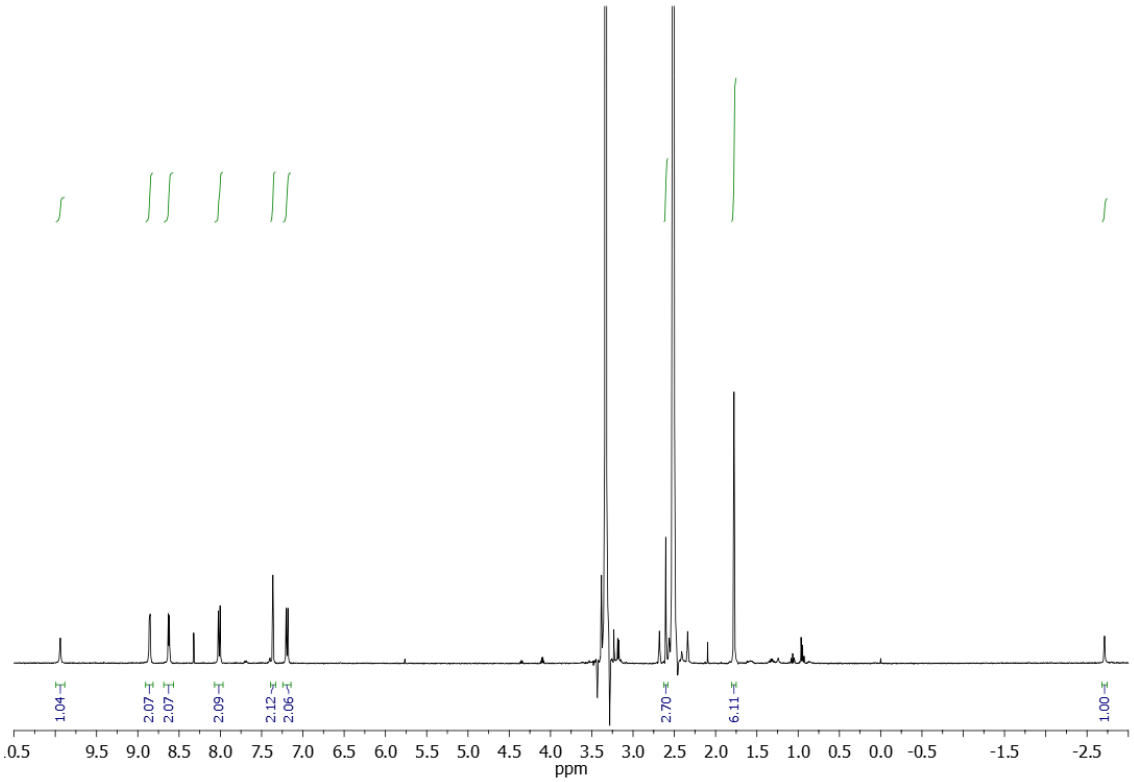
1207.6
1208.6
1209.6
1210.6
1211.6
* E17- LJ316\0_E17\1\C 82 H 78 N 4 O 2 Si 2
Intens. [a.u.]
1000
800
600
400
200
0
1206.6
1207.6
1208.6
1209.6
1210.6
1211.6
1212.6
1204
1206
1208
1210
1212
1214
m/z

Synthesis of compound **2**. Compound **1** (292 mg, 0.24 mmol) was dissolved in THF (100 mL), and tetrabutylammonium fluoride (1.0 M in THF) (350 μL, 1.21 mmol) was added at room temperature. After completion of the reaction, the solution was hydrolyzed with water and extracted with DCM. The organic phase was washed with brine, dried over $MgSO_4$, filtered and solvents were removed by evaporation under vacuum. The crude was washed with cold hexane and filtered, getting a purple solid. The compound **2** (177 mg, 99%) was characterized by ^{1}H, ^{13}C -NMR, FAB and UV/vis.



Compound **2**. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.94 (s, 1H, H_o), 8.86 (d, J = 4.7 Hz, 2H, $H_{e,f}$), 8.62 (d, J = 4.7 Hz, 2H, $H_{g,h}$), 8.01 (d, J = 8.5 Hz, 2H, $H_{c,d}$), 7.36 (s, 2H, $H_{i,j}$), 7.19 (d, J = 8.5 Hz, 2H, $H_{a,b}$), 2.60 (s, 3H, H_l), 1.78 (s, 6H, $H_{k,m}$), -2.71 (s, 1H, H_n). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.9, 138.9, 138.3, 137.9, 136.8, 135.9, 134.9, 129.6, 128.7, 128.3, 127.9, 120.1, 117.9, 114.4, 27.0, 21.6. MS m/z: calculated for $C_{50}H_{42}N_4O_2[M]^+$ 730.3, found FAB+ 730.9. λ_{abs} (DMSO) 422, 518, 554, 595, 650 nm.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2.07
2.07
2.09
2.12
2.06
2.70
6.11
1.00
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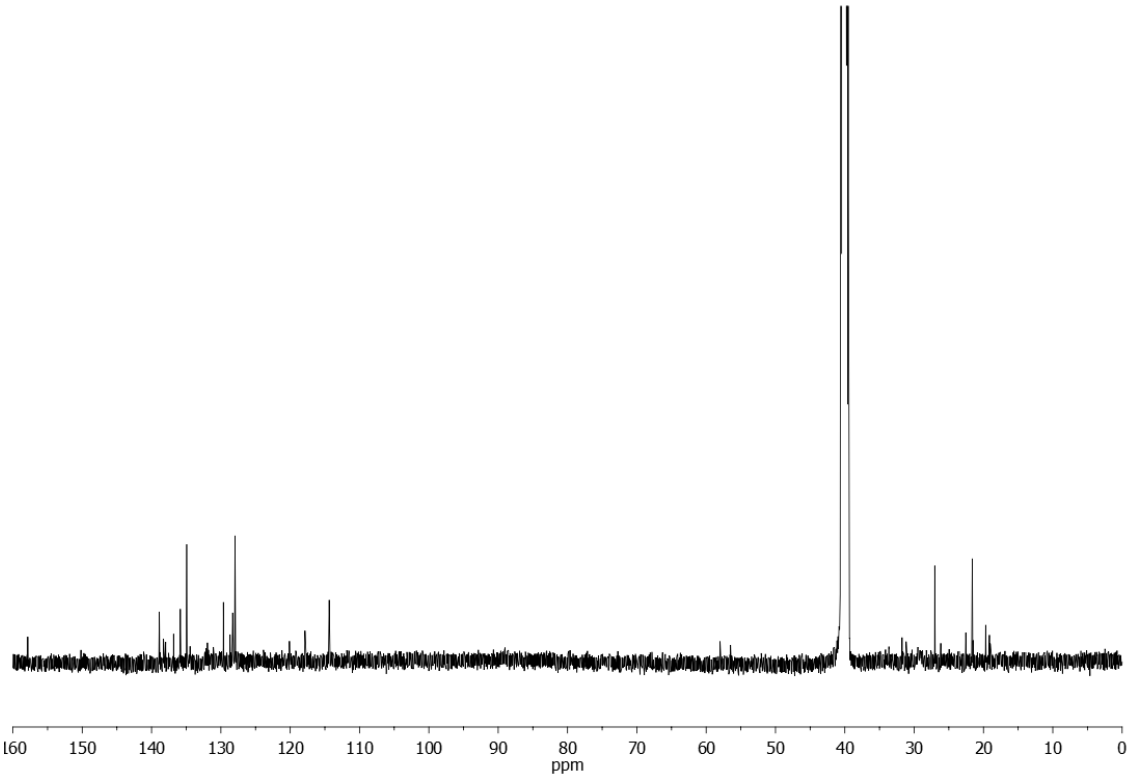
ppm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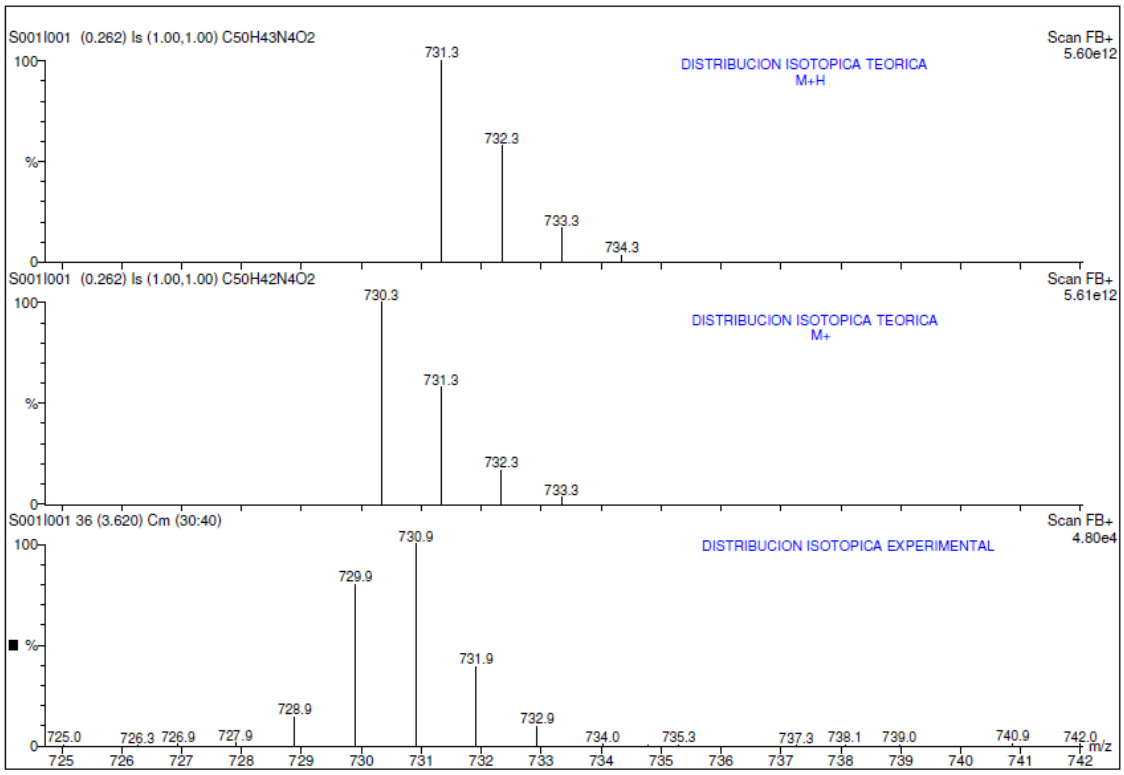
ppm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5.60e12
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731.3
732.3
733.3
734.3
S001I001 (0.262) Is (1.00,1.00) C50H42N4O2
Scan FB+
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DISTRIBUCION ISOTOPICA TEORICA
M+
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731.3
732.3
733.3
S001I001 36 (3.620) Cm (30:40)
Scan FB+
4.80e4
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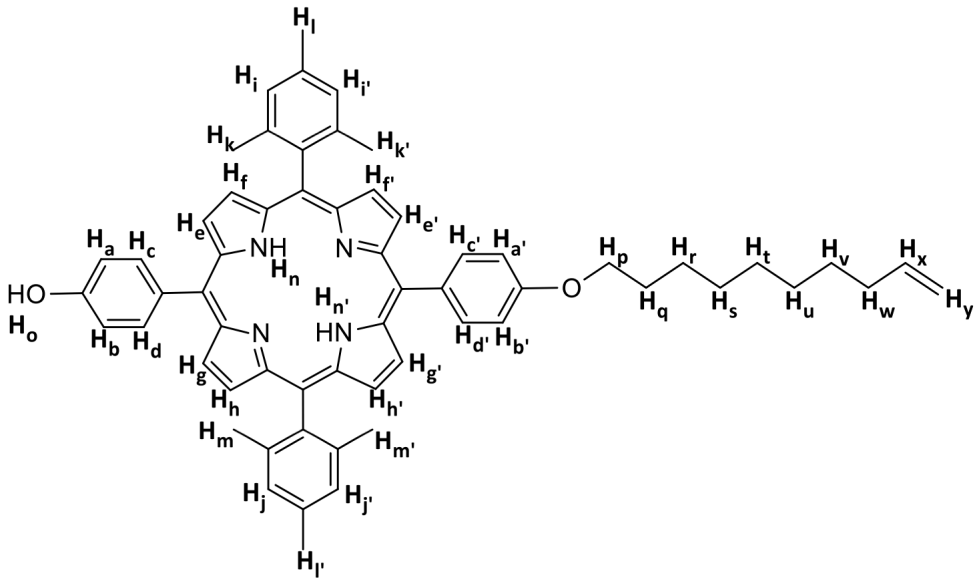
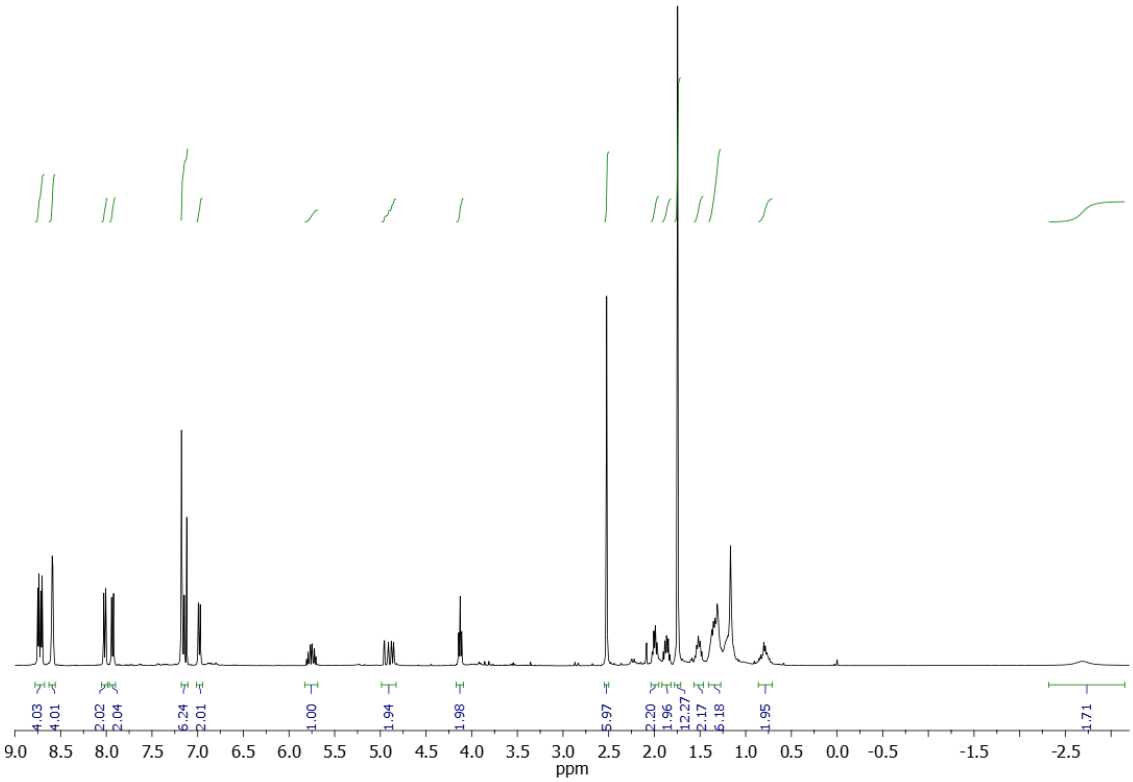
729.9
731.9
728.9
732.9
725.0
726.3
726.9
727.9
734.0
735.3
737.3
738.1
739.0
740.9
742.0
m/z

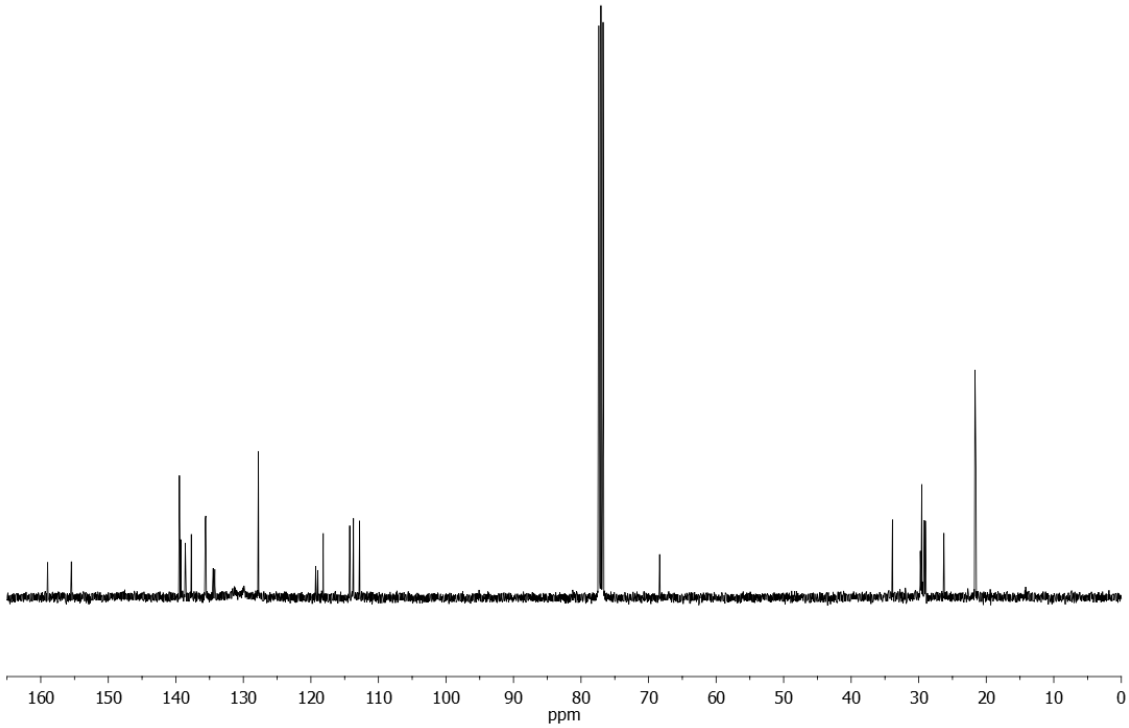
Synthesis of compound **3**. Compound **2** (411 mg, 0.56 mmol) was dissolved in dry DMF (110 mL) under Ar, and dry K_2CO_3 (934 mg, 6.76 mmol) was added at room temperature. The reaction was heated at 55 ºC and a solution of 10-bromo-1-decene (23 μL, 0.11 mmol) in dry DMF (4.5 mL) was added dropwise. After 10 min stirring, 0.11 mmol more of 10-bromo-1-decene in dry DMF were added, and the resulting mixture was stirred at 55 ºC for 3 h. The complete reaction was poured onto cold HCl 1M, the solid was removed by filtration and dissolved in $CHCl_3$ and the filtrate was extracted with $CHCl_3$. The organic phase was washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed under vacuum and the crude product was purified by column chromatography (silica gel, $CHCl_3$). The compound **3** (91 mg, 47%) was characterized by ^1H, ^{13}C -NMR, MALDI and UV/vis.



Compound **3**. ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, J = 13.7, 4.7 Hz, 4H, $H_{e,e',f,f'}$), 8.59 (dd, J = 4.7, 2.0 Hz, 4H, $H_{g,g',h,h'}$), 8.01 (d, J = 8.4 Hz, 2H, $H_{c,d}$), 7.93 (d, J = 8.4 Hz, 2H, $H_{a,b}$), 7.21 – 7.10 (m, 6H, $H_{a',b',i,i',j,j'}$), 6.98 (d, J = 8.4 Hz, 2H, $H_{c'd'}$), 5.76 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, H_x), 4.99 – 4.83 (m, 2H, H_y), 4.13 (t, J = 6.5 Hz, 2H, H_p), 2.52 (s, 6H, $H_{l,l'}$), 2.04 – 1.95 (m, 2H, H_w), 1.92 – 1.81 (m, 2H, H_q), 1.75 (s, 12H, $H_{k,k',m,m'}$), 1.52 (m, 2H, H_v), 1.42 – 1.25 (m, 6H, $H_{r,s,t}$), 0.87 – 0.73 (m, 2H, H_u), -2.69 (s, 2H,

$H_{n,n'}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 155.5, 139.5, 139.3, 138.6, 137.7, 135.6, 135.5, 134.5, 134.2, 127.8, 119.3, 119.0, 118.2, 114.3, 113.7, 112.8, 68.4, 33.9, 29.8, 29.5, 29.2, 29.0, 26.3, 21.7, 21.5. MS m/z: calculated for $C_{60}H_{60}N_4O_2[M]^+$ 868.5, found MALDI 868.5. λ_{abs} ($CHCl_3$) 421, 517, 553, 593, 649 nm.

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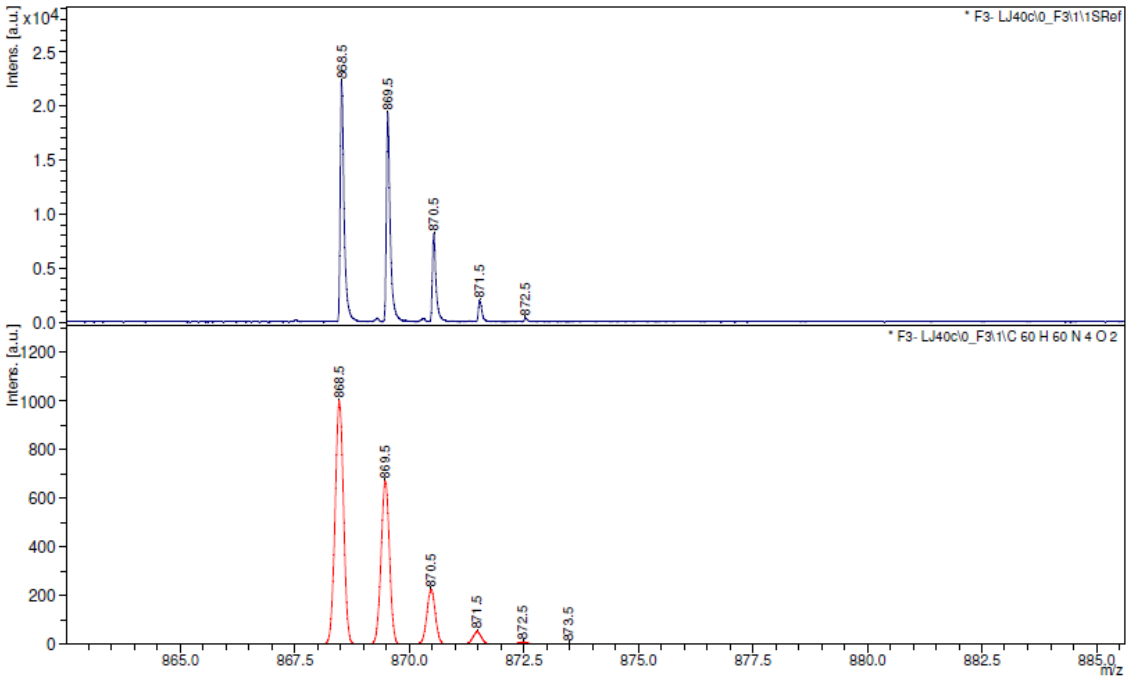
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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0.5
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868.5
869.5
870.5
871.5
872.5
* F3- LJ40c\0_F3\1\1SRef
Intens. [a.u.]
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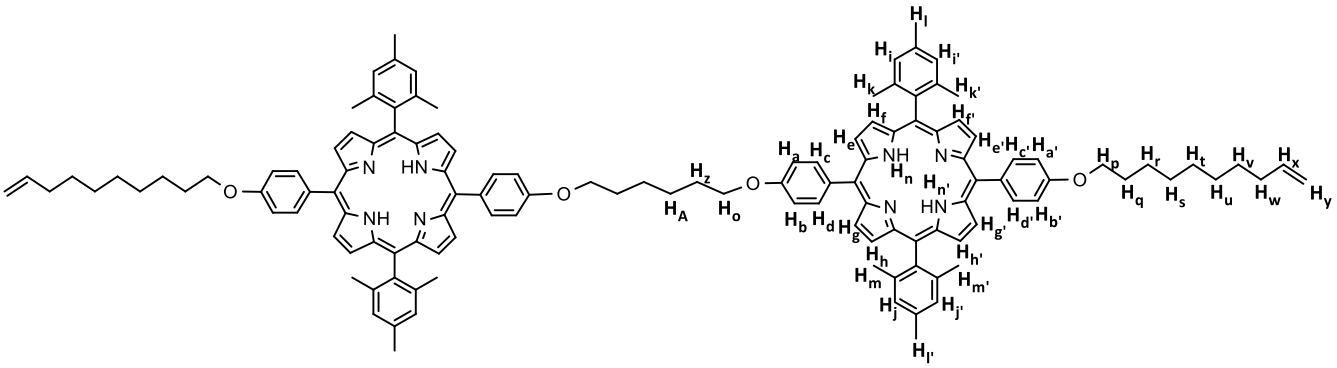
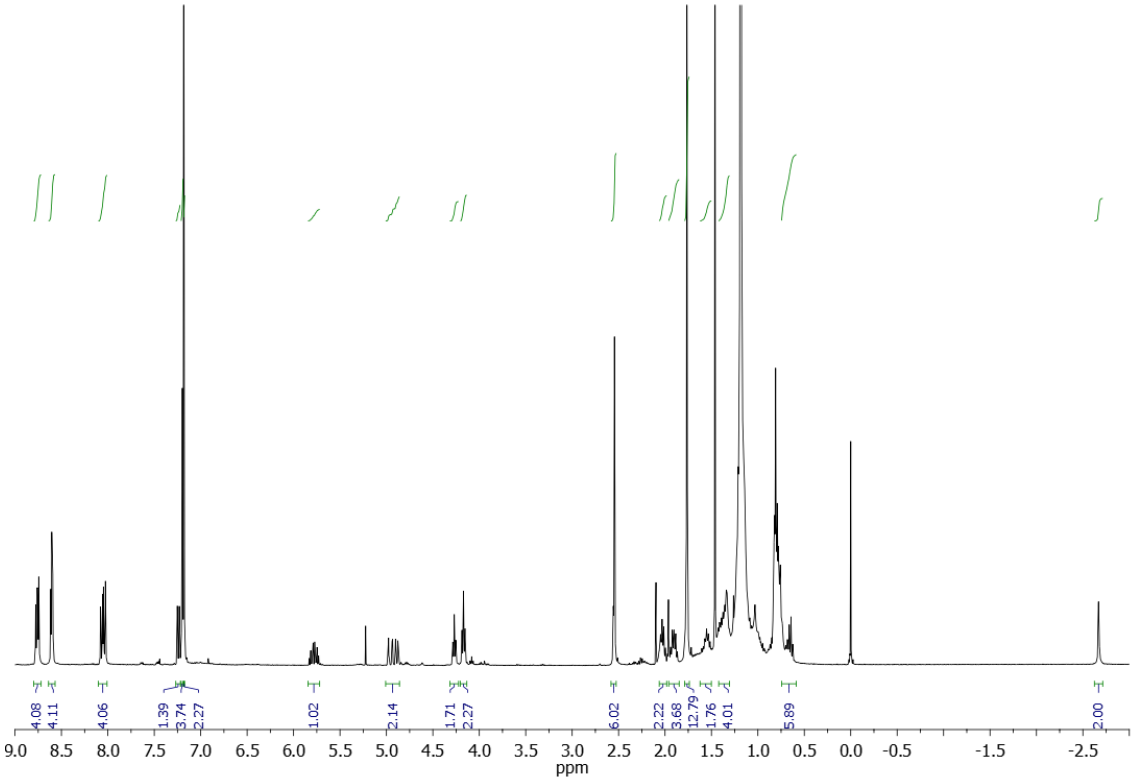
1000
800
600
400
200
0
868.5
869.5
870.5
871.5
872.5
873.5
* F3- LJ40c\0_F3\1\C 60 H 60 N 4 O 2
865.0
867.5
870.0
872.5
875.0
877.5
880.0
882.5
885.0
m/z

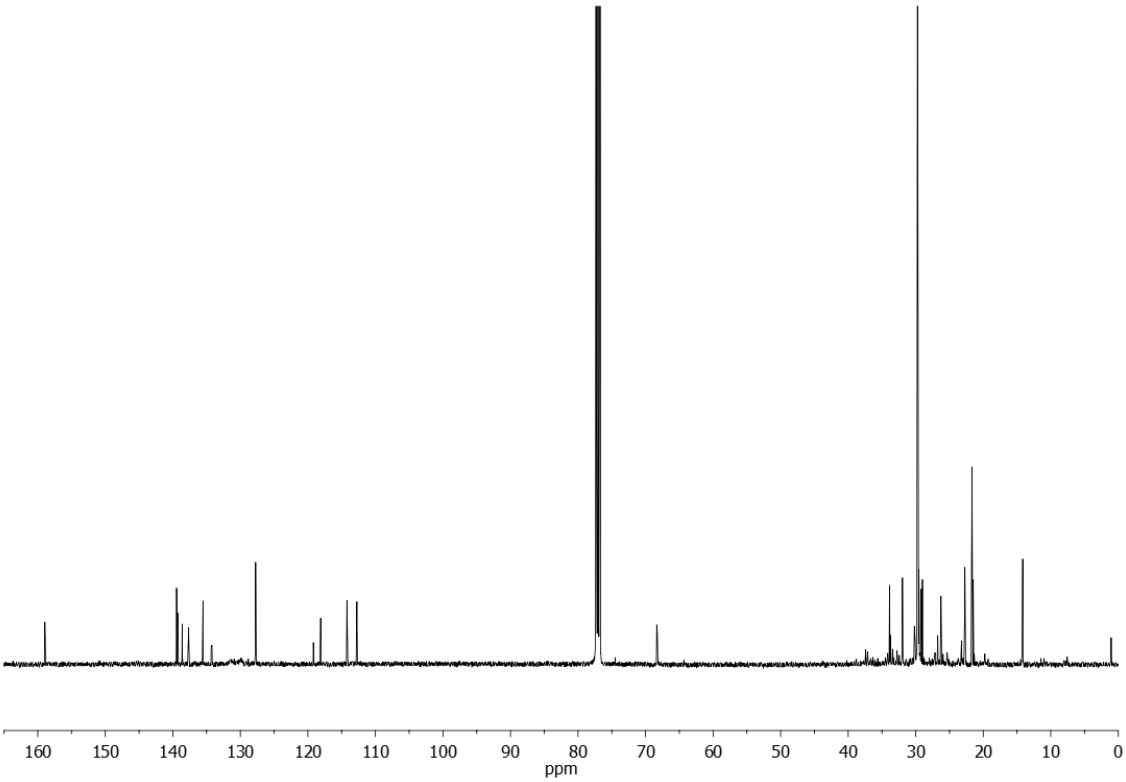
Synthesis of compound **4**. Compound **3** (116 mg, 0.13 mmol) was dissolved in dry 2-butanone (20 mL) under Ar. Dry K_2CO_3 (184 mg, 1.33 mmol) and 1,6-dibromohexane (5 µL, 0.033 mmol) were added, and the resulting mixture was stirred under reflux for 48 h. The reaction was quenched with water and extracted with $CHCl_3$. The organic phase was washed with brine, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, DCM/hexane 2:3) and the purple product **4** (40 mg, 67%) was characterized by ^1H, ^{13}C - NMR, MALDI and UV/vis.



Compound **4**. ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, J = 8.5, 4.7 Hz, 4H, $H_{e,e',f,f'}$), 8.60 (t, J = 4.3 Hz, 4H, $H_{g,g',h,h'}$), 8.05 (dd, J = 12.4, 8.6 Hz, 4H, $H_{a,b,c,d}$), 7.24 (d, J = 8.6 Hz, 2H, $H_{a',b'}$), 7.20 (s, 4H, $H_{i,i',j,j'}$), 7.18 (m, 2H, $H_{c',d'}$), 5.78 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, H_x), 4.97 – 4.82 (m, 2H, H_y), 4.27 (t, J = 6.3 Hz, 2H, H_o), 4.17 (t, J = 6.5 Hz, 2H, H_p), 2.54 (s, 6H, $H_{l,l'}$), 2.06 – 1.99 (m, 2H, H_w), 1.94 – 1.86 (m, 4H, $H_{q,z}$), 1.76 (s, 12H, $H_{k,k',m,m'}$), 1.61 – 1.50 (m, 2H, H_v), 1.44 – 1.30 (m, 4H, $H_{r,A}$), 0.78 – 0.66 (m, 6H, $H_{s,t,u}$), -2.67 (s, 2H, $H_{n,n'}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 139.4, 139.3, 138.6, 137.7, 135.6, 135.5, 134.3, 134.2, 127.7, 119.2, 119.1, 118.1, 114.2, 112.8, 112.7, 68.3, 68.2, 33.9, 32.0, 29.7, 29.5, 29.4, 29.2, 29.0, 26.3, 22.7, 21.7, 21.5, 14.2. MS m/z: calculated

for $C_{126}H_{130}N_8O_4[M]^+$ 1820.0, found MALDI 1819.9. λ_{abs} ($CHCl_3$) 421, 517, 553, 594, 649 nm.

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60
50
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30
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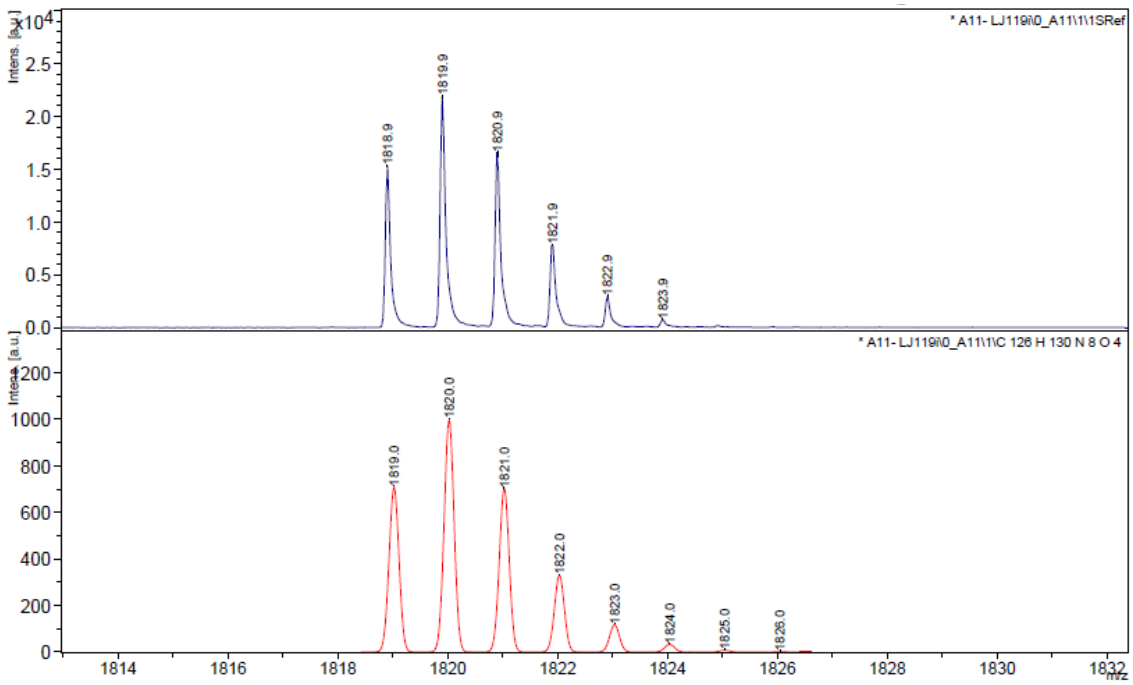
10
0
ppm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2.0
1.5
1.0
0.5
0.0
1818.9
1819.9
1820.9
1821.9
1822.9
1823.9
* A11- LJ119\0_A11\1\C 126 H 130 N 8 O 4
Intens. [a.u.]
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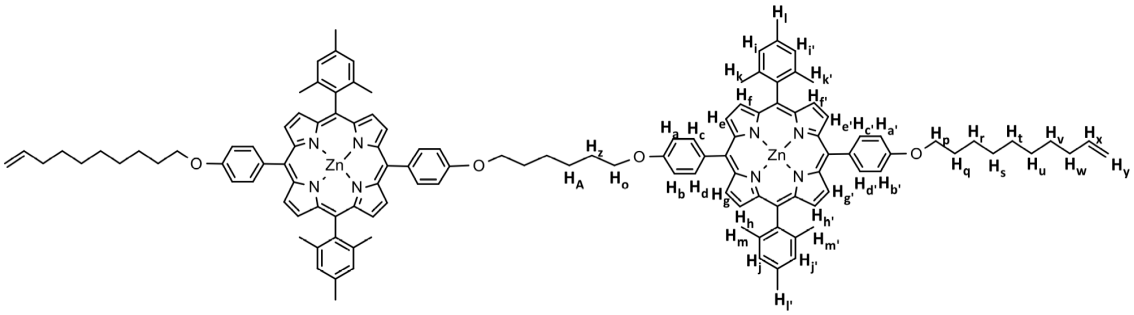
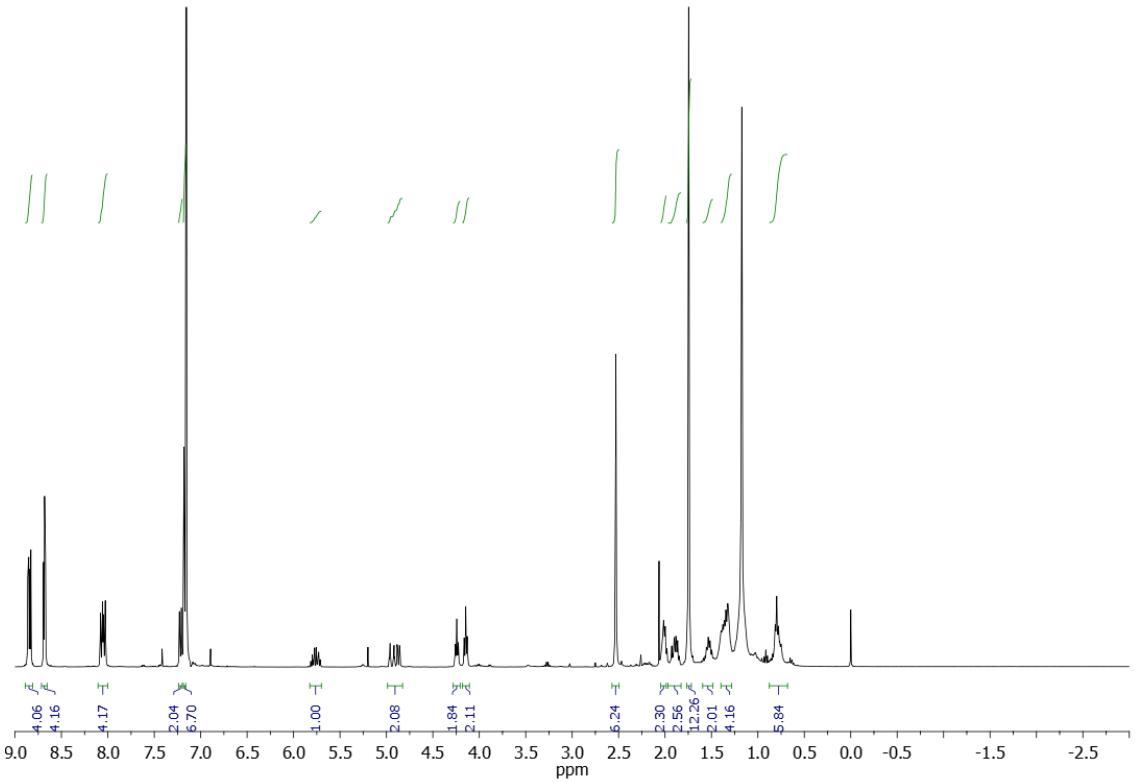
1000
800
600
400
200
0
1819.0
1820.0
1821.0
1822.0
1823.0
1824.0
1825.0
1826.0
1814
1816
1818
1820
1822
1824
1826
1828
1830
1832
m/z

Synthesis of compound **5**. Compound **4** (44 mg, 0.024 mmol) was dissolved in $CHCl_3$ (10 mL) and a solution of zinc acetate (14 mg, 0.078 mmol) in methanol (0.5 mL) was added. The resulting mixture was stirred at room temperature. After completion of the reaction, the solvent was removed under vacuum, and the product was dissolved in $CHCl_3$ and extracted with water several times. The combined organic phases were washed with brine, dried over $MgSO_4$ and the solvent was removed under vacuum. The compound **5** (46 mg, 99%) was characterized by ^1H, ^{13}C -NMR, MALDI and UV/vis.



Compound **5**. ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, J = 9.0, 4.6 Hz, 4H, $H_{e,e',f,f'}$), 8.68 (t, J = 4.3 Hz, 4H, $H_{g,g',h,h'}$), 8.05 (dd, J = 12.3, 8.6 Hz, 4H, $H_{a,b,c,d}$), 7.22 (d, J = 8.5 Hz, 2H, $H_{a',b'}$), 7.18 – 7.16 (m, 6H, $H_{i,i',j,j',c',d'}$), 5.76 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, H_x), 4.99 – 4.84 (m, 2H, H_y), 4.24 (t, J = 6.3 Hz, 2H, H_o), 4.15 (t, J = 6.5 Hz, 2H, H_p), 2.53 (s, 6H, $H_{l,l'}$), 2.05 – 1.98 (m, 2H, H_w), 1.95 – 1.83 (m, 4H, $H_{q,z}$), 1.75 (s, 12H, $H_{k,k',m,m'}$), 1.60 – 1.48 (m, 2H, H_v), 1.43 – 1.29 (m, 4H, $H_{r,A}$), 0.86 – 0.74 (m, 6H, $H_{s,t,u}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 150.5, 149.9, 139.3, 139.2, 139.1, 137.4, 135.5, 135.4, 135.1, 135.0, 132.4, 130.6, 127.7, 120.1, 119.1, 114.2, 112.7, 112.6, 68.3, 68.2, 33.9, 32.0, 29.8, 29.5, 29.2, 29.0, 26.3, 22.7, 21.7, 21.5, 14.2. MS m/z: calculated for $C_{126}H_{126}N_8O_4Zn_2[M+H]^+$ 1946.8, found MALDI 1946.8. λ_{abs} ($CHCl_3$) 424, 554, 599 nm.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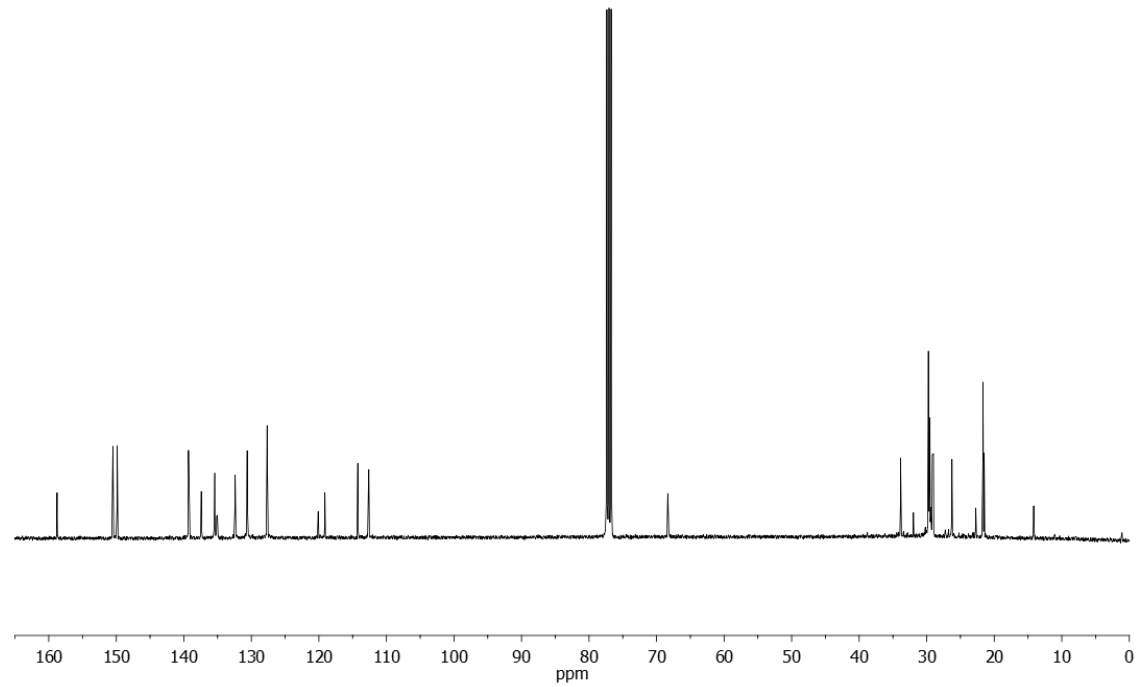
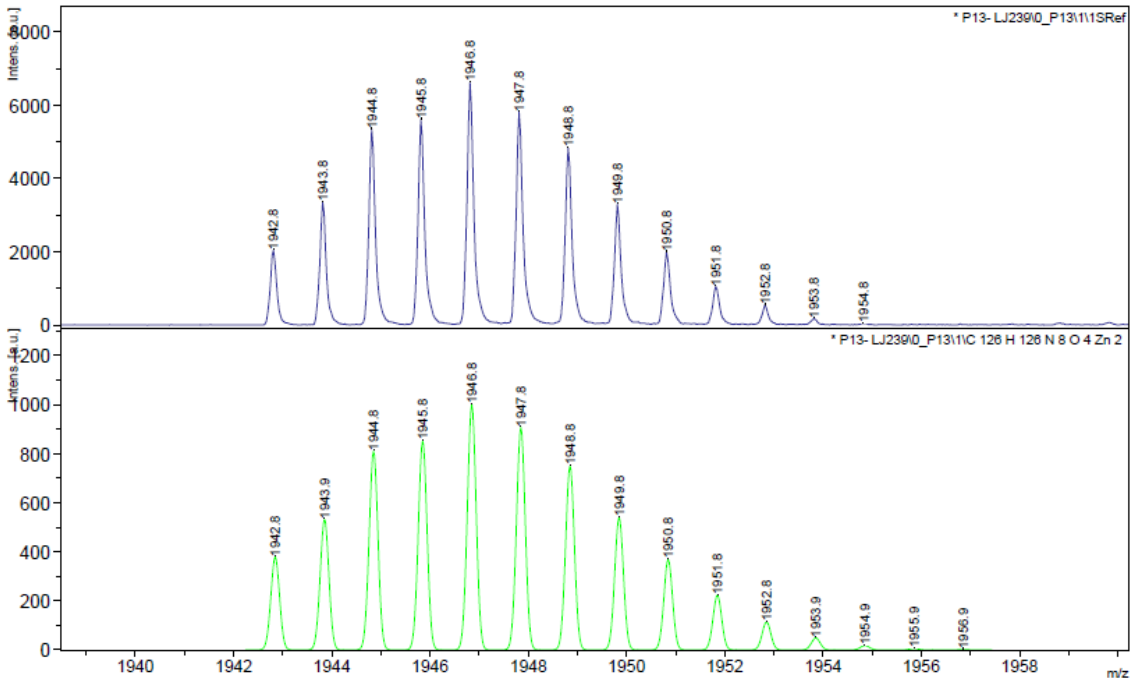
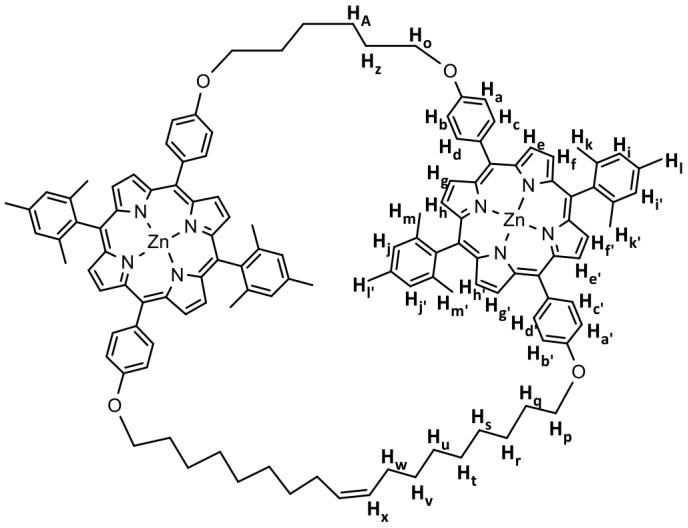
4.16
4.17
2.04
6.70
1.00
2.08
1.84
2.11
6.24
2.30
2.56
12.26
2.01
4.16
5.84
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5 -2.5
ppm

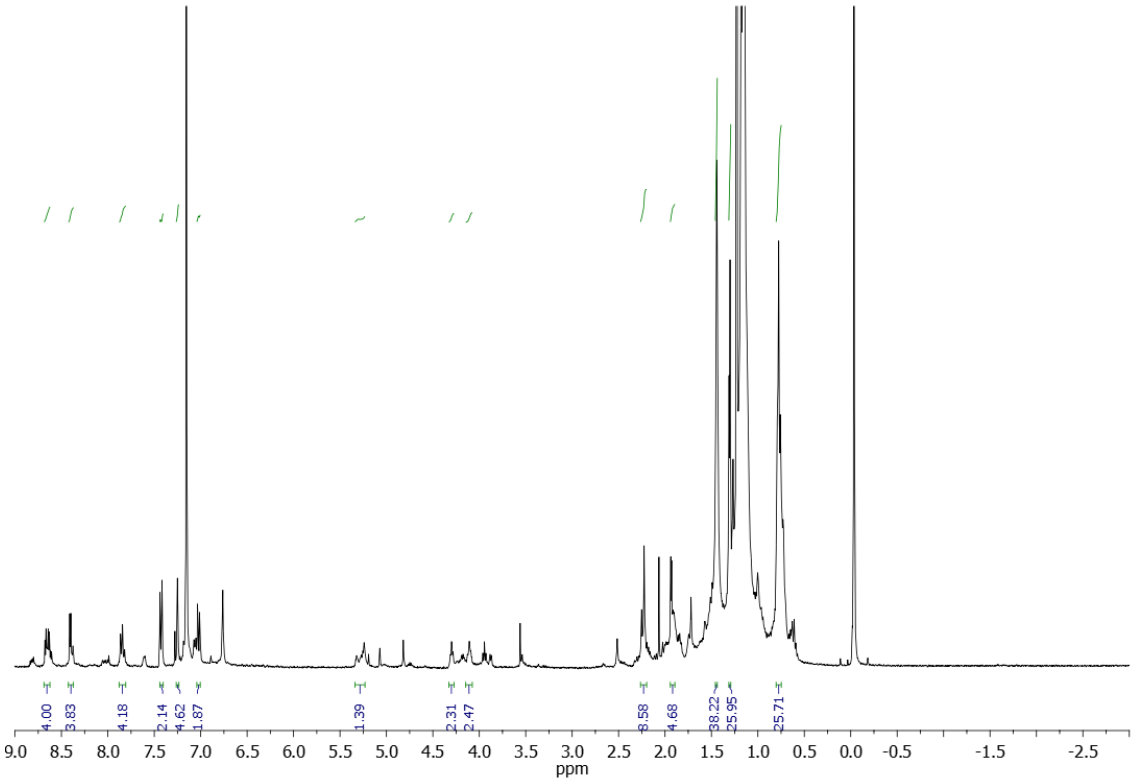

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


* P13- LJ239\0_P13\1\1\SRef
Intens. [a.u.]
8000
6000
4000
2000
0
1942.8
1943.8
1944.8
1945.8
1946.8
1947.8
1948.8
1949.8
1950.8
1951.8
1952.8
1953.8
1954.8
* P13- LJ239\0_P13\1\C 126 H 126 N 8 O 4 Zn 2
Intens. [a.u.]
1200
1000
800
600
400
200
0
1942.8
1943.9
1944.8
1945.8
1946.8
1947.8
1948.8
1949.8
1950.8
1951.8
1952.8
1953.9
1954.9
1955.9
1956.9
1940
1942
1944
1946
1948
1950
1952
1954
1956
1958
m/z

Synthesis of compound **6**. Compound **5** (19 mg, 0.0097 mmol) was dissolved in dry DCM (97 mL) and degassed for 30 min. Grubbs' 1st generation catalyst (4.8 mg, 0.0058 mmol) was added and the solution was stirred under reflux. The progress of the reaction was monitored by TLC (hexane/toluene 1:4). The reaction was then stopped, filtered through a pad of celite and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane/toluene 1:4) and the purple product **6** (7.6 mg, 41%) was characterized by ^{1}H NMR, MALDI and UV/vis.



Compound **6**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.62 (m, 4H, $H_{e,e',f,f'}$), 8.42 – 8.36 (m, 4H, $H_{g,g',h,h'}$), 7.84 (d, *J* = 8.8 Hz, 4H, $H_{a,b,c,d}$), 7.43 (d, *J* = 8.6 Hz, 2H, $H_{a',b'}$), 7.25 (s, 4H, $H_{i,i',j,j'}$), 7.02 (dd, *J* = 8.6, 2.4 Hz, 2H, $H_{c',d'}$), 5.35 – 5.26 (m, 1H, H_x), 4.30 (t, 2H, H_o), 4.11 (t, 2H, H_p), 2.27 – 2.20 (m, 8H, $H_{l,l',w}$), 1.95 – 1.89 (m, 4H, $H_{q,z}$), 1.44 (s, 12H, $H_{k,k',m,m'}$), 1.33 – 1.28 (m, 6H, $H_{v,r,A}$), 0.83 – 0.73 (m, 6H, $H_{s,t,u}$) (cis/trans isomers). MS m/z: calculated for $C_{124}H_{122}N_8O_4Zn_2[M+H]^+$ 1918.8, found MALDI 1918.8. λ_{abs} ($CHCl_3$) 421, 553, 598 nm.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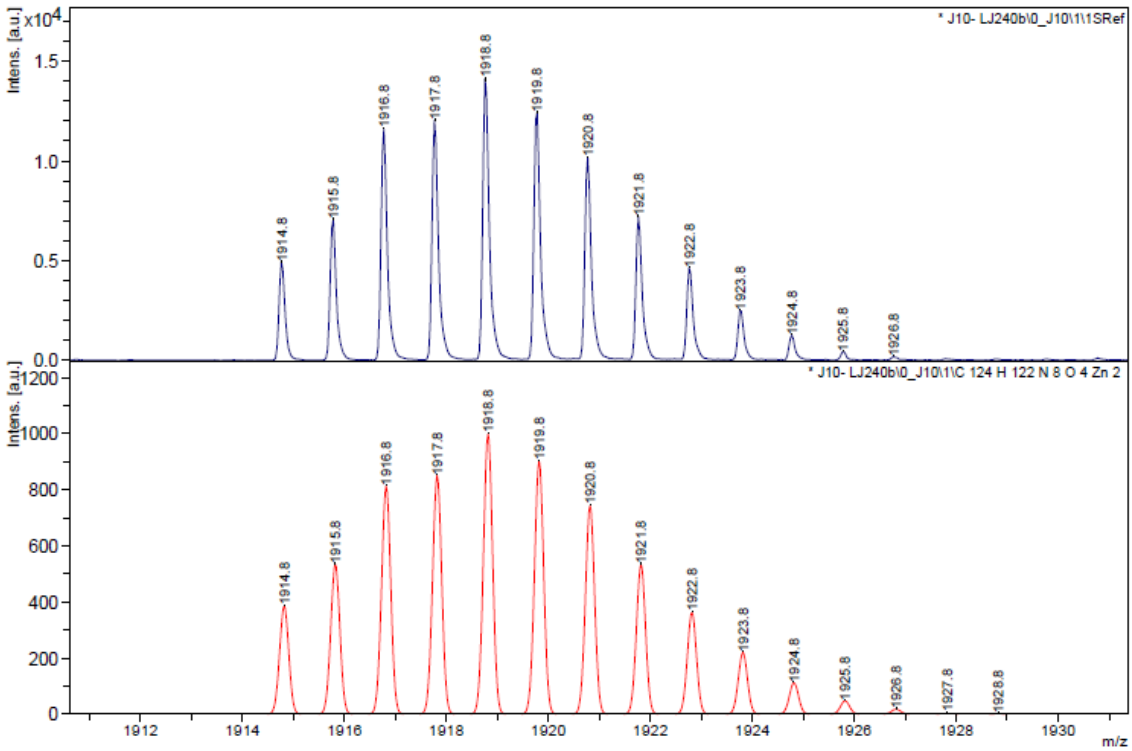
3.83
4.18
2.14
4.62
1.87
1.39
2.31
2.47
8.58
4.68
38.22
25.95
25.71
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5 -2.5
ppm


Intens. [a.u.]
x10^4
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1.0
0.5
0.0
* J10- LJ240b\0_J10\1\1SRef
1914.8
1915.8
1916.8
1917.8
1918.8
1919.8
1920.8
1921.8
1922.8
1923.8
1924.8
1925.8
1926.8
Intens. [a.u.]
1200
1000
800
600
400
200
0
* J10- LJ240b\0_J10\1\C 124 H 122 N 8 O 4 Zn 2
1914.8
1915.8
1916.8
1917.8
1918.8
1919.8
1920.8
1921.8
1922.8
1923.8
1924.8
1925.8
1926.8
1927.8
1928.8
1912 1914 1916 1918 1920 1922 1924 1926 1928 1930
m/z

General procedure for SWCNTs functionalization.

The (6,5)-enriched SWCNTs purchased from Sigma Aldrich Co were purified previously. 50 mg of (6,5)-enriched SWCNTs were suspended in 34 mL of 35% HCl and sonicated for 15 min. The mixture was poured onto milliQ water and filtered through a polycarbonate membrane of 0.2 μm pore size. The solid was washed with water to neutral pH and then dried in an oven at 350 ºC for 30 min.

The SWCNTs (2 mg) were suspended in tetrachloroethane (TCE, 2 mL) through sonication for 10 min and mixed with **U-por** (16.3 mg, 0.0084 mmol) and Grubbs' 2nd generation catalyst (7.2 mg, 0.0084 mmol) at room temperature for 72 hours. After this time, the suspension was filtered through a polytetrafluoroethylene membrane with a pore size of 0.2 μm, and the solid was washed profusely with DCM. The solid was re-suspended in 20 mL of DCM through sonication (10 min) and filtered through a PTFE membrane of 0.2 μm pore size again. This purification step was repeated three times.

General procedure for SWCNTs functionalization (varying the relative concentration of U-por with respect to SWCNTs).

The SWCNTs were suspended in TCE (1 mg/mL) through sonication for 10 min and mixed with **U-por** (1.06 mM, 2.1 mM, 4.2 mM or 8.4 mM), and Grubbs' 2nd generation catalyst at room temperature for 72 hours. After this time, the suspension was filtered through a PTFE membrane with a pore size of 0.2 μm, and the solid was washed profusely with DCM. The solid was re-suspended in 20 mL of DCM through sonication (10 min) and filtered through a PTFE membrane of 0.2 μm pore size again. This purification step was repeated three times.

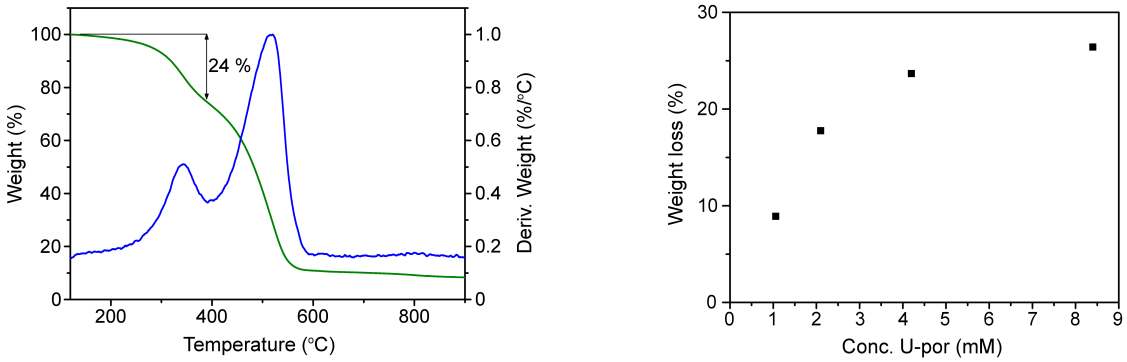

Fig. S1. Left: TGA (air, 10 ºC min^{-1}) of **MINT-por**. Note that the derivative shows a single peak for the porphyrinic material, indicating little or no participation of oligomers in the functionalization (see main text). Right: Degree of functionalization of **MINT-por** samples from TGA: relative weight loss versus concentration of linear precursor.

General procedure for SWCNTs functionalization (control experiments).

The SWCNTs (2 mg) were suspended in tetrachloroethane (TCE, 2 mL) through sonication for 10 min and mixed with **U-por** (16.3 mg) at room temperature for 72 hours. After this time, the suspension was filtered through a PTFE membrane with a pore size of 0.2 µm, and the solid was washed profusely with DCM. The solid was re-suspended in 20 mL of DCM through sonication (10 min) and filtered through a PTFE membrane of 0.2 µm pore size again. This purification step was repeated three times.

General procedure for de-threading functionalized SWCNTs.

The functionalized nanotubes (1.1 mg) were suspended in 2.8 mL of TCE by sonication for 5 min and then heated to reflux (bp = 147 ºC) for 30 min. The suspension was filtered through a PTFE membrane of 0.2 μm pore size, and the solid was washed profusely with DCM.

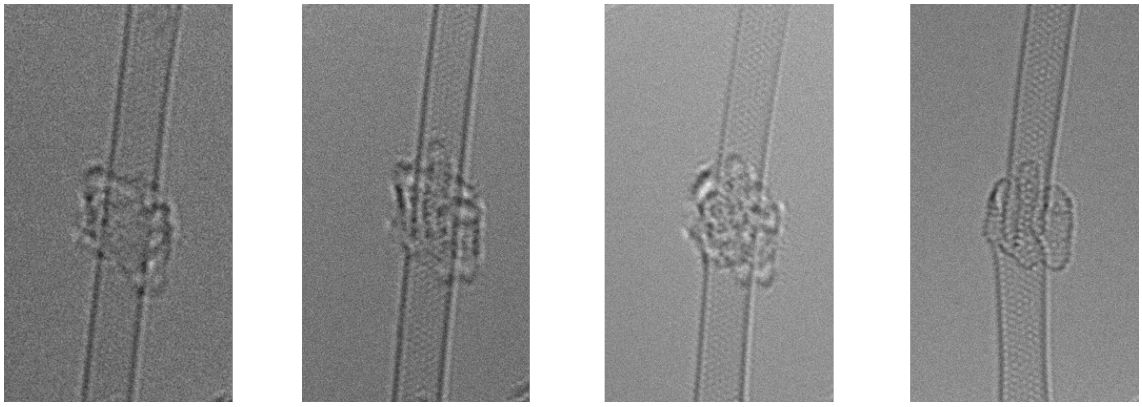

Fig. S2. Modification of **mac-por** during TEM imaging by the impact of the e-beam (60 kV).

General procedure for dispersion preparation of (6,5)-enriched SWCNTs and MINT-por.

The pristine or functionalized nanotubes (0.4 mg) were suspended in 4 mL of methanol, DMF or D_2O/SDBS (1 wt%) by sonication for 1 h (20 min for DMF), followed by 10 min of centrifugation at 5 kG and subsequent sonication for 2 min. The centrifugation and short sonication steps were repeated 3 times.

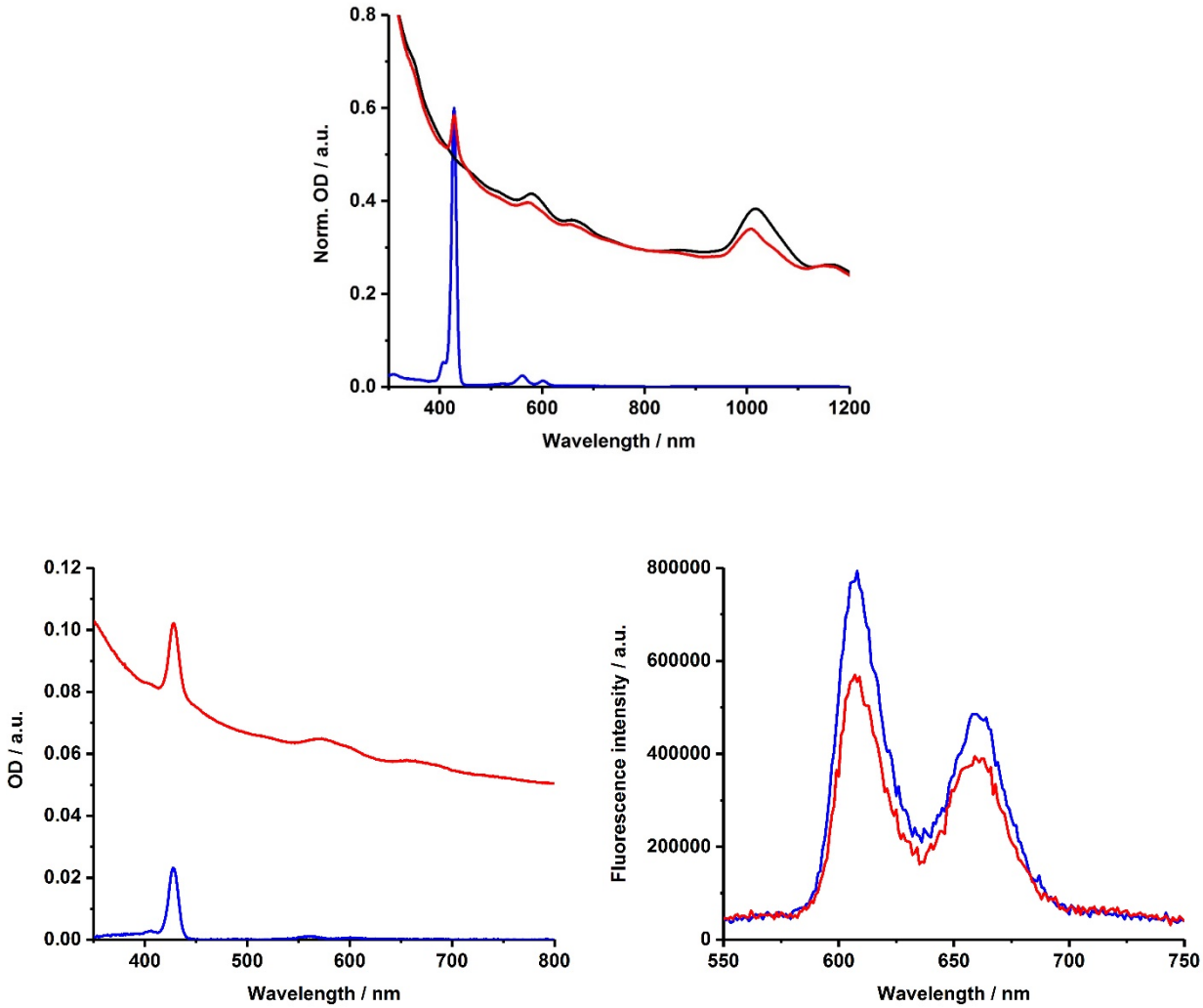

Fig. S3. Normalized absorption spectra (top) of **U-por** (blue), pristine (6,5)-enriched SWCNTs (black), and **MINT-por** (red) in DMF at room temperature. Absorption

spectra (bottom left) of diluted **MINT-por** (red) and **U-por** (blue) in DMF at room temperature, and the respective fluorescence (bottom right), excited at 428 nm.

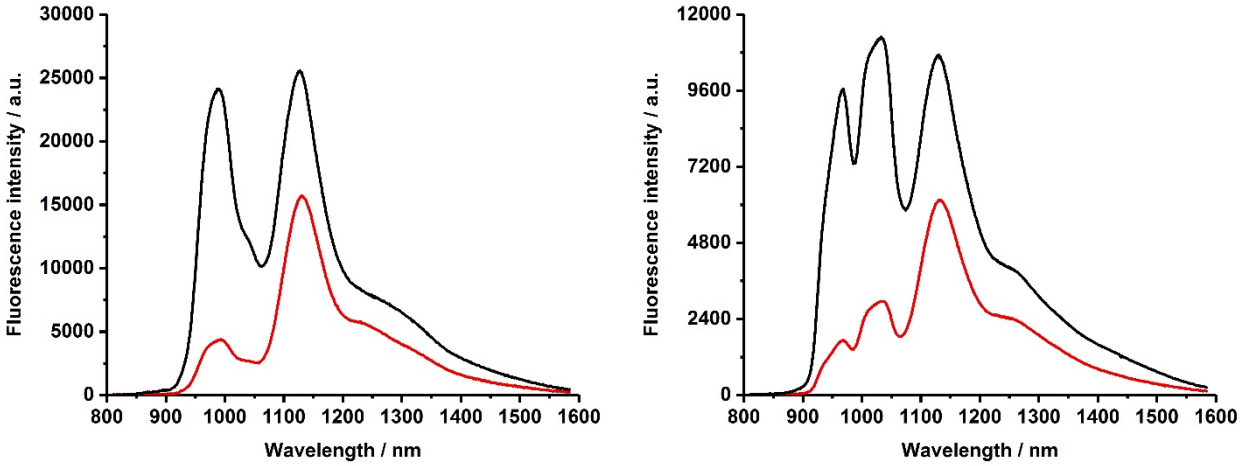

Fig. S4. nIR fluorescence spectra of (6,5)-enriched SWCNTs (black) and **MINT-por** (red) in D_2O/SDBS (1 wt%) at room temperature, measured with an OD of 0.21 at 570 nm, with an excitation wavelength of 570 (left) and 660 nm (right).

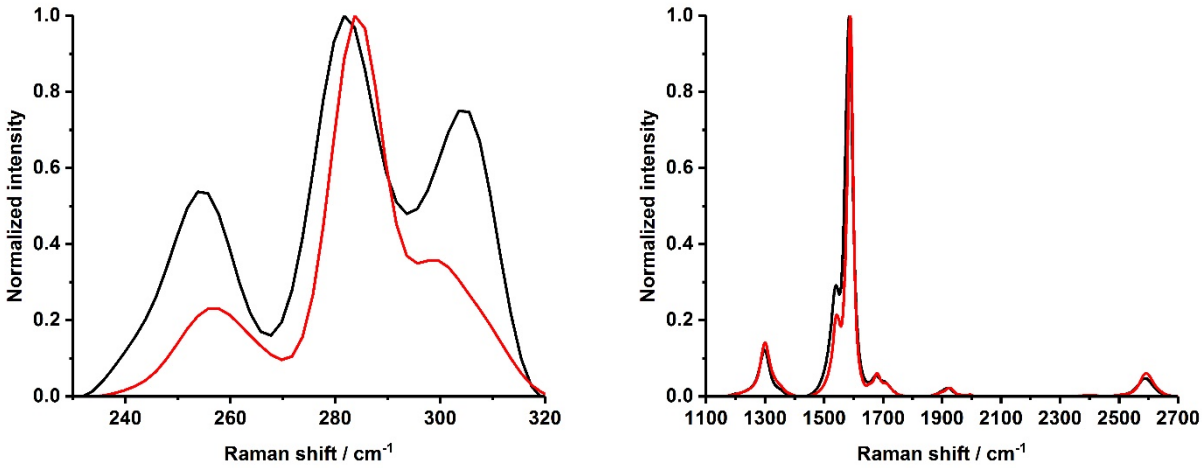

Fig. S5. Radial breathing modes (left), and D, G and 2D modes (right) of drop-casted SWCNT (black) and **MINT-por** (red) from methanol, with 633 nm laser excitation, normalized to (7,5).

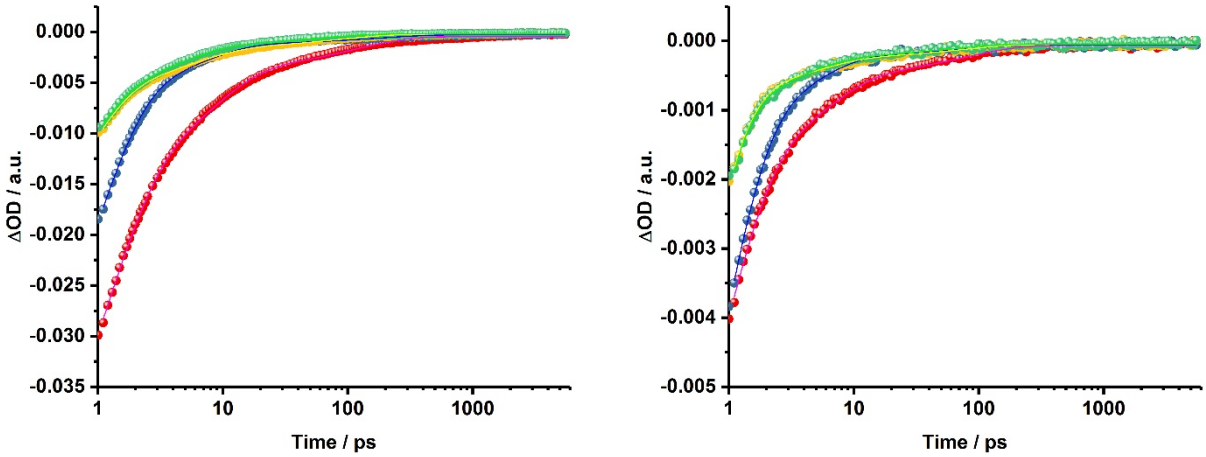

Fig. S6. Time absorption profiles and the respective three exponential fits following 420 nm laser excitation of (6,5)-enriched SWCNTs (left) and **MINT-por** (right) in D_2O/SDBS (1 wt%) at 983 (red, (6,5)), 1021 (blue, (7,5)), 1118 (yellow, (8,4)) and 1139 nm (green, (7,6)).

Table S1. Lifetimes from three exponential fitting of the respective time absorption profiles.

(6,5)-enriched SWCNTs			
6,5	7,5	8,4	7,6
1.08 ± 0.03	0.88 ± 0.01	0.65 ± 0.02	0.63 ± 0.03
7.38 ± 0.27	6.03 ± 0.21	5.41 ± 0.21	4.15 ± 0.15
113.32 ± 5.27	168.21 ± 11.50	85.03 ± 3.89	58.55 ± 2.89

MINT-por			
6,5	7,5	8,4	7,6
0.79 ± 0.03	0.72 ± 0.03	0.50 ± 0.03	0.43 ± 0.03
5.20 ± 0.30	3.99 ± 0.32	4.35 ± 0.52	3.02 ± 0.30
77.62 ± 4.80	80.52 ± 11.71	71.91 ± 8.44	51.72 ± 5.81

[1] R. Sure, S. Grimme, *J. Comput. Chem.* **2013**, *34*, 1672-1685.

[2] E. M. Perez, *Chem. Eur. J.* **2017**, *23*, 12681-12689.