Supporting Information

New Strapped Porphyrins as Hosts for Fullerenes: Synthesis and Complexation Study

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1. General procedure

Chemical reagents were purchased from Sigma-Aldrich Co. Canada, Alfa Aesar Co. or TCI America Co. and were used as received. Solvents used for organic synthesis were obtained from Fisher Scientific and purified with a Solvent Purifier System (SPS) (Vacuum Atmosphere Co., Hawthorne, USA) except CH_2Cl_2 for porphyrin synthesis was used as received. Other solvents were obtained from Fisher Scientific and were used as received. Analytical thin-layer chromatography was performed with silica gel 60 F_{254}, 0.25 mm pre-coated TLC plates (Silicycle, Québec, Canada). Flash column chromatographies were performed on 230-400 mesh silica gel R10030B (Silicycle, Québec, Canada). Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz (^1H), 376 MHz (^{19}F) and 100 MHz (^{13}C). Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublet) and br s (broad singlet) and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak or TMS. High-resolution mass spectra (HRMS) were recorded with a Agilent 6210 Time-of-Flight (TOF) LC-MS apparatus equipped with a ESI or APPI ion source (Agilent Technologies, Toronto, Canada). UV-visible absorption spectra were recorded on a Varian diode-array spectrophotometer (model Cary 500). Molecular geometry optimizations were done using HyperChem^{TM} with Amber molecular force field *in vacuo*.

2. Experiment Details for the Complexation Study of hosts H1-H7 with Fullerenes

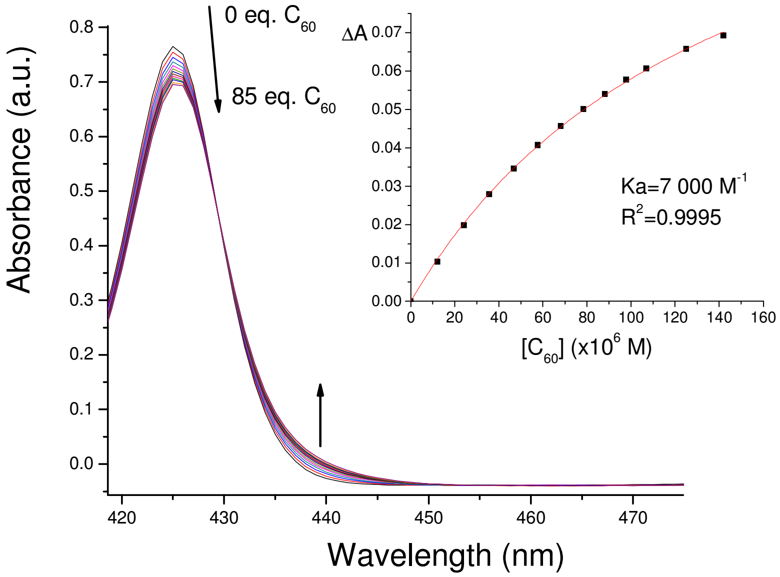
General Procedure

UV-visible titration experiments were carried out with solutions of porphyrin hosts **H1-H7** (1.2 µM to 1.7 µM) in toluene or in acetonitrile/toluene 1:1 (3 mL) in a quartz cuvette (1 cm path length). For C_{60} titration experiments, a C_{60} solution ($7.5x10^{-4}$ M) containing the same host concentration as the sample cell (1.2 – 1.7 µM) was added in aliquots (10 to 50 µL) to the sample cell and the same volume of a C_{60} stock solution ($7.5x10^{-4}$ M) was added to the reference cell. For C_{70} titration experiments, a stock solution ($5.9x10^{-4}$ M) was added in aliquots (5 to 50 µL) to both the sample cell and the reference cell and the absorbance was corrected for dilution. The absorbance of the Soret band (415-425 nm) was recorded after each addition and a plot of ΔA versus [fullerene] was carried out and the binding constant (*Ka*) was evaluated by non-linear curve fitting with OriginPro 8.0 (OriginLab) using the equation[1]:

$$\Delta A = \frac{\Delta A_{\infty}\left((1 + K_a[F] + [H]K_a) - \sqrt{(1 + K_a[F] + [H]K_a)^2 - 4K_a^2[F][H]}\right)}{2K_a[H]}$$

where $\Delta A = A - A_0$, [H] is the concentration of the host solution and [F] is the concentration of the fullerene solution and ΔA_{∞} the absorbance difference at saturation of the binding sites.

Complexation of C_{60} by H1 [1.6 μM] in MeCN/Toluene 1:1



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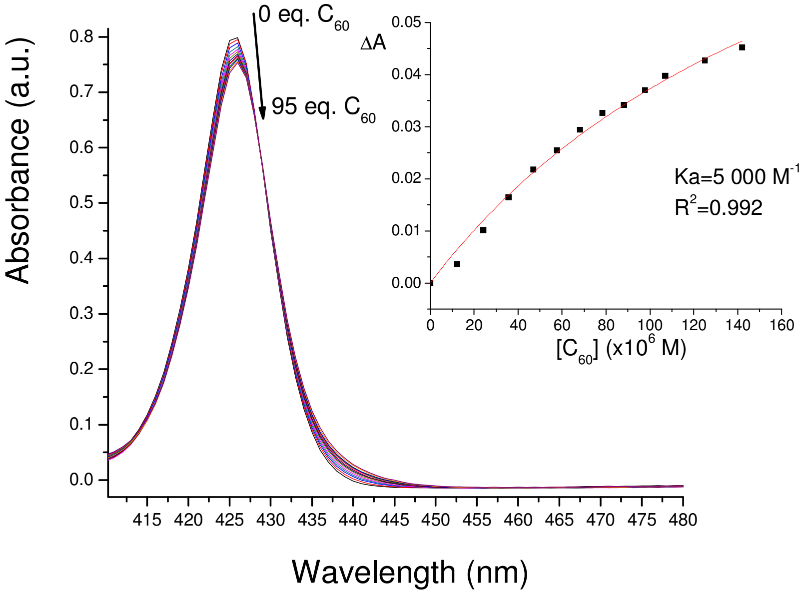

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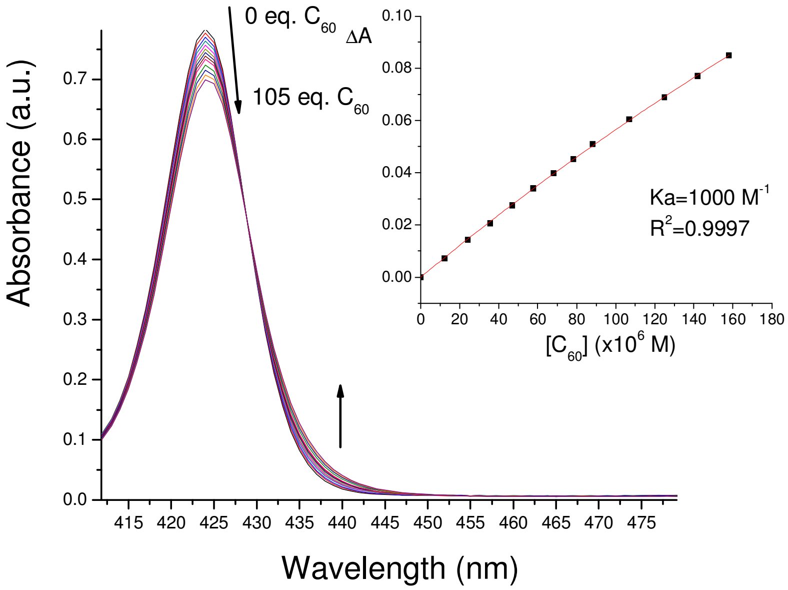

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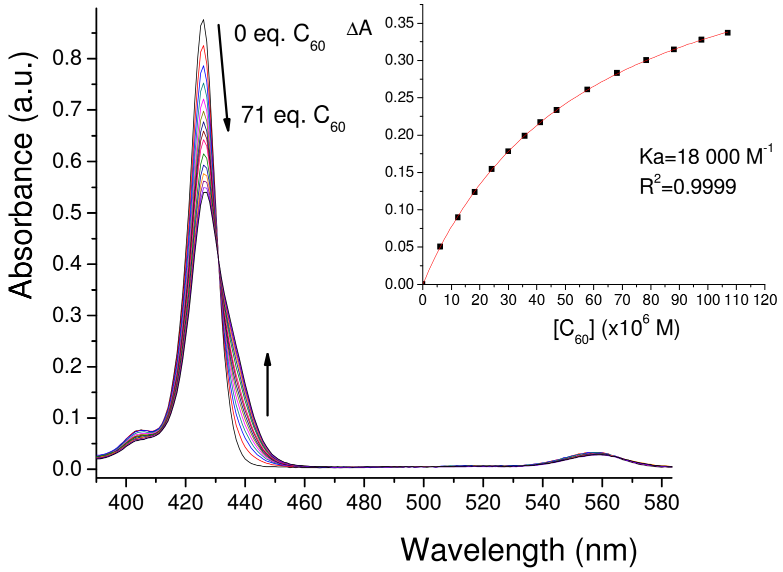

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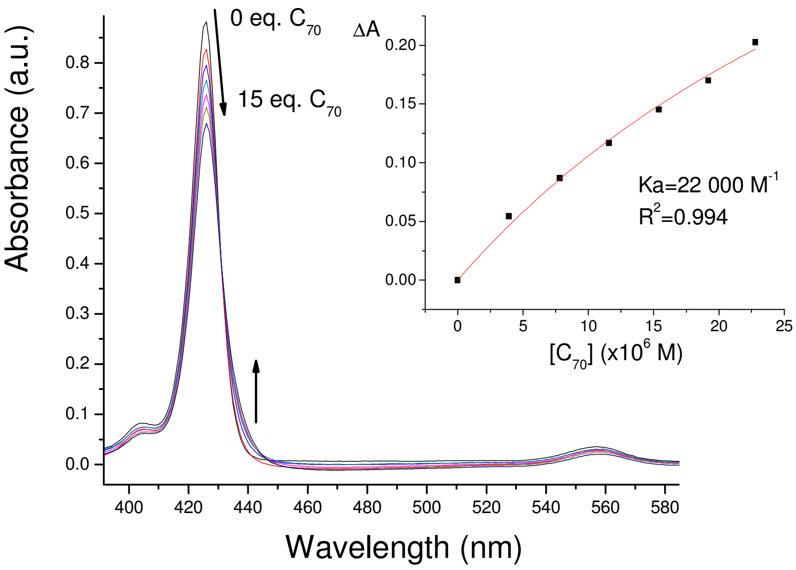
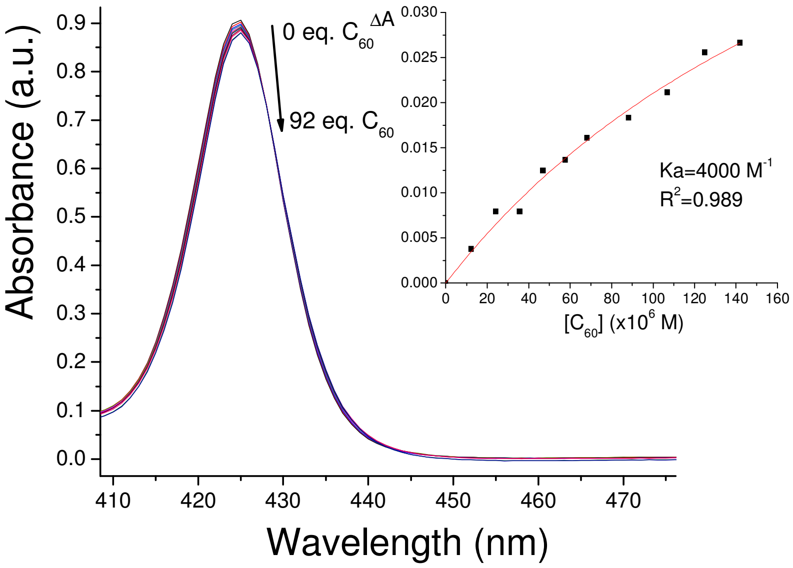
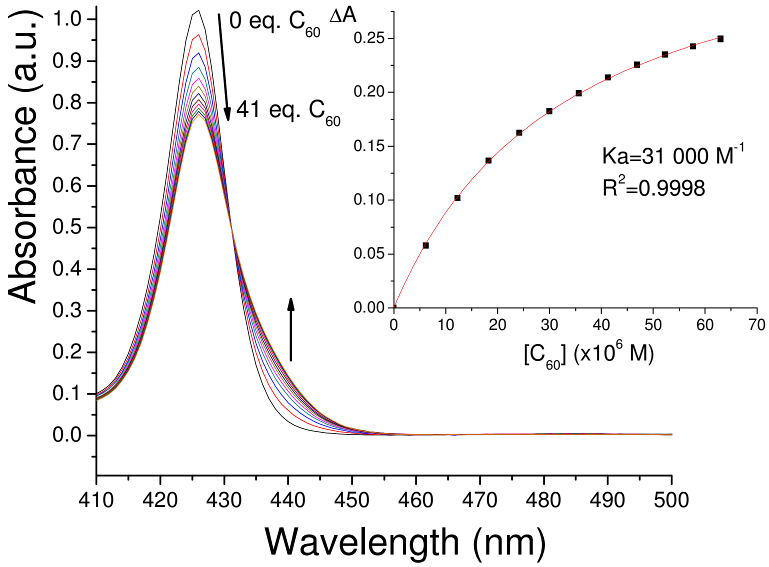


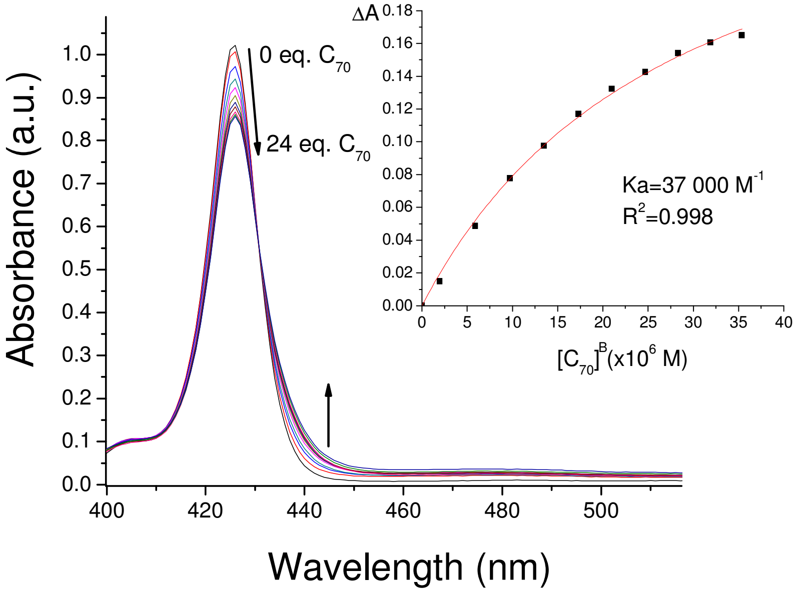
Complexation of C_{60} by H5 [1.5 μM] in Toluene



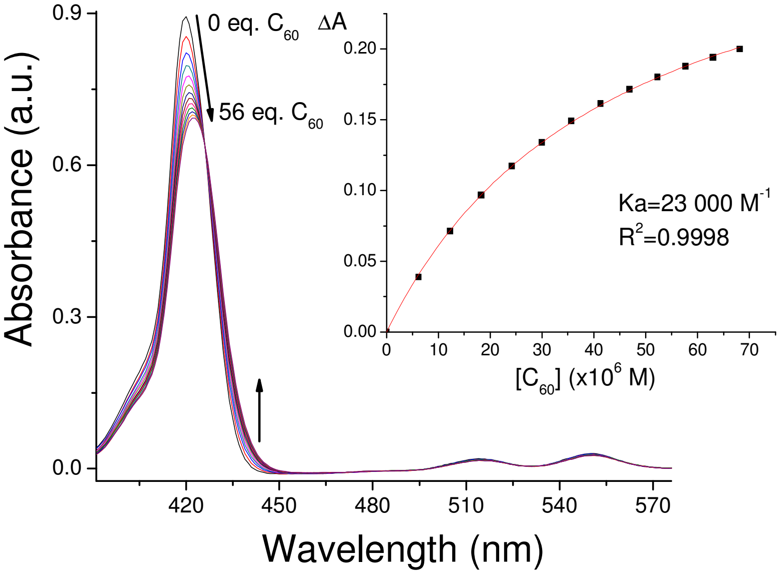
Complexation of C_{60} by H5 [1.5 μM] in MeCN/Toluene 1:1



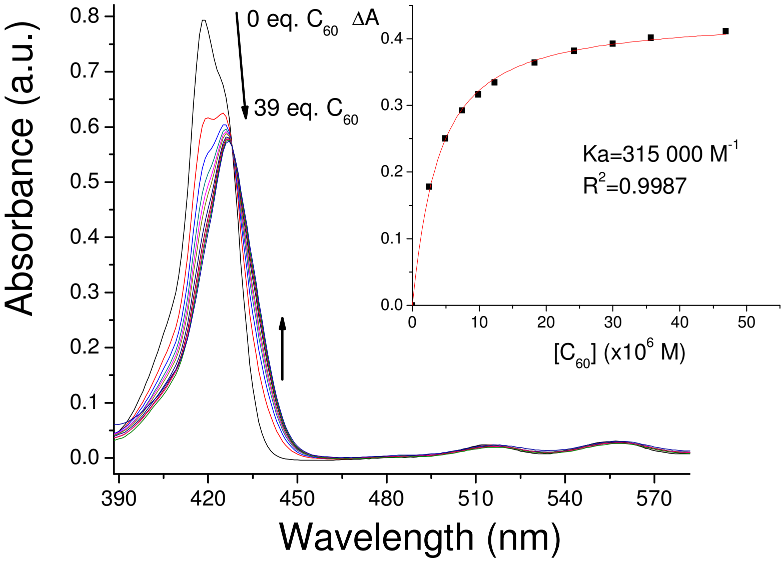
Complexation of C_{70} by H5 [1.5 μM] in MeCN/Toluene 1:1



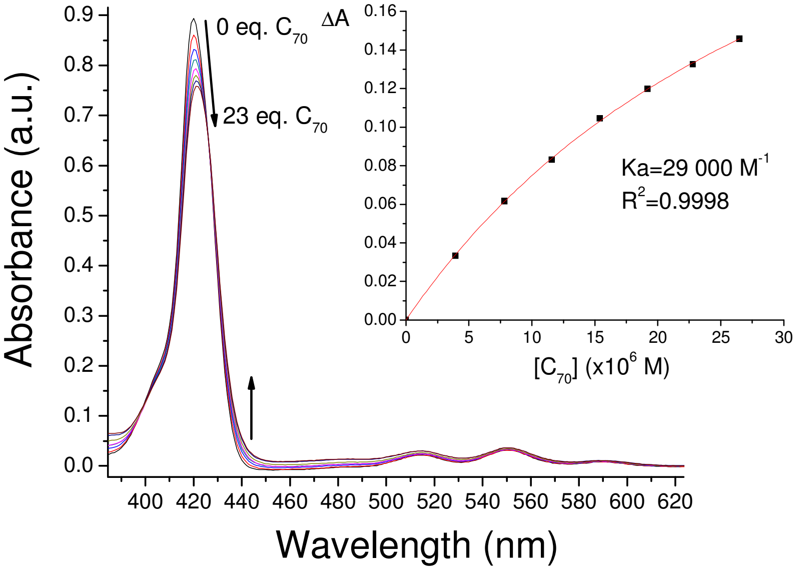
Complexation of C_{60} by H6 [1.2 µM] in Toluene



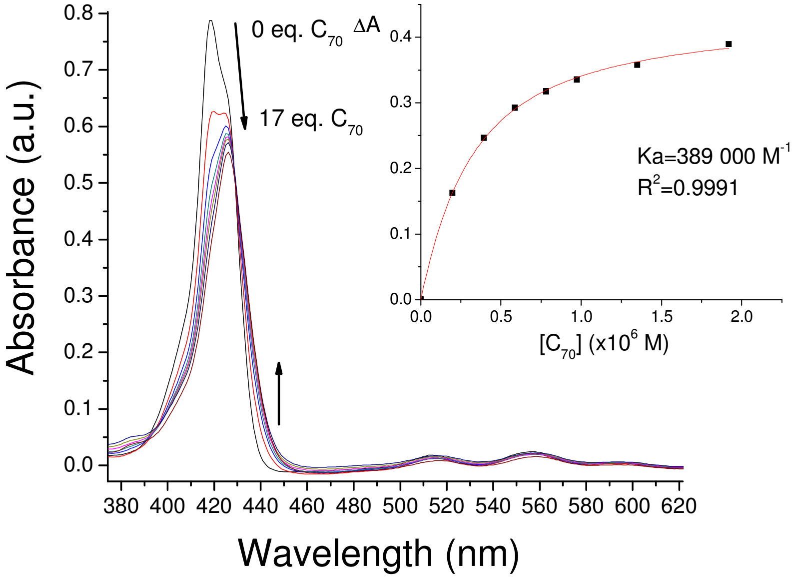
Complexation of C_{60} by H6 [1.2 µM] in MeCN/Toluene 1:1



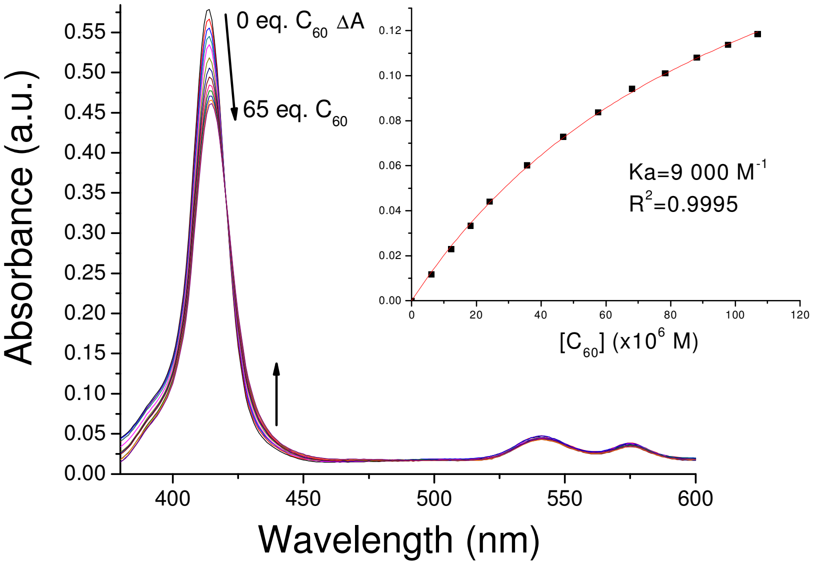
Complexation of C_{70} by H6 [1.2 μM] in Toluene



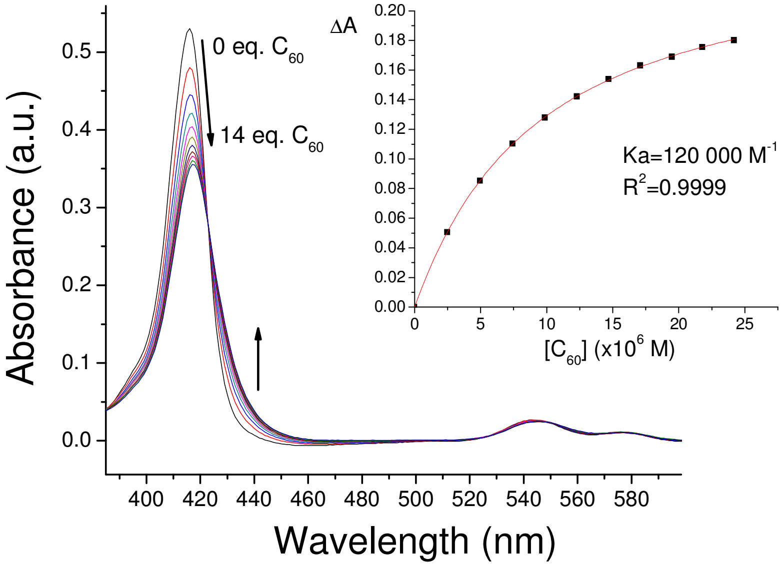
Complexation of C_{70} by H6 [1.2 μM] in MeCN/Toluene 1:1



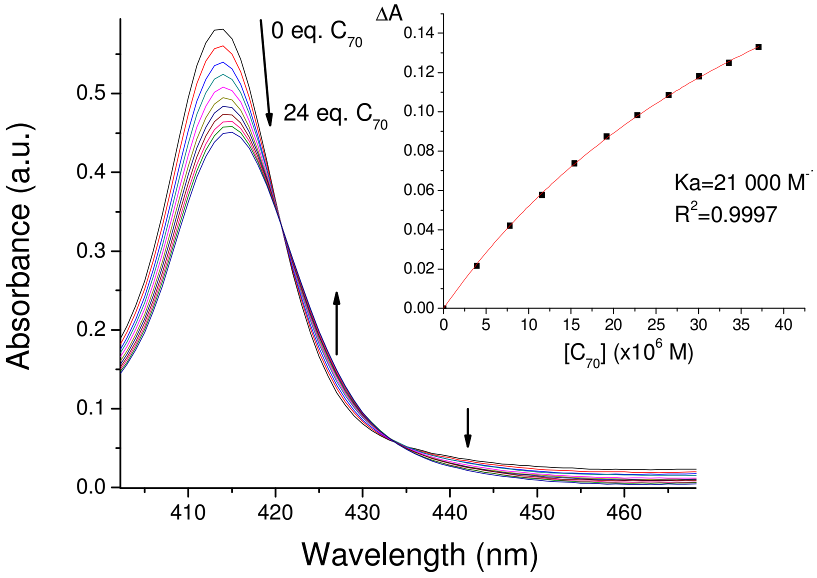
Complexation of C_{60} by H7 [1.7 μM] in Toluene



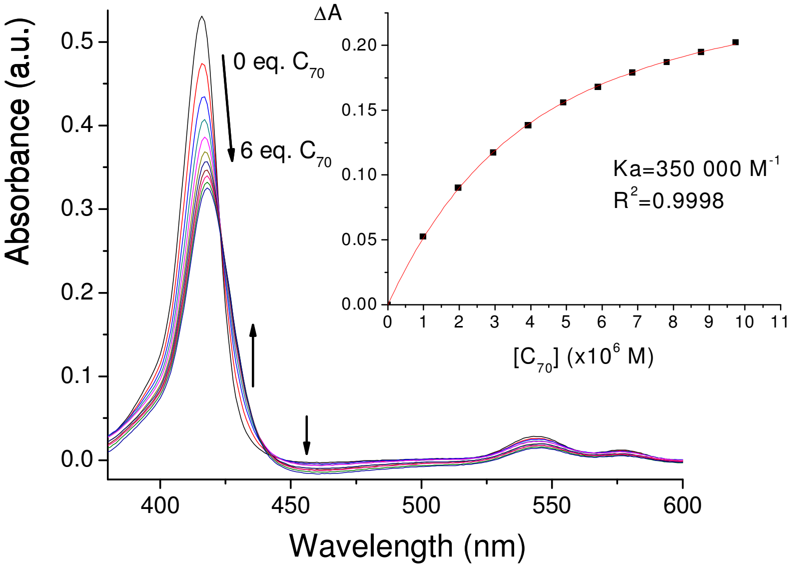
Complexation of C_{60} by H7 [1.7 μM] in MeCN/Toluene 1:1



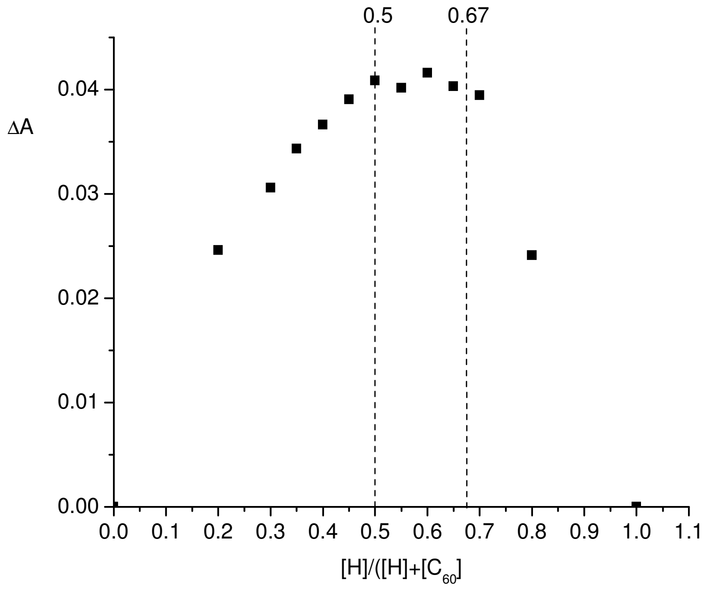
Complexation of C_{70} by H7 [1.7 µM] in Toluene



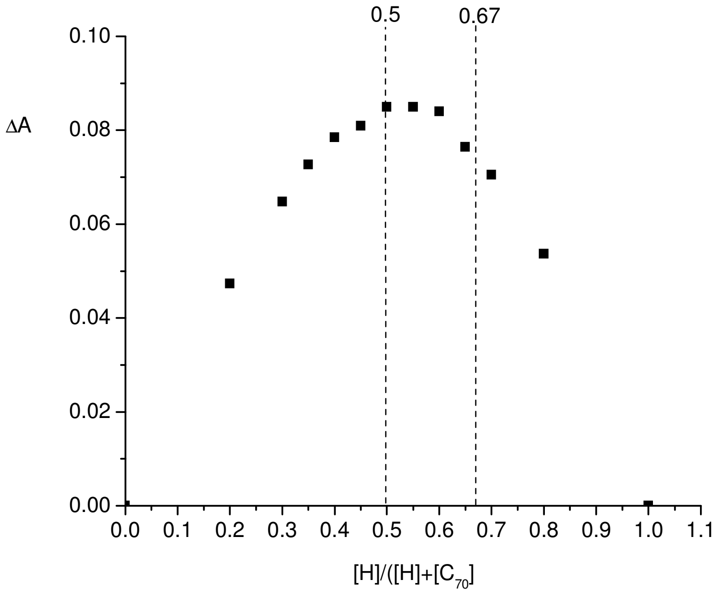
Complexation of C_{70} by H7 [1.7 µM] in MeCN/Toluene



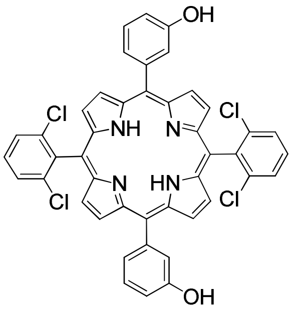
Job's plot of H7 with C_{60} in MeCN/Toluene 1:1 at a fixed [H7]+[C_{60}]=4x10^{-6} M.



Job's plot of H7 with C_{70} in MeCN/Toluene 1:1 at a fixed [H7]+[C_{70}]=4x10^{-6} M.



3. Experimental data for compounds 2-6, 8, 9, 12, H1-H7.



Synthesis of compound 2a:

To a 500 mL round bottom flask equipped with a stir bar and sealed with a septum was added 3-hydroxybenzaldehyde (293 mg, 2.40 mmol), 5-(2,6-dichlorophenyl)dipyrromethane **1** (700 mg, 2.40 mmol) and CH_2Cl_2 (240 mL) and the mixture was degassed with a flow of nitrogen for 15 minutes. Trifluoroacetic acid (263 mg, 2.31 mmol) was added dropwise and the reaction was stirred for 60 minutes. Then, *p*-chloranil (480 mg, 1.95 mmol) was added and the solution was stirred for 30 minutes at room temperature and afterward heated to reflux for 2 hours. The acid was neutralized with triethylamine (494 mg, 4.90 mmol) and silica gel (3.5 g) was added and the solvent evaporated under pressure. The product adsorbed on silica gel was loaded on the top of a silica gel chromatography column and eluted with toluene followed by 7% AcOEt/93% toluene. The product obtained was dissolved in a mixture CH_2Cl_2 and MeOH and layered with hexanes. A purple precipitate appeared and it was recovered via filtration to afford 485 mg of compound **2a** (51% yield) as a purple solid. Mp: >250 °C. ^{1}H NMR (DMSO, 300 MHz): 9.90 (s, 2H), 8.92 (d, 2H, *J* = 4.7 Hz),), 8.71 (d, 2H, *J* = 4.8 Hz), 8.02 (m, 4H), 7.92 (m, 2H), 7.70-7.56 (m, 6H), 7.24 (m, 2H), -2.84 (s, 2H). ^{13}C NMR: 155.88, 141.79, 138.56, 137.46, 132.34 (2C), 131.94, 129.94 (2C), 128.37, 127.98, 125.80, 121.93, 120.29, 115.28, 113.82. HRMS (APPI$^+$): calcd. for $C_{44}H_{26}Cl_4N_4O_2$: 782.0804, found: 782.0802 $(M)^+$.

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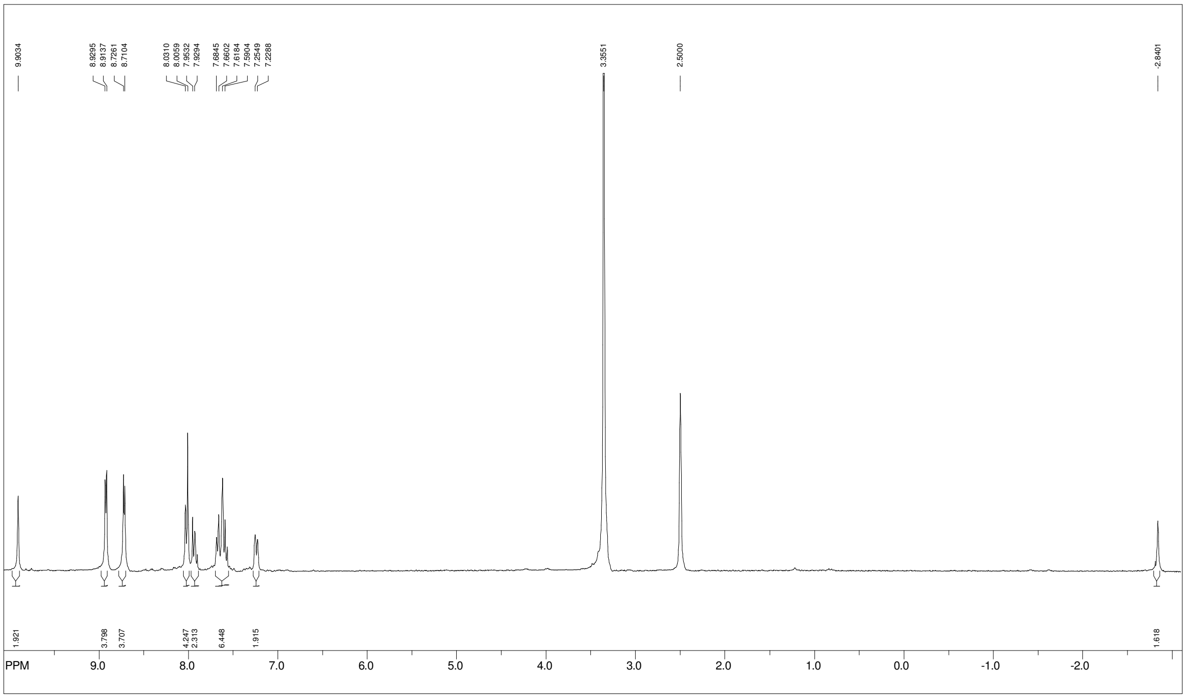

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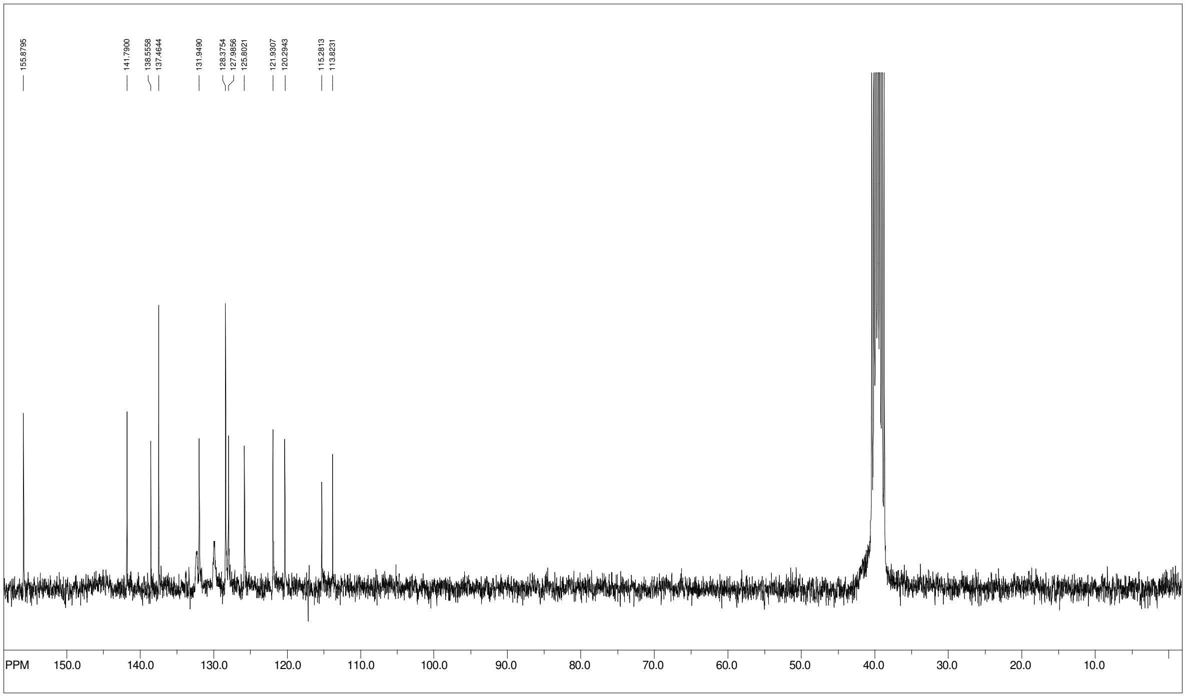

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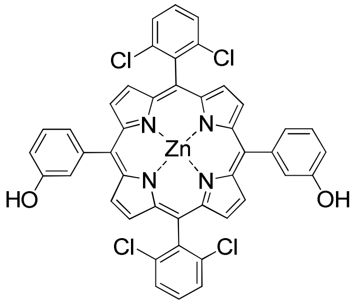

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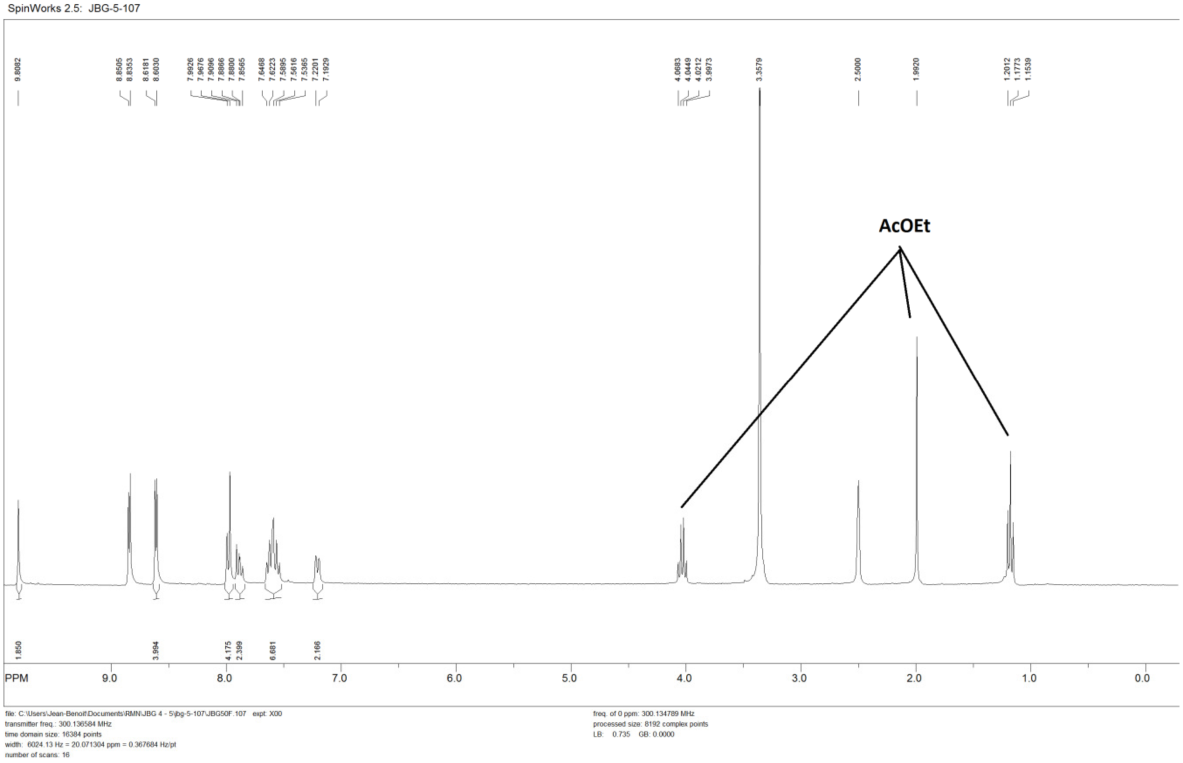
Synthesis of compound 2b:

To a round bottom flask equipped with a stir bar and sealed with a septum was added free base porphyrin **2a** (250 mg, 0.32 mmol), $Zn(OAc)_2.2H_2O$ (700 mg, 3.20 mmol), CH_2Cl_2 (10 mL) and MeOH (10 mL) and the mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: AcOEt) to afford 277 mg (quant. yield) of compound **2b** as a purple solid.

Mp: >250 °C. ^{1}H NMR (DMSO, 300 MHz): 9.81 (s, 2H), 8.84 (d, 2H, *J* = 4.5 Hz), 8.61 (d, 2H, *J* = 4.6 Hz), 8.00-7.94 (m, 4H), 7.92-7.85 (m, 2H), 7.65-7.53 (m, 6H) 7.20 (m, 2H). ^{13}C NMR: 155.52, 149.47, 148.40, 143.58, 140.08, 137.62, 132.59, 131.27, 129.84, 128.05, 127.47, 125.78, 121.93, 120.44, 114.62, 114.13. HRMS (APPI$^+$): calcd. for $C_{44}H_{25}Cl_4N_4O_2Zn$: 845.0018, found: 845.0002 $(M+H)^+$.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1.1539
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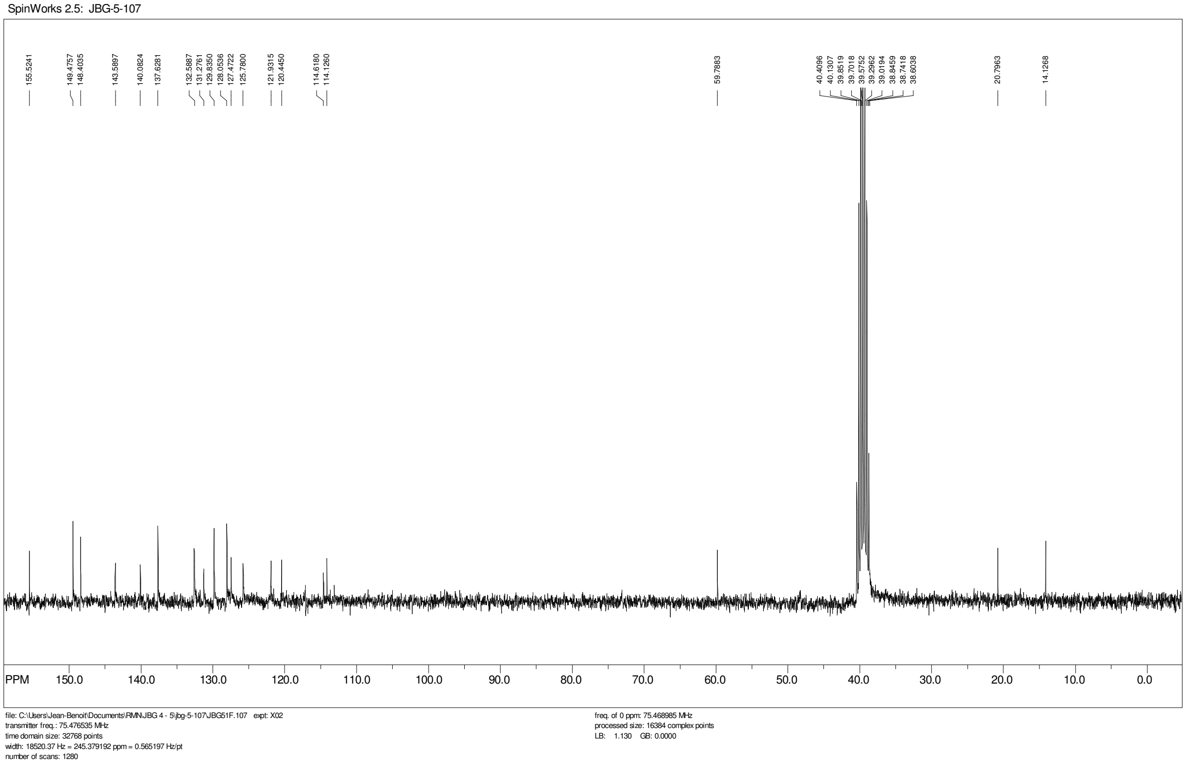
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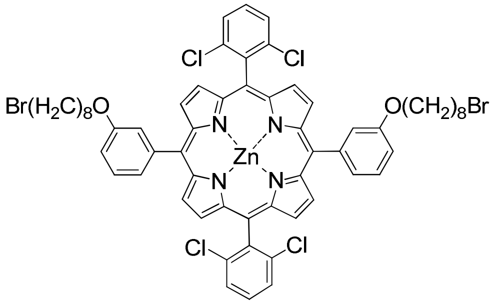
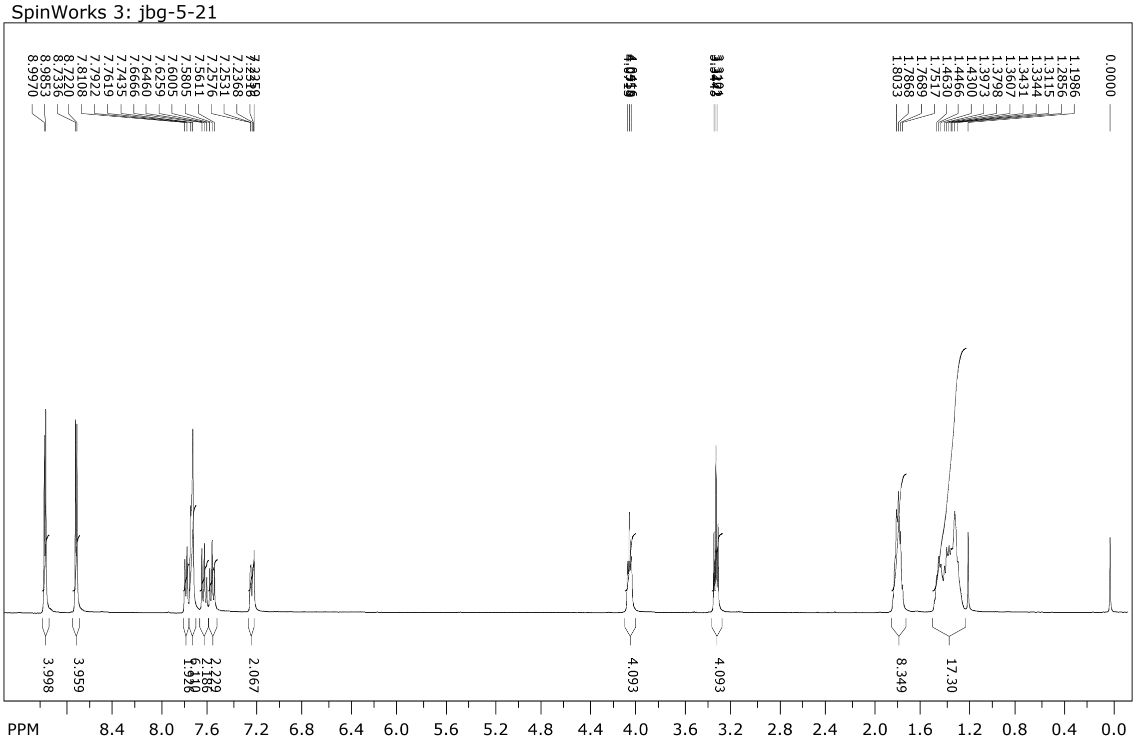


Synthesis of compound 4:

To a 500 mL round bottom flask equipped with a stir bar and sealed with a septum was added 3-(8-bromooctyloxy)benzaldehyde (750 mg, 2.39 mmol), 5-(2,6-Dichlorophenyl)dipyrromethane **1** (700 mg, 2.40 mmol) and CH_2Cl_2 (240 mL) and the mixture was degassed with a continuous flow of nitrogen for 15 minutes. Trifluoroacetic acid (486 mg, 4.27 mmol) was added dropwise and the reaction was stirred for 60 minutes. Then, *p*-chloranil (884 mg, 3.60 mmol) was added and the reaction allowed to stir overnight. The acid was neutralized with triethylamine (ca. 1.5 mL) and the solvent was removed under reduced pressure. The crude solid was triturated with methanol and run through a silica gel column chromatography on using 50% toluene/50% hexanes as eluent. This afforded the free base porphyrin (ca. 600 mg) that was dissolved in CH_2Cl_2 (15 mL) and methanol (5 mL) and $Zn(OAc)_2.2H_2O$ (470 mg, 2.14 mg) was added to the resulting solution. The reaction was heated at 40 °C overnight, the solvent was removed and the crude product was purified by column chromatography on silica gel (eluent: 40% CH_2Cl_2/60% hexanes) to afford 585 mg (40% yield) of compound **4** as a purple solid.

Mp: 135-137 °C, ^{1}H NMR ($CDCl_3$, 400 MHz): 8.99 (d, 2H, *J* = 4.6 Hz), 8.73 (d, 4H, *J* = 4.6 Hz), 7.80 (d, 2H, *J* = 7.2 Hz), 7.77-7.72 (m, 6H), 7.67-7.62 (m, 2H), 7.58 (t, 2H, *J* = 8.1 Hz), 7.24 (dd, 2H, *J* = 4.43 Hz, *J* = 2.0 Hz), 4.05 (t, 4H, *J* = 6.3 Hz), 3.32 (t, 4H, *J* = 6.9 Hz), 1.83-1.73 (m, 8H), 1.48-1.25 (m, 16 H). ^{13}C NMR: 157.53, 150.69, 149.41, 143.41, 140.68, 138.87, 138.84, 138.81, 133.41, 130.32, 127.99, 127.79, 127.54, 121.33, 121.16, 115.17, 114.45, 114.42, 68.41, 34.27, 33.00, 29.55, 29.45, 28.92, 28.32, 26.24. HRMS (APPI$^+$): calcd. for $C_{60}H_{55}Cl_4N_4O_2Zn$: 1225.0732, found: 1225.0683 $(M+H)^+$.



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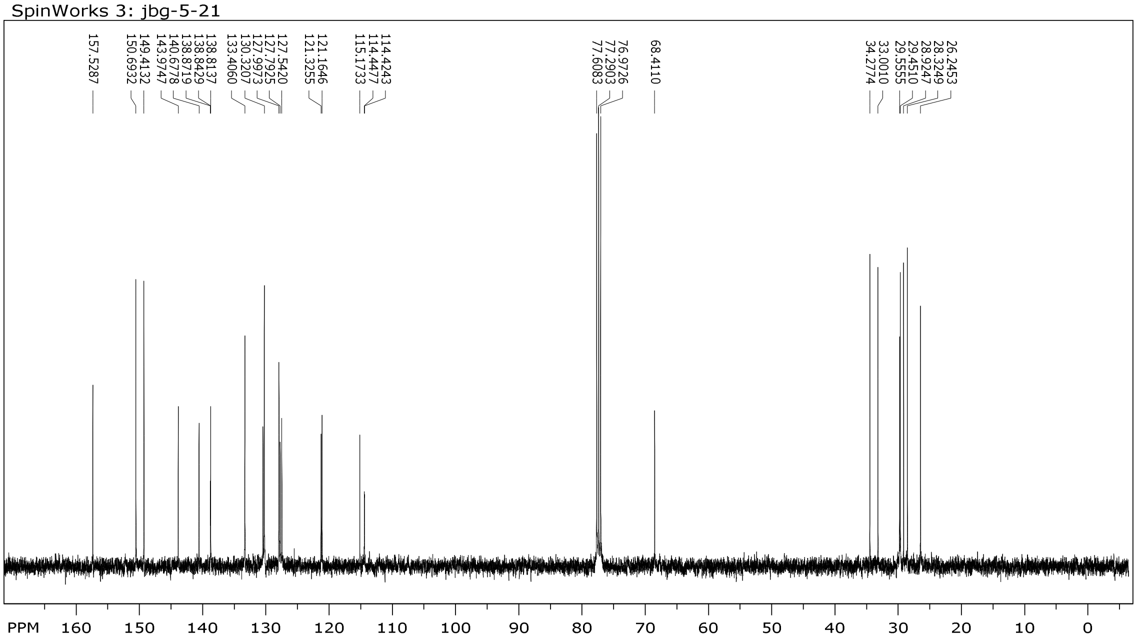

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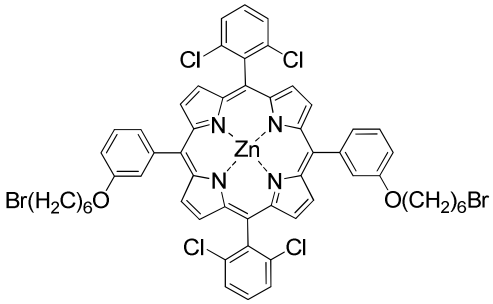
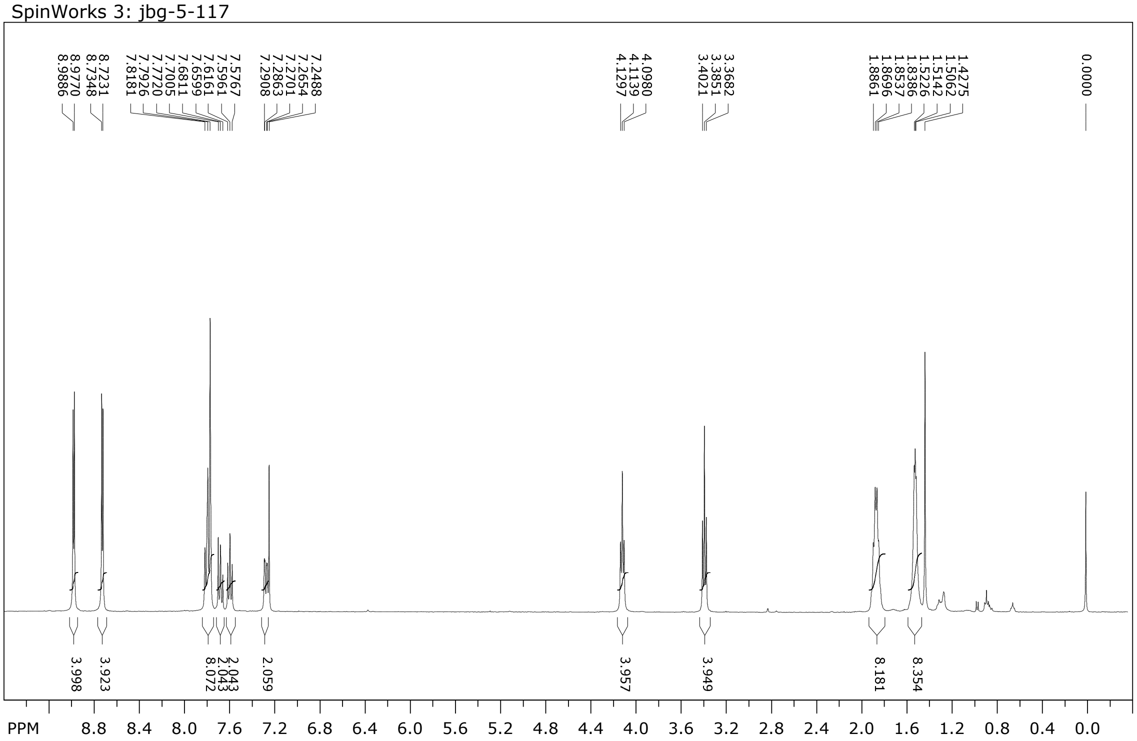


Synthesis of compound 3:

To a 500 mL round bottom flask equipped with a stir bar and sealed with a septum was added 3-(8-bromohexyloxy)benzaldehyde (370 mg, 1.30 mmol), 5-(2,6-dichlorophenyl)dipyrromethane **1** (380 mg, 1.30 mmol) and CH_2Cl_2 (130 mL) and the mixture was degassed with a continuous flow of nitrogen for 15 minutes. Trifluoroacetic acid (263 mg, 2.31 mmol) was added dropwise and the reaction was stirred for 60 minutes. Then, *p*-chloranil (480 mg, 1.95 mmol) was added and the reaction heated to reflux for 60 minutes. The acid was neutralized with triethylamine (256 mg, 2.54 mmol) and $Zn(OAc)_2.2H_2O$ (1,42 g, 6.50 mmol) and methanol (20 mL) were added and the resulting solution was heated to reflux for 60 minutes. The solvent was removed under reduced pressure and the crude product triturated with methanol (30 mL) and the residue was purified by column chromatography on silica gel (eluent: gradient from 30% CH_2Cl_2/70% hexanes to 45% CH_2Cl_2/55% hexanes) to afford 316 mg (41% yield) of compound **3** as a purple solid. Mp: 171-173 °C. ^1H NMR ($CDCl_3$, 400 MHz): 8.98 (d, 2H, J = 4.7 Hz), 8.72 (d, 4H, J = 4.6 Hz), 7.82-7.75 (m,8H), 7.77-7.72 (m, 6H), 7.67 (t, 2H, J = 8.2 Hz), 7.59 (t, 2H, J = 8.1 Hz), 7.27 (dd, 2H, J = 4.4 Hz, J = 2.0 Hz), 4.11 (t, 4H, J = 6.5 Hz), 3.38 (t, 4H, J = 6.7 Hz), 1.91-1.80 (m, 8H), 1.55-1.47 (m, 8 H). ^{13}C NMR: 157.48, 150.63, 149.37, 144.05, 140.72, 138.87, 138.85, 138.82, 133.32, 130.50, 130.27, 127.98, 127.52, 121.22, 121.13, 115.10, 114.33, 68.19, 34.07, 32.93, 29.45, 28.21, 25.60. HRMS (APPI$^+$): calcd. for $C_{56}H_{47}Cl_4N_4O_2Zn$: 1169.0106, found: 1169.0136 $(M+H)^+$.

SpinWorks 3: jbg-5-117



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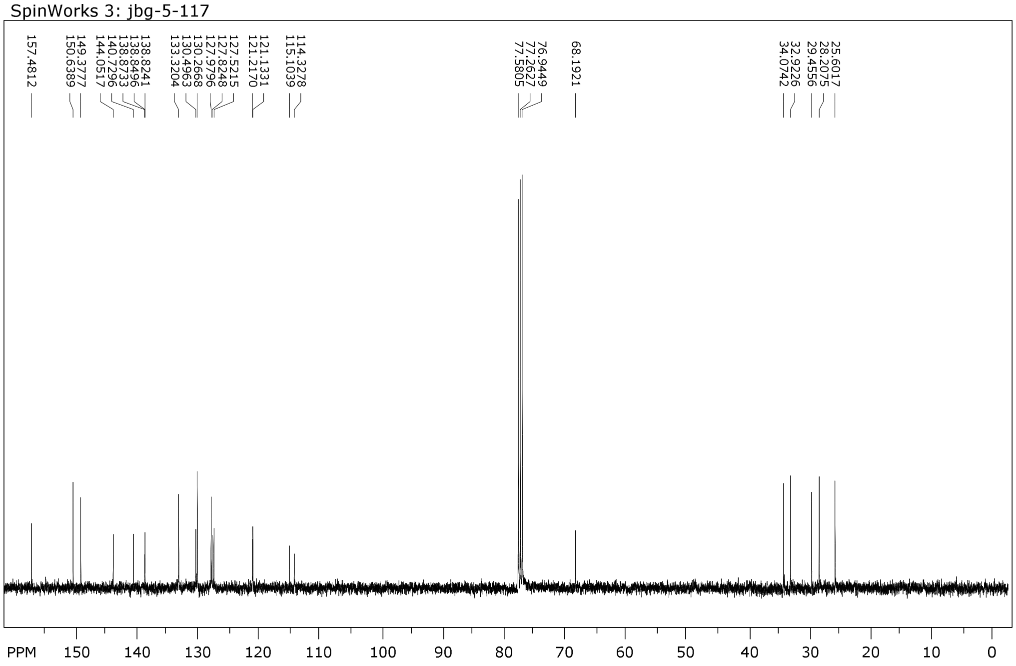
SpinWorks 3: jbg-5-117



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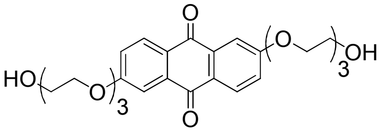
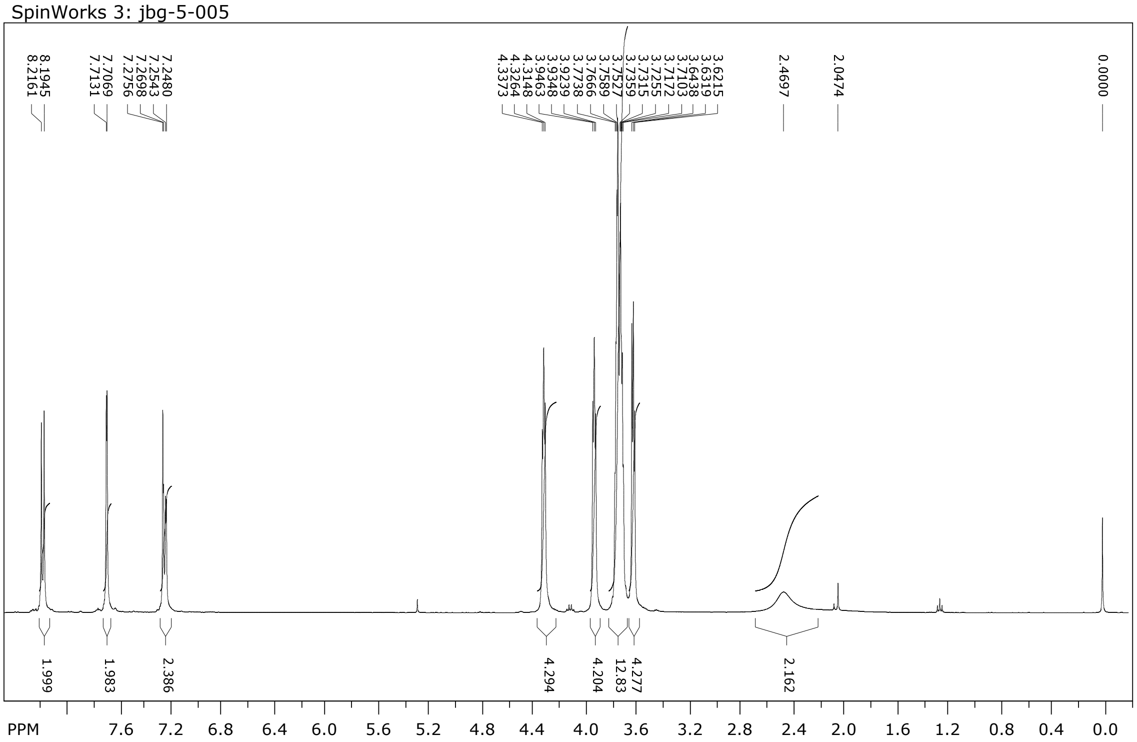


Synthesis of compound 5:

To a 10 mL round bottom flask equipped with a stir bar and sealed with a septum was added anthraflavic acid (300 mg, 1.25 mmol), 2-[2-(2-chloroethoxy)ethoxy]ethanol (527 mg, 3.13 mmol), K_2CO_3 (431 mg, 3.13 mmol) and NaI (47 mg, 0.31 mmol) and DMF (3 mL). The reaction mixture was heated and stirred at 120 °C for 2 hours. Once cooled, CH_2Cl_2 and EtOAc were added and the organic layer was washed twice with water, dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was recrystallized from EtOAc (ca. 25 mL) to afford 466 mg (76% yield) of compound **5** as an off-white solid.

Mp: 119-121 °C. ^1H NMR ($CDCl_3$, 400 MHz): 8.21 (d, 2H, *J* = 8.6 Hz), 7.71 (d, 2H, *J* = 2.4 Hz), 7.26 (dd, 2H, *J* = 4.3 Hz, *J* = 2.5 Hz), 4.31 (t, 4H, *J* = 4.3 Hz), 3.93 (t, 4H, *J* = 4.6 Hz) 3.80-3.69 (m, 12H), 3.63 (t, 4H, *J* = 4.6 Hz) 2.47 (bs, 2H). ^{13}C NMR: 182.34, 163.79, 135.95, 129.92, 127.49, 121.40, 110.76, 72.74, 71.15, 70.60, 69.66, 68.27, 62.00. HRMS (APPI$^+$): calcd. for $C_{26}H_{33}O_{10}$: 505.2068, found: 505.2041 $(M+H)^+$.



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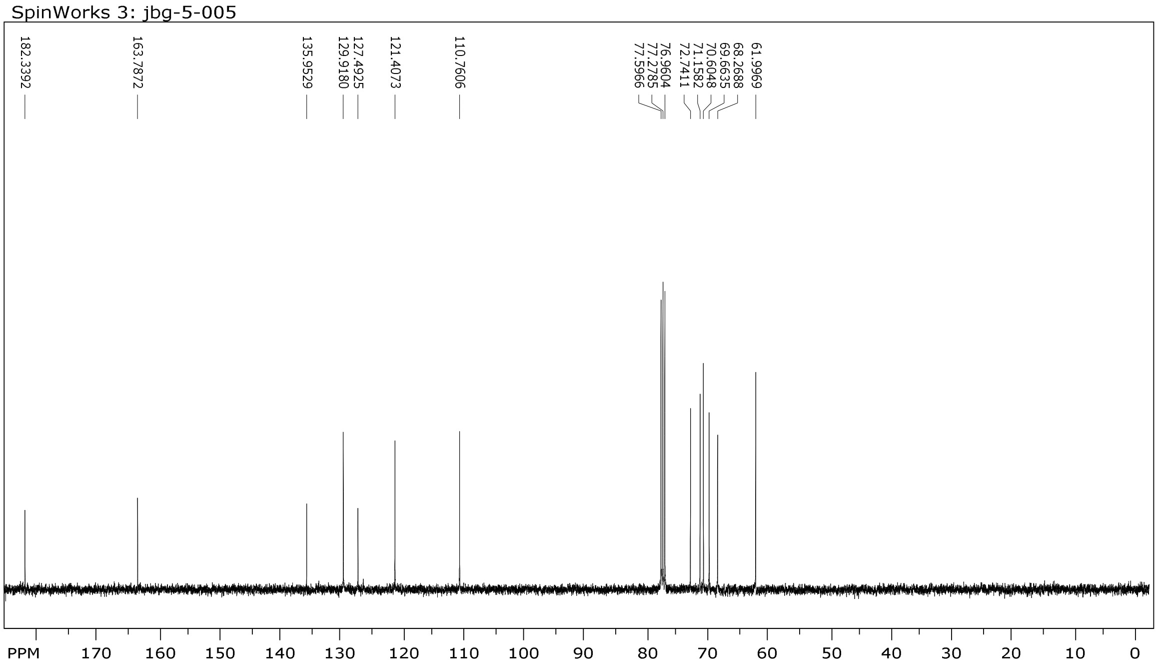

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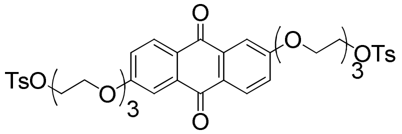
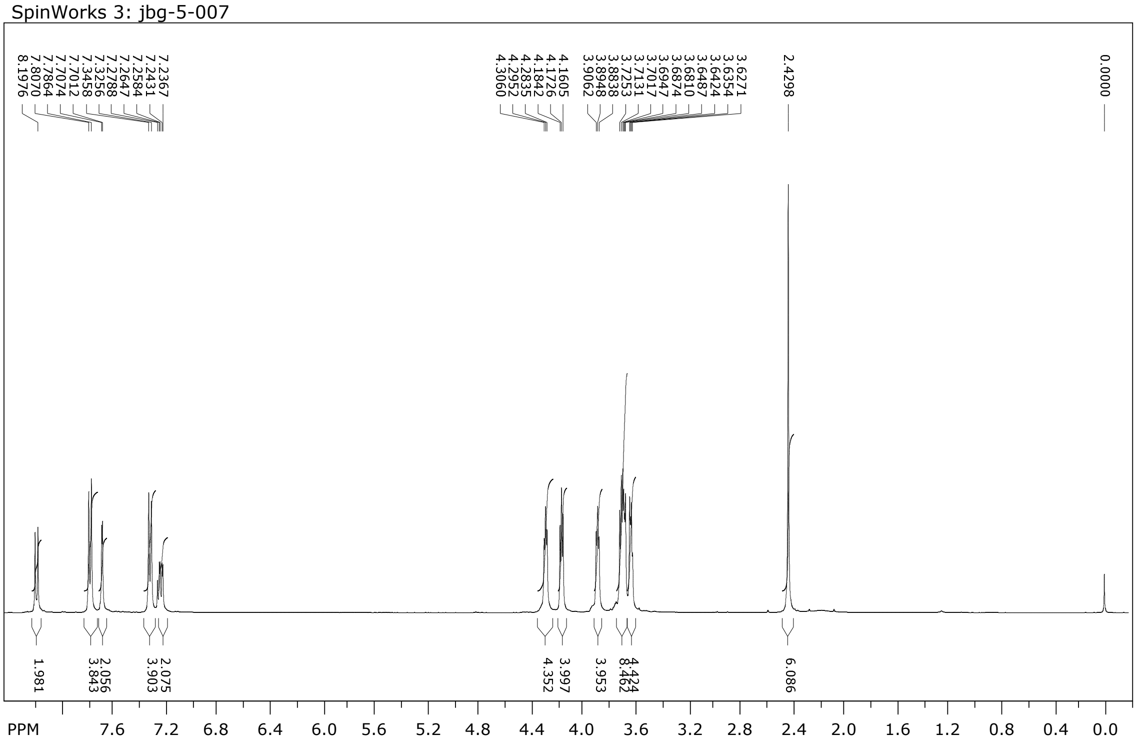


Synthesis of compound 6:

To a flame dried 10 mL round bottom flask equipped with a stir bar and sealed with a septum was added anthraquinone **5** (250 mg, 0.495 mmol), triethylamine (200 mg, 1.98 mmol) and anhydrous CH_2Cl_2 (2 mL). The reaction vessel was then cooled to 0 °C using an ice bath and tosyl chloride (236 mg, 1.24 mmol) was added. The reaction was left to warm to room temperature overnight. The solvent was removed under reduce pressure and the crude product was purified by column chromatography on silica gel using (eluent: 3% MeOH/97% CH_2Cl_2) to afford 380 mg (94% yield) of compound **6** as a yellow solid.

Mp: 98-101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.21 (d, 2H, J = 8.6 Hz), 7.79 (d, 4H, J = 8.3 Hz), 7.70 (d, 2H, J = 2.3 Hz), 7.33 (d, 4H, J = 7.7 Hz), 7.25 (dd, 2H, J=4.4 Hz, J=2.5 Hz), 4.29 (t, 4H, J = 4.3 Hz), 4.17 (t, 4H, J = 4.7), 3.89 (t, 4H, J = 4.7 Hz), 3.73-3.66 (m, 8H), 3.66-3.61 (m, 4H), 2.43 (s, 6H). ^{13}C NMR: 182.31, 163.83, 145.08, 135.95, 133.15, 130.07, 129.91, 128.20, 127.45, 121.29, 110.85, 71.06, 71.03, 69.70, 69.48, 68.99, 68.32, 21.89. HRMS (APPI$^+$): calcd. for $C_{40}H_{45}O_{14}S_2$: 813.2245, found: 813.2210 $(M+H)^+$.



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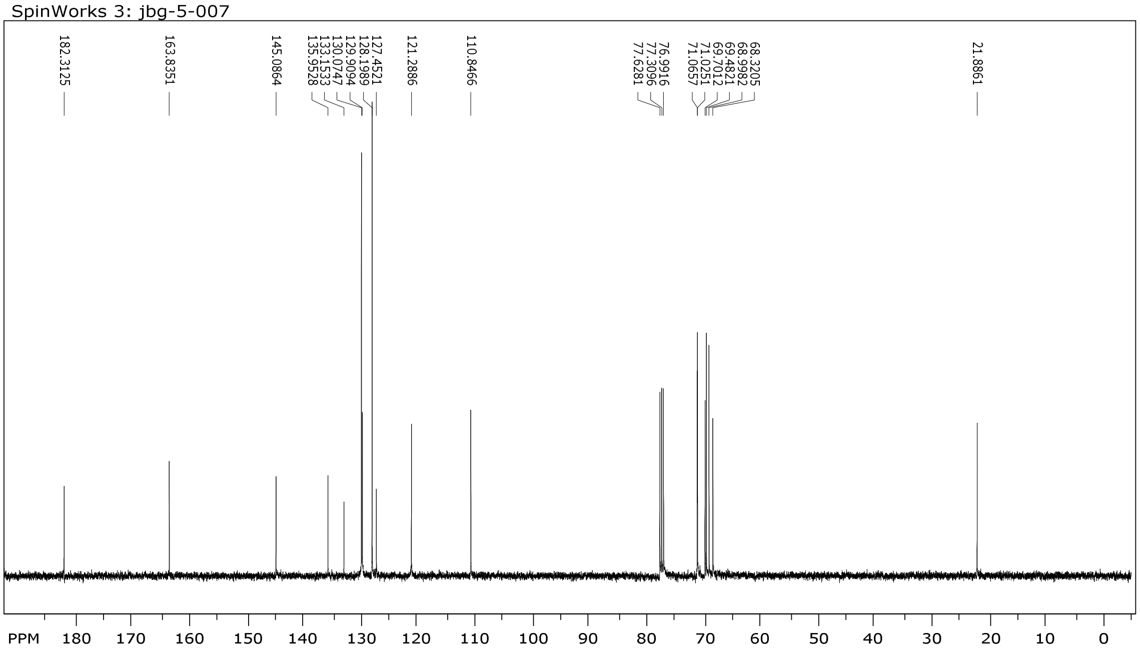

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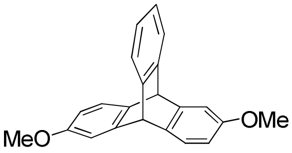
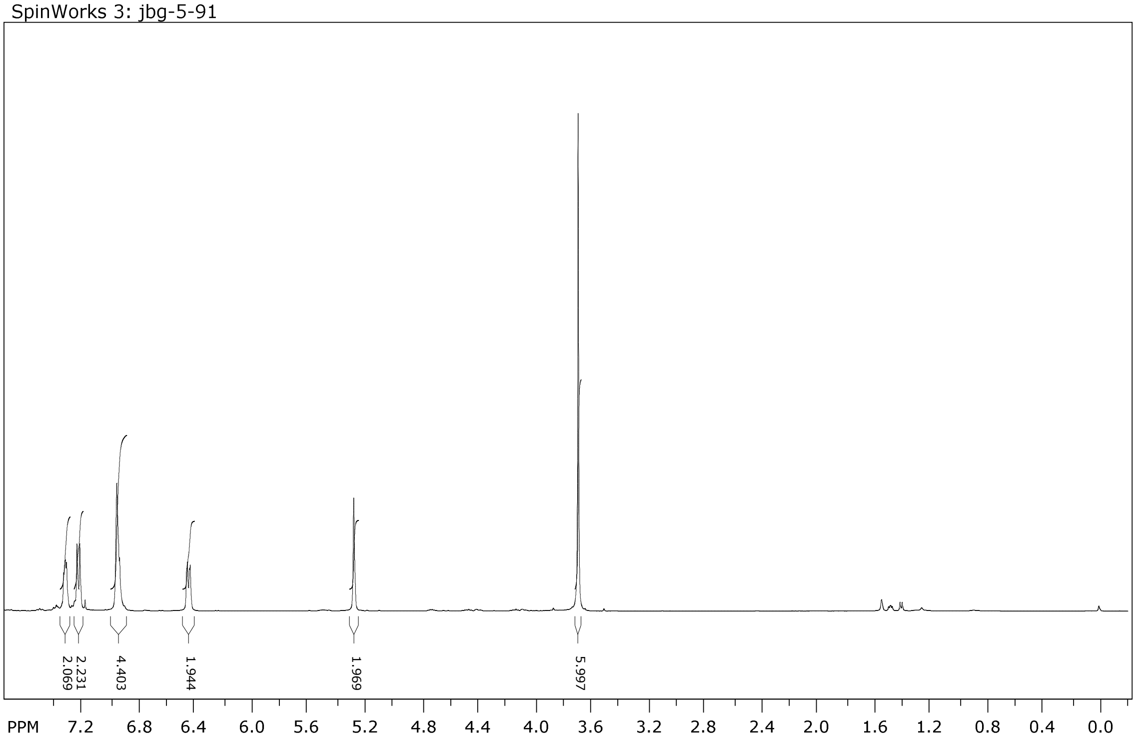


Synthesis of compound 8:

To a 25 mL round bottom flask equipped with a stir bar and sealed with a septum was added 2,6-dimethoxyanthracene (180 mg, 0.75 mmol), 2-carboxybenzenediazonium chloride (696 mg, 3.77 mmol), 1,2-epoxypropane (1,5 mL) and dichloroethane (15 mL). The reaction vessel was put under a low vacuum and backfilled with nitrogen 4 times and refluxed for 2 hours. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: gradient from 25% CH_2Cl_2/75% hexanes to 35% CH_2Cl_2/65% hexanes) to afford 212 mg (89% yield) of compound **8** as a white solid.

Mp: 168-172 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.33 (m, 2H), 7.23 (d, 2H, *J* = 7.5 Hz), 6.96 (m, 4H), 6.45 (dd, 2H, *J* = 3.2 Hz, *J* = 1.9 Hz), 5.29 (s, 2H), 3.69 (s, 6H). ^{13}C NMR: 157.56, 147.49, 145.78, 137.73, 125.39, 124.33, 123.64, 110.96, 109.31, 55.70, 53.69. HRMS (APPI$^+$): calcd. for $C_{22}H_{18}O_2$: 314.1301, found: 314.1260 $(M)^+$.



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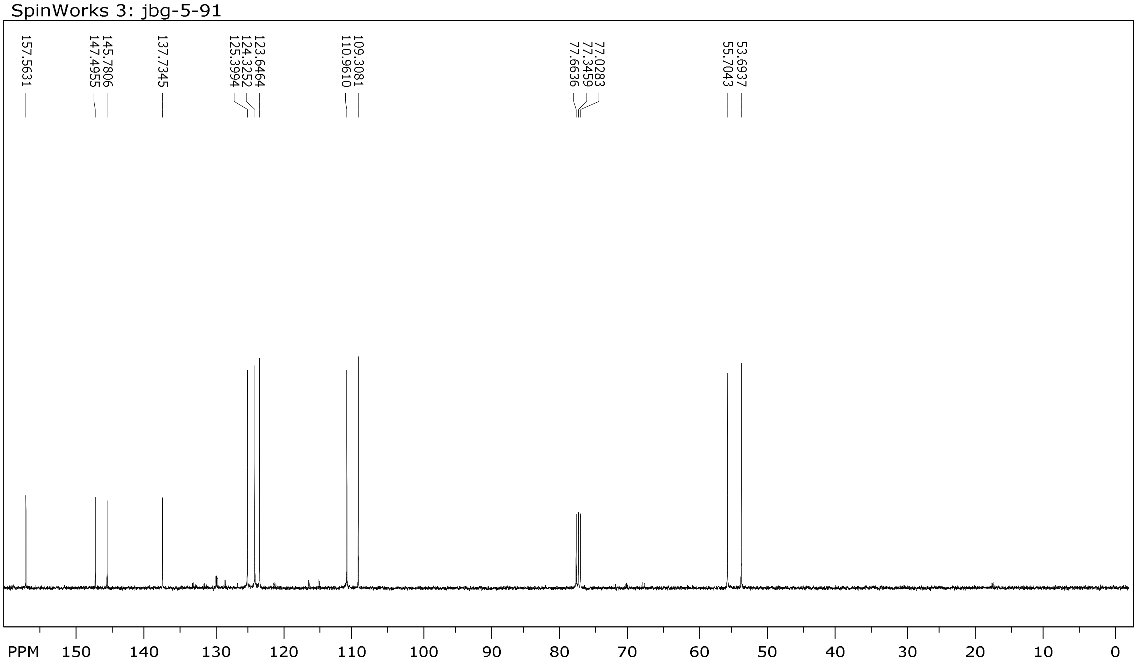

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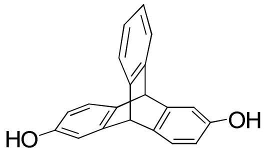
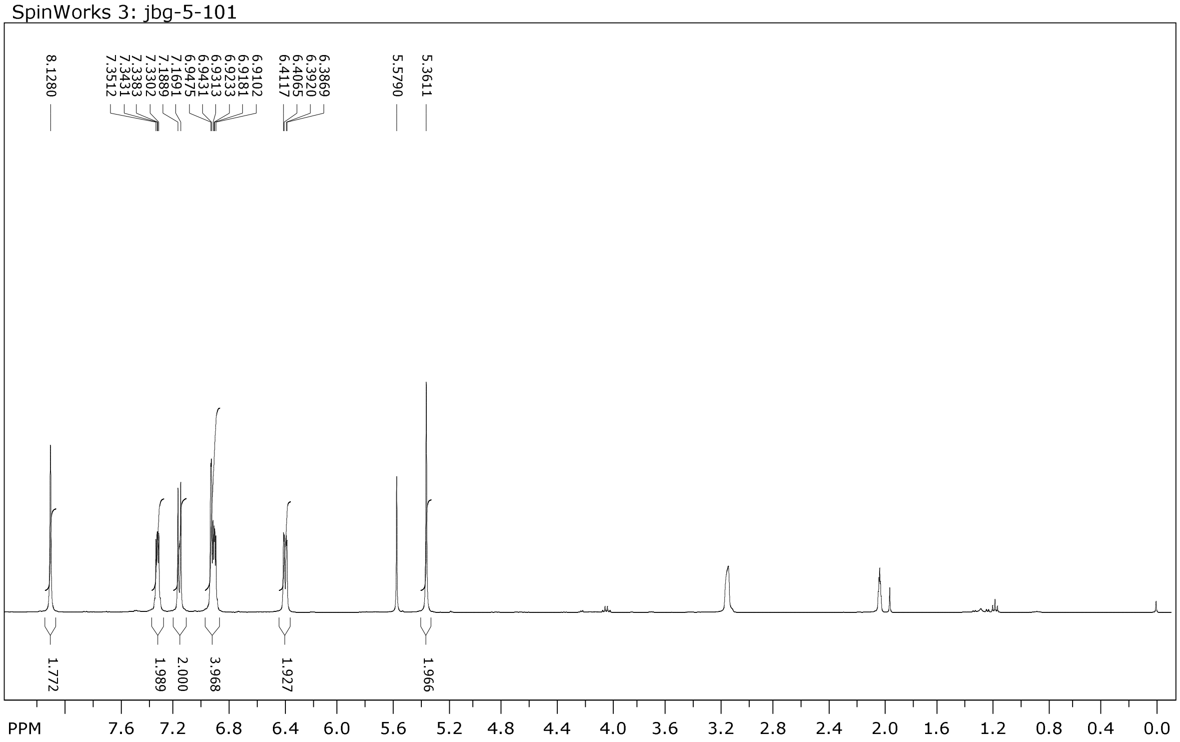


Synthesis of compound 9:

To a flame dried 25 mL round bottom flask equipped with a stir bar and sealed with a septum under nitrogen was added 2,6-dimethoxytriptycene **6** (212 mg,0.67 mmol), and anhydrous CH_2Cl_2 (7 mL) and the reaction vessel was cooled to 0 °C with an ice bath. Boron tribromide (1.00 g, 4.02 mmol) was added dropwise and the solution was allowed to warm to room temperature over 2 hours. The reaction was quenched with water and extracted three times with a mixture of CH_2Cl_2/EtOAc (1:1, 3x15 mL). The organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: 10% AcOEt/90% CH_2Cl_2) to afford 133 mg (70% yield) of compound **9** as an off-white solid.

Mp: >250 °C. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz): 8.14 (s, 2H), 7.35 (dd, 2H, *J* = 2.7 Hz, *J* = 3.3 Hz), 7.19 (d, *J* = 7.8 Hz), 6.95 (d, 2H, *J* = 1.7 Hz), 6.93 (dd, 2H, *J* = 2.7 Hz, *J* = 3.3 Hz), 6.41 (dd, 2H, *J* = 4.1 Hz, *J* = 2.0 Hz), 5.37 (s, 2H). ^{13}C NMR: 154.98, 148.07, 146.54, 136.90, 124.90, 124.23, 123.34, 111.68, 110.53. HRMS (APPI$^+$): calcd. for $C_{20}H_{14}O_2$: 286.0988, found: 286.0975 $(M)^+$.



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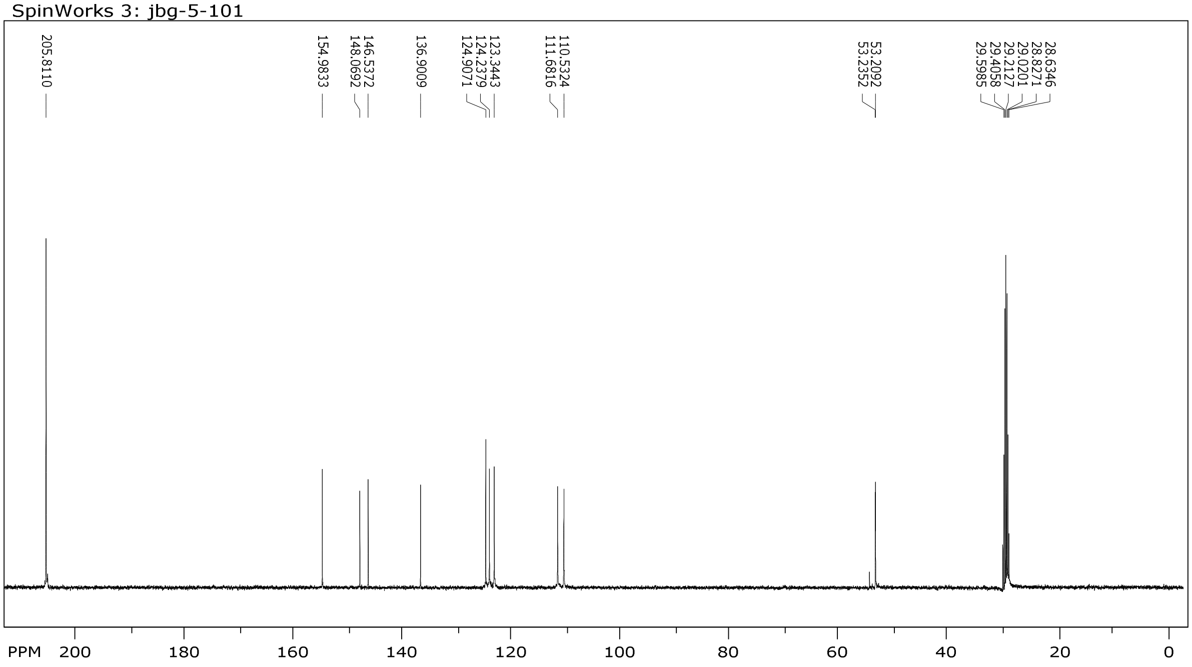

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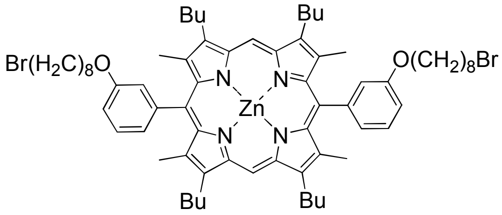
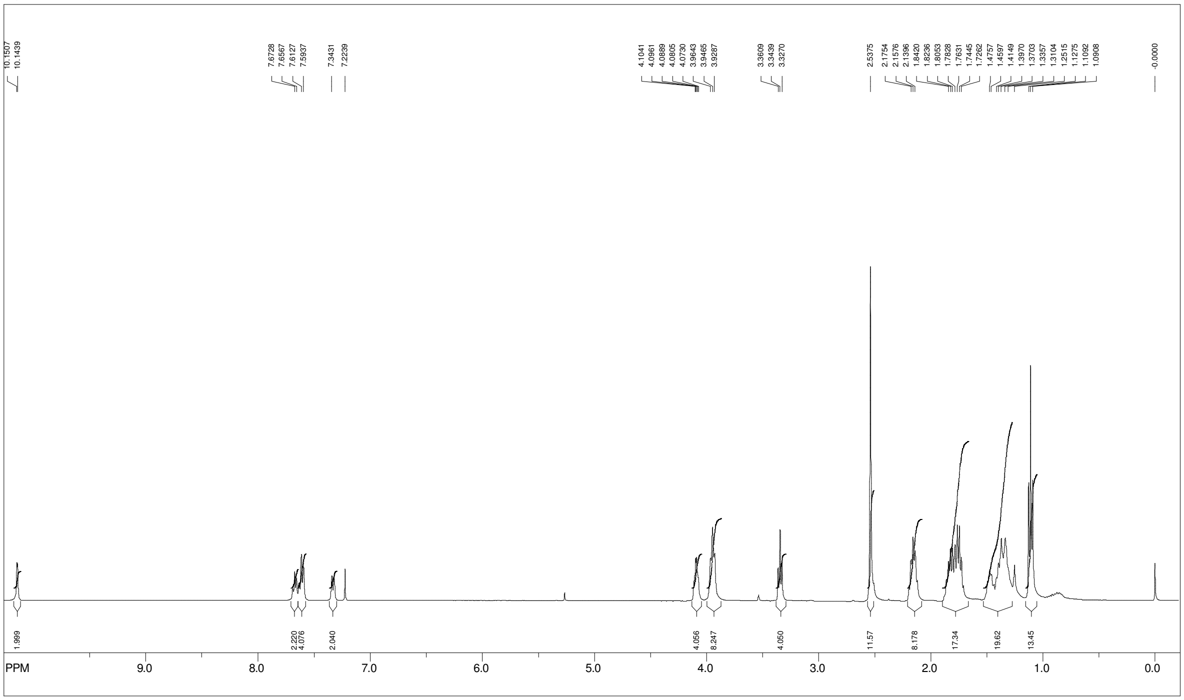


Synthesis of compound 12

To a 250 mL round bottom flask equipped with a stir bar and sealed with a septum was added 3-(8-bromooctyloxy)benzaldehyde (274 mg, 0.874 mmol), 4,4´-dimethyl-3,3´-dibutyl-2,2´-dipyrrylmethane **12** (250 mg, 0.874 mmol) and CH_2Cl_2 (140 mL) and the mixture was degassed with a flow of nitrogen for 15 minutes. Trifluoroacetic acid (29 mg, 0.25 mmol) was added and the reaction was stirred for 2 hours at room temperature. Then, *p*-chloranil (318 mg, 1.30 mmol) was added and the reaction was stirred overnight. The acid was neutralized with triethylamine (ca. 0.5 mL) and $Zn(OAc)_2.2H_2O$ (952 mg, 4.35 mmol) and methanol (20 mL) were added. The resulting solution was heated to reflux for 30 minutes. Once cooled, the reaction mixture was washed successively with NaOH aq. (0.1 M), water, brine and then dried over Na_2SO_4. The solvent was evaporated under reduced pressure and purified by a first column chromatography on silica gel (eluent 30% CH_2Cl_2/70% hexanes) and a second column chromatography on silica gel (eluent 50% toluene/50% texanes) to afford a purple gummy solid that was triturated with cold methanol to afford a 304 mg (60% yield) of compound **12** as a purple solid. Mp: 155-157 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 10.15 (d, 2H, *J*= 2.6 Hz), 7.67 (t, 2H, *J* = 6.7 Hz), 7.61 (m, 4H), 7.33(m, 2H), 4.09 (m, 4H), 3.95 (t, 8H, *J* = 8 Hz), 3.34 (t, 4H, *J* = 6.7 Hz), 2.54 (s, 12H), 2.16 (m, 8H), 1.87-1.72 (m, 16 H), 1.50-1.28 (m, 18H), 1.11 (t, 12H, *J* = 7.4 Hz). ^{13}C NMR: 158.81, 147.83, 146.61, 145.09, 143.64, 138.44, 128.64, 126.55, 119.84, 119.46, 115.25, 97.83, 68.52, 35.78, 34.22, 33.00, 29.58, 29.48, 28.94, 28.33, 29.72, 26.21, 23.66, 15.33, 14.54. HRMS (APPI$^+$): calcd. for $C_{68}H_{91}Br_2N_4O_2Zn$: 1217.4800, found: 1217.4748 $(M+H)^+$.

SpinWorks 2.5: jbg-5-169



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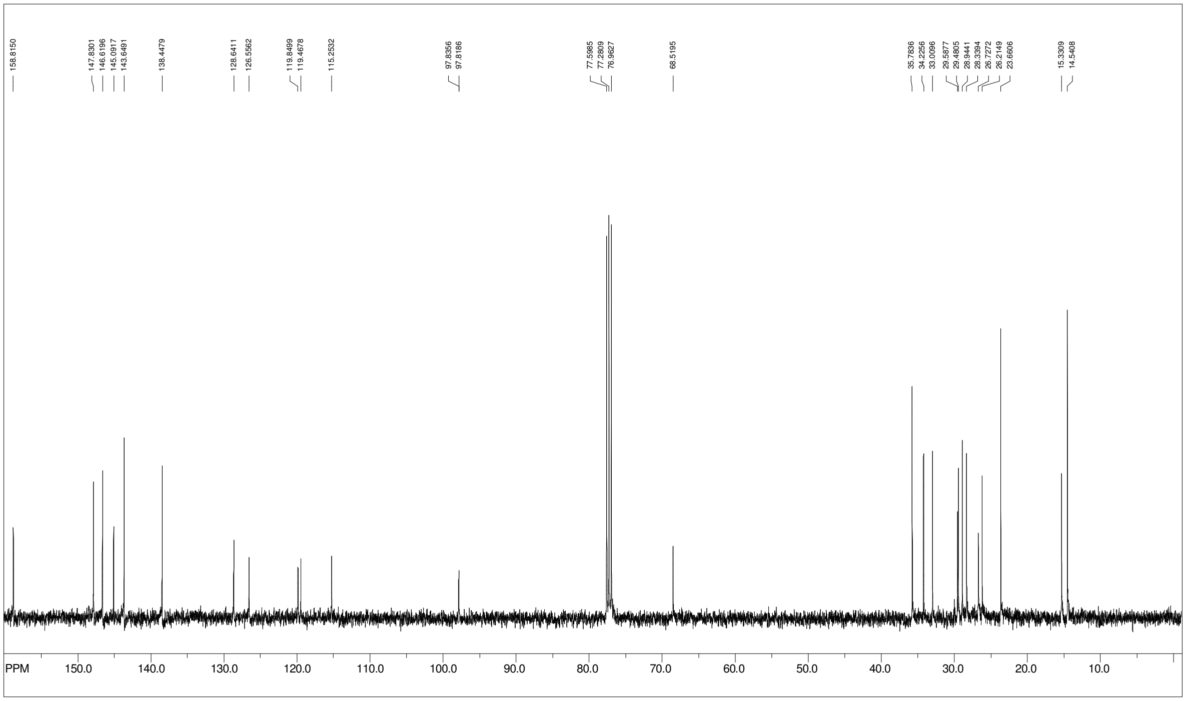
SpinWorks 2.5: jbg-5-169



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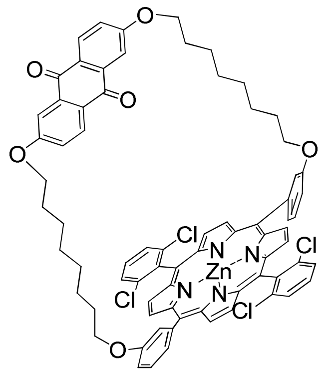
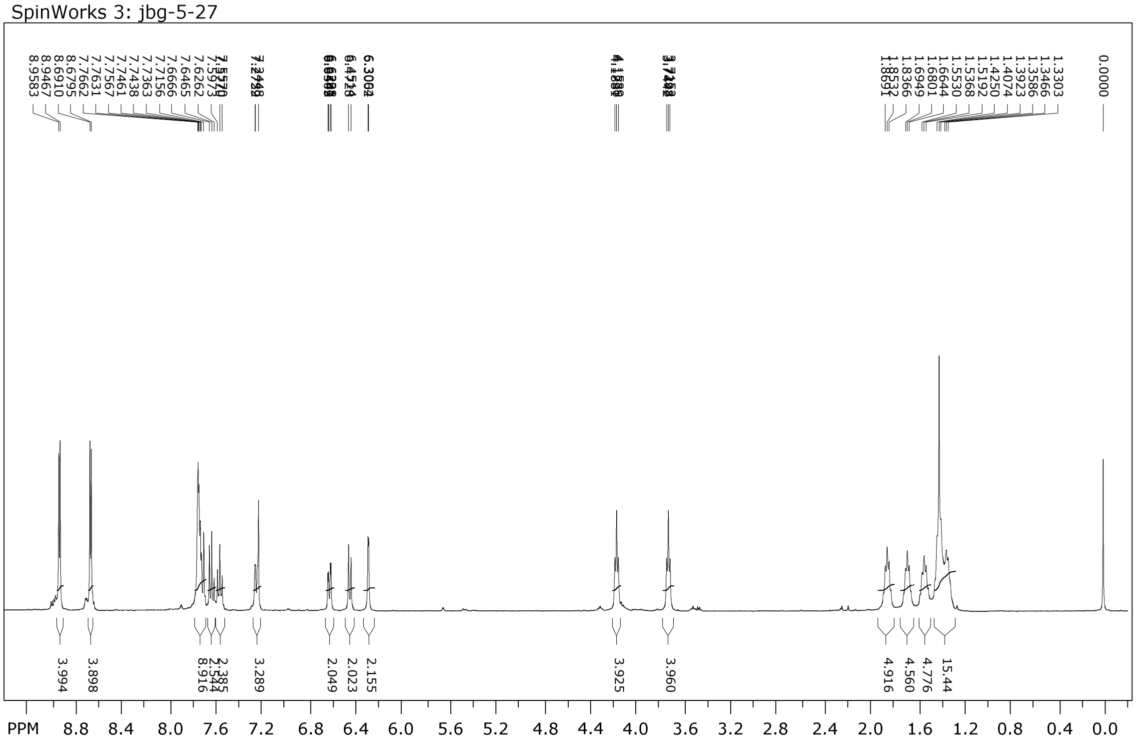


Synthesis of compound H1:

To a 250 mL round bottom flask equipped with a stir bar and sealed with a septum was added porphyrin **4** (150 mg, 0.122 mmol), anthraflavic acid (21 mg, 0.86 mmol), K_2CO_3 (67 mg, 0.49 mmol), NaI (18 mg, 0.12 mmol) and DMF (100 mL). The reaction vessel was put under a low vacuum and backfilled with nitrogen 4 times. The solution was then heated at 80 °C overnight. Once cooled, the solvent was evaporated under reduced pressure and the residue was dissolved in toluene, filtered and the solvent evaporated. The residue was purified by column chromatography on silica gel (eluent: toluene) to afford 81 mg (50% yield) of compound **H1** as a purple solid.

^{1}H NMR (($CDCl_3$, 400 MHz): 8.95 (d, 4H, *J*= 4.6 Hz), 8.68 (d, 4H, *J*= 4.5 Hz), 7.78-7.70 (m, 8H), 7.64 (t, 2H, *J* = 7.9 Hz), 7.57 (t, 2H, *J* = 7.7 Hz), 7.26 (dd, 2H, *J* = 4.2 Hz, *J* = 1.9 Hz), 6.63 (dd, 2H, *J* = 4.4 Hz, *J* = 2.1 Hz), 6.46 (d, 2H, *J* = 6.5 Hz), 6.30 (d, 2H, *J* = 2.3 Hz), 4.17 (t, 4H, *J* = 6.0 Hz), 3.73 (t, 4H, *J* = 5.6 Hz), 1.90-1.81 (m, 4H), 1.71-1.63 (m, 4H), 1.58-1.49 (m, 4H), 1.44-1.29 (m, 12H). ^{13}C NMR: 181.64, 163.63, 157.49, 150.58, 149.31, 144.29, 140.93, 138.89, 138.85, 134.79, 133.1, 130.34, ,30.17, 129.13, 127.88, 127.85, 127.38, 125.81, 122.31, 121.05, 121.03, 115.01, 112.79, 109.56, 68.37, 67.92, 28.76, 28.32, 28.08, 27.92, 25.13, 24.99. HRMS (APPI$^+$): calcd. for $C_{74}H_{61}Cl_4N_4O_6Zn$: 1305.2631, found: 1305.2646 $(M+H)^+$.



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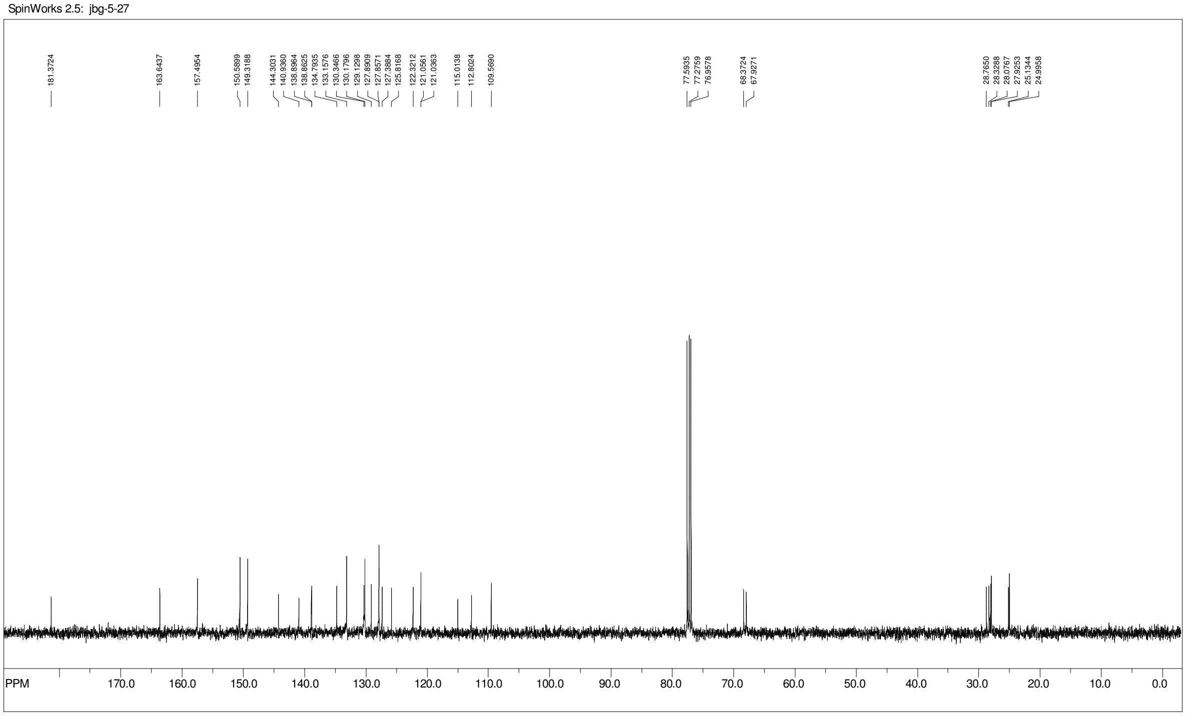

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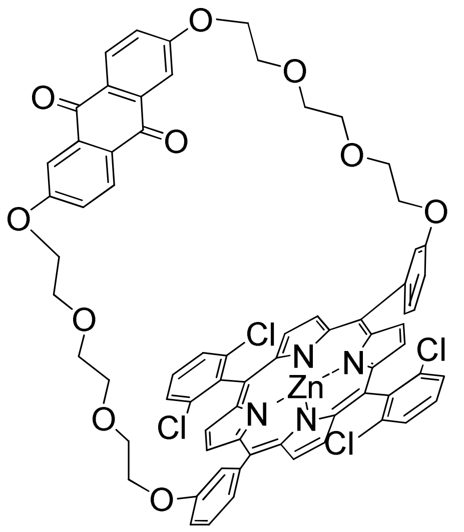
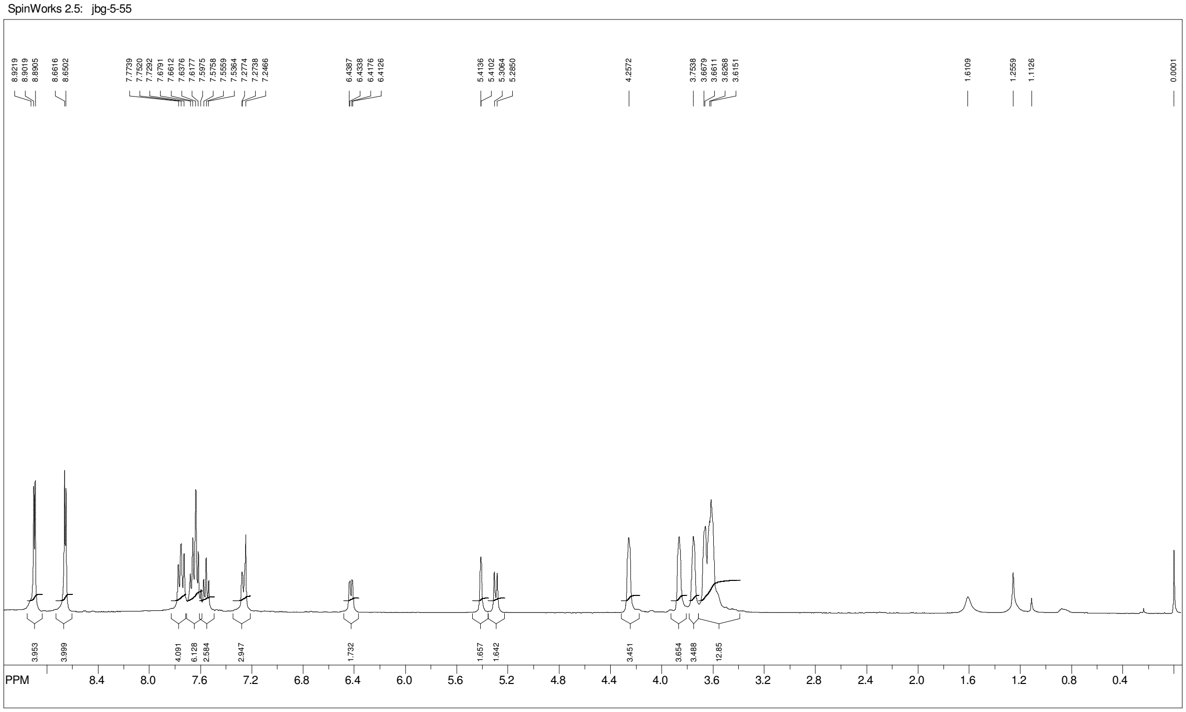


Synthesis of compound H2:

To a 100 mL round bottom flask equipped with a stir bar and sealed with a septum was added porphyrin **2a** (96 mg, 0.123 mmol), bis-tosyl anthraquinone **6** (100 mg, 0.123 mmol), K_2CO_3 (340 mg, 2.46 mmol) and DMF (30 mL). The reaction vessel was put under a low vacuum and backfilled with nitrogen 4 times. The reaction was then heated at 75 °C overnight. Once cooled, the solvent was evaporated under reduced pressure. This residue was purified by column chromatography on silica gel (eluent: 40% AcOEt/60% toluene). The porphyrin was dissolved in CH_2Cl_2 (20 mL), MeOH (4 mL) and $Zn(OAc)_2.2H_2O$ (88 mg, 0.40 mmol) and the solution was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue purified by chromatography column on silica gel (eluent: 50% AcOEt/50% CH_2Cl_2) to afford 49 mg (29% yield) of compound **H2** as a purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): 8.90 (d, 4H, *J* = 4.6 Hz), 8.65 (d, 4H, *J* = 4.6 Hz), 7.75 (t, 4H, *J* = 8.8 Hz), 7.69-7.59 (m, 6H), 7.56 (t, 2H, *J* = 7.9 Hz), 7.26 (m, 2H), 6.42 (dd, 2H *J* = 4.6 Hz, *J* = 2.0 Hz), 5.29 (d, 2H, *J* = 8.4), 4.26 (t, 4H, *J* = 4.3 Hz), 3.86 (m, 4H), 3.75 (m, 4H), 3.68-3.58 (m, 12H). ^{13}C NMR: 180.64, 163.00, 157.16, 150.50, 149.29, 144.46, 141.06, 138.86, 138.83, 133.94, 132.94, 130.27, 128.84, 128.02, 127.88, 127.76, 127.39, 125.13, 121.72, 120.92, 120.87, 114.99, 113.45, 109.07, 71.46, 71.22, 70.12, 69.39, 68.09, 68.03. HRMS (APPI$^+$): calcd. for $C_{70}H_{53}Cl_4N_4O_{10}Zn$: 1313.1802, found: 1313.1804 $(M+H)^+$.



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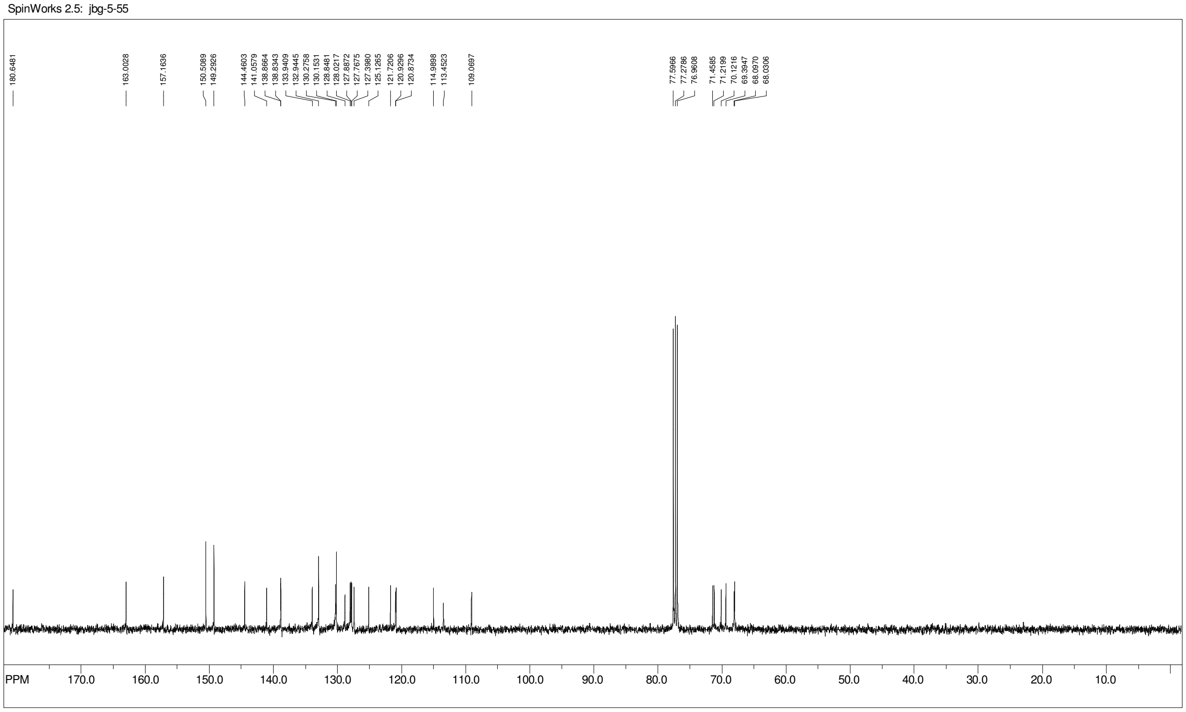
width: 6396.42 Hz = 16.000012 ppm = 0.133548 Hz/pt
number of scans: 8

freq. of 0 ppm: 399.773436 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.0000



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number of scans: 512

freq. of 0 ppm: 100.523085 MHz
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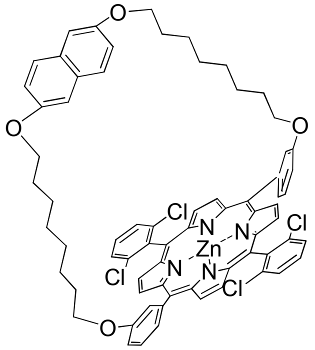
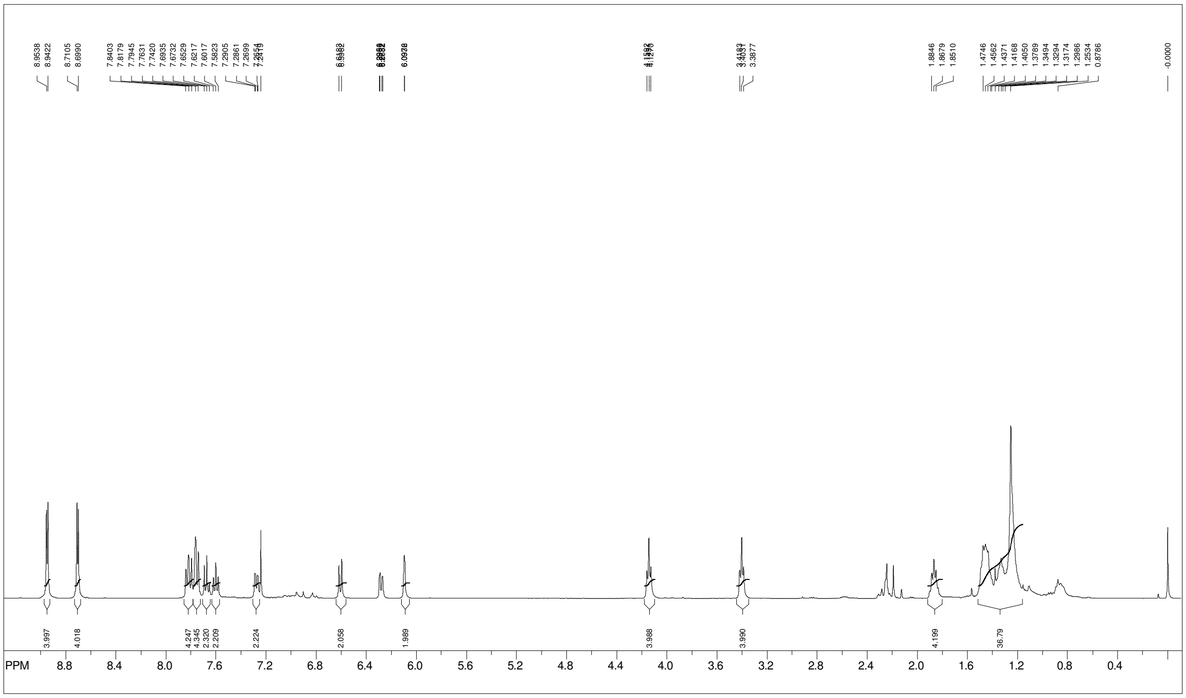


Synthesis of compound H3:

To a 250 mL round bottom flask equipped with a stir bar and sealed with a septum was added porphyrin **4** (76 mg, 0.061 mmol), 2,6-dihydroxynaphthalene (10 mg, 0.061 mmol), K_2CO_3 (90 mg, 0.65 mmol), NaI (24mg, 0.16 mmol) and DMF (80 mL). The reaction vessel was degassed using a low vacuum and backfilled with nitrogen 4 times and heated to 80 °C overnight. Once cooled, the solvent was evaporated under reduced pressure and the residue was dissolved in toluene, filtered and the solvent was evaporated. The residue was purified by column chromatography on silica gel (eluent: toluene) to afford 16 mg (22 % yield, 95% purity) of host **H3** as a purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): 8.95 (d, 4H, *J* = 4.5 Hz), 8.70 (d, 4H, *J* = 4.5 Hz), 7.81 (t, 4H, *J* = 8.9 Hz), 7.75 (m, 4H), 7.67 (d, 2H, *J* = 8.1 Hz), 7.60 (d, 2H, *J* = 8.0 Hz), 7.28 (dd, 2H, *J* = 4.2 Hz, *J* = 1.9 Hz), 6.61 (d, 2H, *J* = 8.7 Hz), 6.28 (dd, 2H, *J* = 4.4 Hz, *J* = 2.0 Hz), 6.10 (d, 2H, *J* = 1.9 Hz), 4.14 (t, 4H, *J* = 6.5 Hz), 3.40 (t, 4H, 6.1 Hz), 1.86 (m, 4H), 1.50-1.20 (m, 20H). ^{13}C NMR: 157.41, 154.68, 150.61, 149.30, 144.09, 140.80, 139.07, 138.65, 133.29, 130.46, 130.46, 130.13, 128.69, 128.00, 127.97, 127.45, 127.40, 127.09, 121.97, 121.15, 118.59, 114.99, 113.79, 106.30, 106.27, 68.20, 67.73, 29.96, 29.02, 28.83, 28.79, 28.54, 25.39. HRMS (APPI$^+$): calcd. for $C_{70}H_{60}Cl_4N_4O_6Zn$: 1223.2631, found: 1226.2638 (M)$^+$.

SpinWorks 2.5: jbg-5-69



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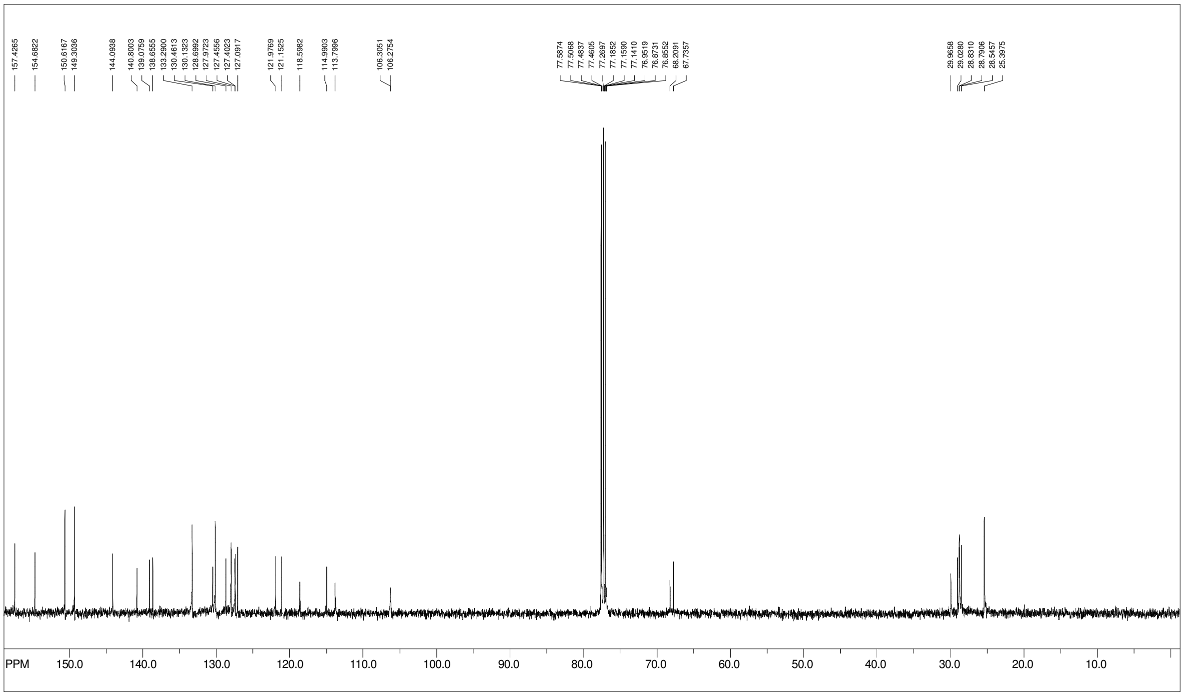
number of scans: 16

freq. of 0 ppm: 399.773438 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.5: jbg-5-69



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time domain size: 60288 points
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number of scans: 1000

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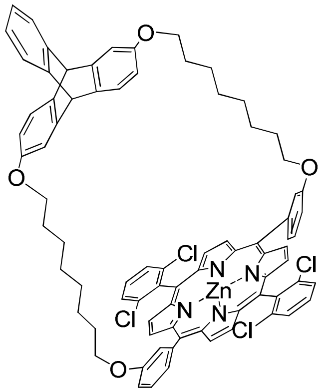
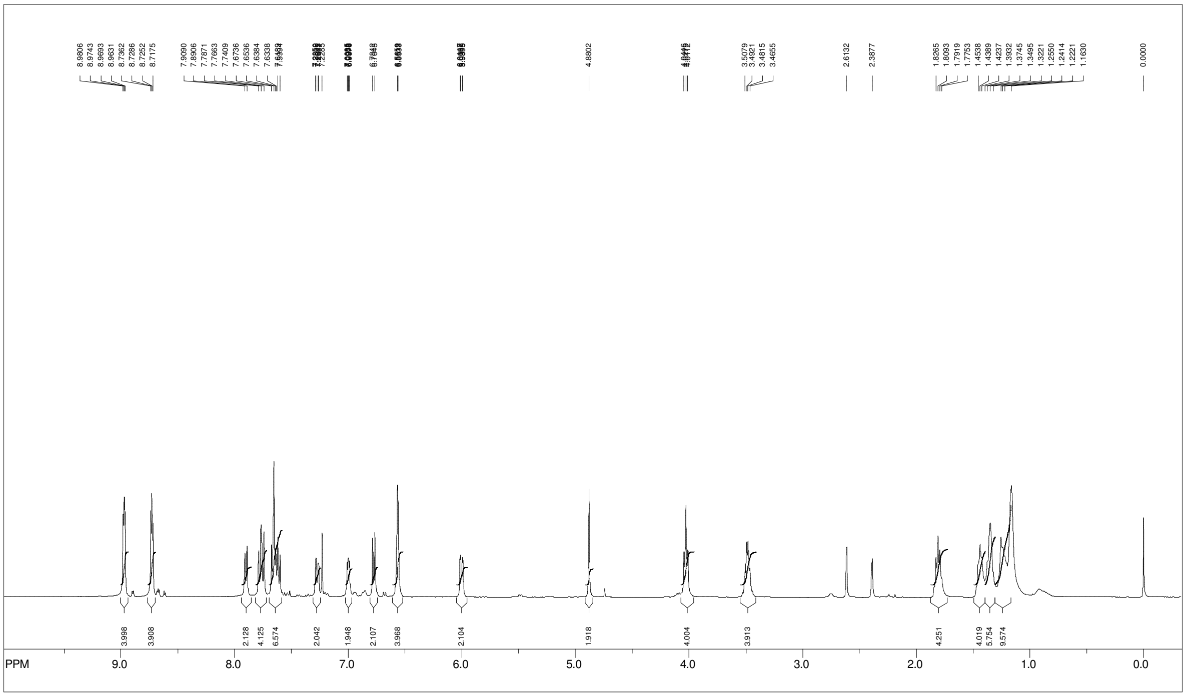


Synthesis of compound H4:

To a 250 mL round bottom flask equipped with a stir bar was added porphyrin **4** (100 mg, 0.081 mmol), K_2CO_3 (90 mg, 0.65 mmol) and DMF (40 mL). The reaction vessel was put under low vacuum and backfilled with nitrogen 4 times and heated to 80 °C. The 2,6-dihydroxytriptycene **9** (23 mg, 0.081 mmol) was dissolved in DMF (10 mL) under nitrogen and added to reaction vessel over 14 hours at a rate of 0.7 mL/h using a syringe pump. After the addition the reaction vessel was heated for 2 hours. Once cooled, the solvent was removed under reduced pressure and the residue was dissolved in toluene, filtered and the solvent was evaporated. This residue was purified by a first column chromatography on silica gel (eluent: toluene) and a second column chromatography on silica gel (eluent: 50% CH_2Cl_2/50% hexanes) to afford 45 mg (41% yield, 95% purity) of host **H4** as a purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): 9.00 (m, 4H), 8.76 (m, 4H), 7.94 (d, 4H, *J* = 7.3 Hz), 7.71-7.62 (m, 6H), 7.31 (dd, 2H, *J* = 4.2 Hz, *J* = 1.9 Hz), 7.03 (dd, 2H, *J* = 2.6 Hz, *J* = 3.1 Hz), 6.81 (d, 2H, *J* = 7.9 Hz), 6.60 (m, 4H), 6.04 (dd, 2H, *J* = 4 Hz, *J* = 2.1 Hz), 4.92 (s, 2H), 4.06 (t, 4H, *J* = 6.7 Hz), 3.52 (m, 4H), 1.80 (m, 4H), 1.47-1.10 (m, 24H). ^{13}C NMR: 157.45, 146.59, 150.69, 149.41, 146.68, 145.55, 144.05, 140.78, 138.94, 137.15, 133.35, 130.50, 130.28, 128.01, 127.97, 127.59, 127.30, 124.96, 123.88, 123.27, 121.28, 121.23, 115.13, 114.69, 111.08, 109.80, 68.97, 68.08, 53.34, 29.34, 29.17, 29.05, 25.99, 25.60. HRMS (APPI$^+$): calcd. for $C_{80}H_{66}Cl_4N_4O_4Zn$: 1350.3130, found: 1350.3124 (M)$^+$.

SpinWorks 2.5: jbg-5-123



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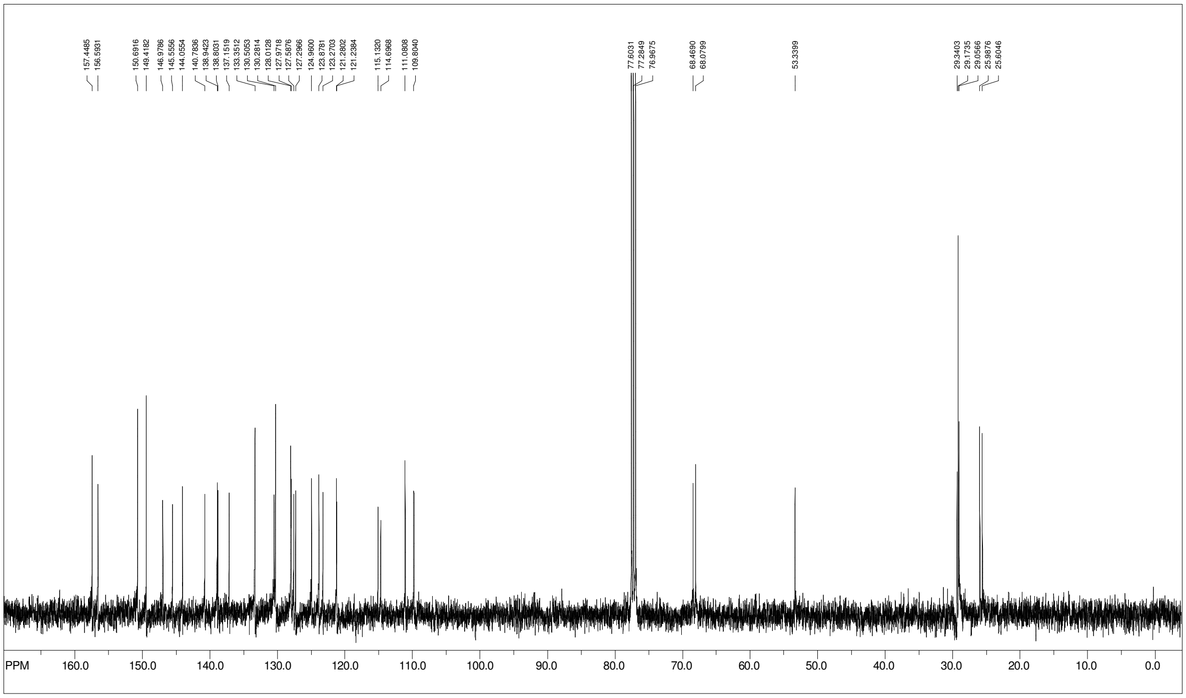
number of scans: 8

freq. of 0 ppm: 399.773443 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.5: jbg-5-123



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time domain size: 60288 points
width: 25133.52 Hz = 249.999864 ppm = 0.416891 Hz/pt
number of scans: 256

freq. of 0 ppm: 100.523085 MHz
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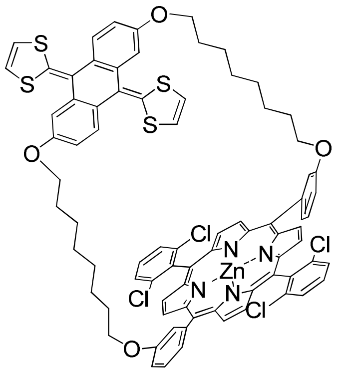
LB: 1.000 GB: 0.0000



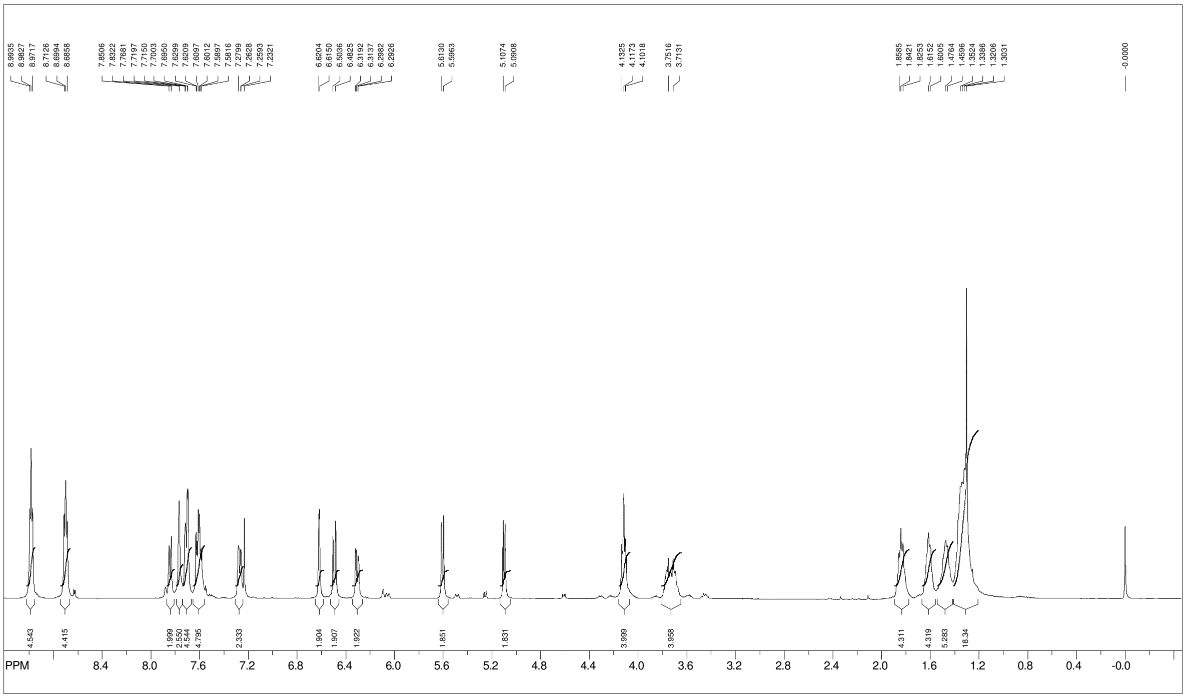
Synthesis of compound H5:

To a 100 mL round bottom flask equipped with a stir bar was added porphyrin **4** (100 mg, 0.081 mmol), K_2CO_3 (90 mg, 0.65 mmol) and DMF (40 mL). The reaction vessel was put under a low vacuum and backfilled with nitrogen 4 times and heated to 80 °C. The 2,6-dihydroxy-exTTF **10** (34 mg, 0.081 mmol) was dissolved in DMF (12 mL) under nitrogen and added to reaction vessel over 15 hours at a rate of 0.8 mL/h using a syringe pump. After the addition, the reaction vessel was heated for an additional 2 hours. Once cooled, the solvent was evaporated under reduced pressure and the residue dissolved in toluene, filtered and the solvent evaporated. This residue was purified by column chromatography on silica gel (eluent: toluene) and afforded 28 mg (23% yield, 95% purity) of host **H5** as a purple solid.

Note: This product is sensitive to acids and decomposes when kept in chloroform.

^{1}H NMR ($CDCl_3$, 400 MHz): 8.97 (t, 4H, *J* = 4.2 Hz), 8.70 (t, 4H, *J* = 5.2 Hz), 7.84 (d, 2H, *J* = 7.3 Hz), 7.77 (s, 2H), 7.70 (m, 4H), 7.60 (m, 4H), 7.27 (m, 2H), 6.52 (d, 2H, *J* = 2.2 Hz), 6.49 (d, 2H, *J* = 8.5 Hz), 6.31 (dd, 2H, *J* = 4.2 Hz, *J* = 2.2 Hz), 5.61 (d, 2H, *J* = 6.5 Hz), 5.10 (d, 2H, *J* = 6.6 Hz), 4.12 (t, 4H, *J* = 6.2 Hz), 3.73 (m, 4H), 1.84 (m 4H), 1.61 (m, 4H), 1.47 (m, 4H), 1.38-1.28 (m, 12H). ^{13}C NMR: 157.55, 156.78, 150.75, 150.64, 149.40, 149.37, 144.16, 140.69, 138.99, 138.78, 136.35, 133.36, 132.64, 130.42, 130.30, 127.95, 127.91, 127.67, 127.62, 127.50, 125.80, 122.41, 121.68, 121.24, 116.53, 116.28, 115.16, 113.56, 112.35, 110.49, 68.18, 68.02, 29.17, 28.75, 28.64, 28.52, 25.56, 25.36. HRMS (APPI$^+$): calcd. for $C_{88}H_{101}N_4O4S_4Zn$: 1469.5992, found: 1469.5860 $(M+H)^+$.

SpinWorks 2.5: jbg-5-133



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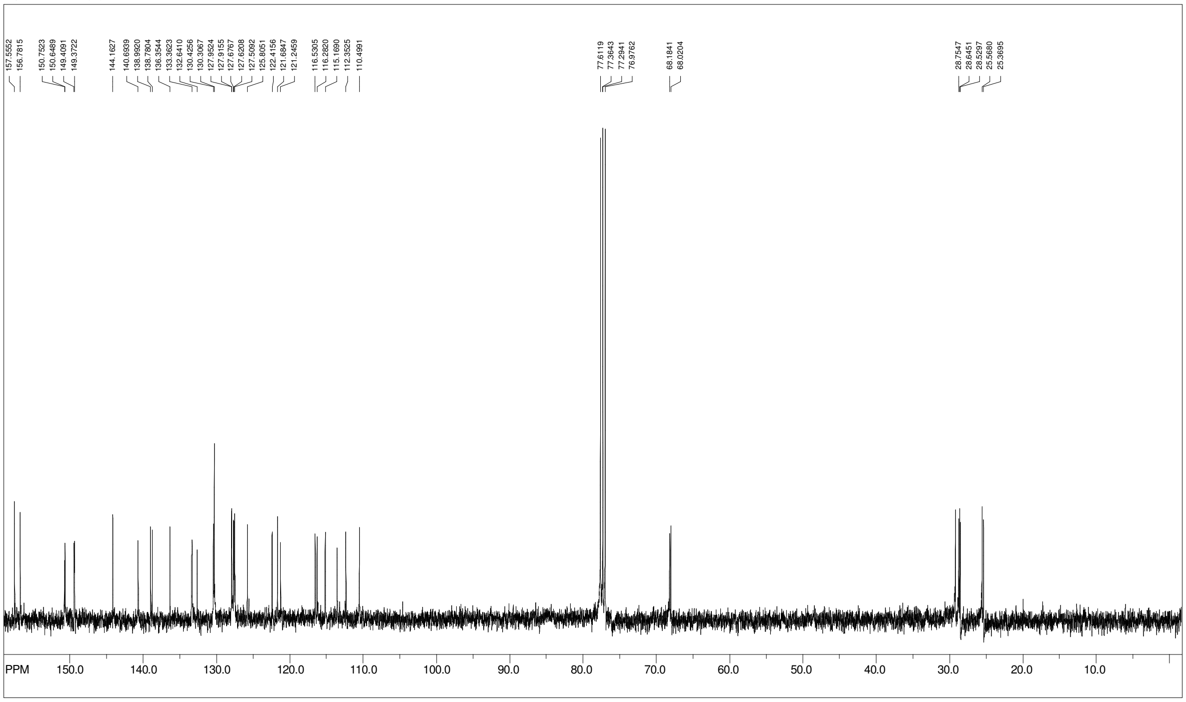
number of scans: 8

freq. of 0 ppm: 399.773441 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.5: jbg-5-133



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time domain size: 60288 points
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number of scans: 256

freq. of 0 ppm: 100.523085 MHz
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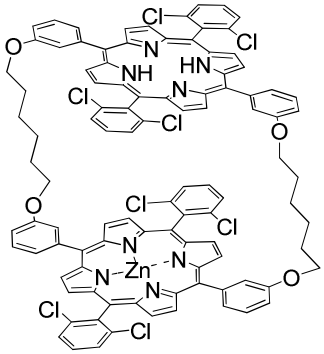
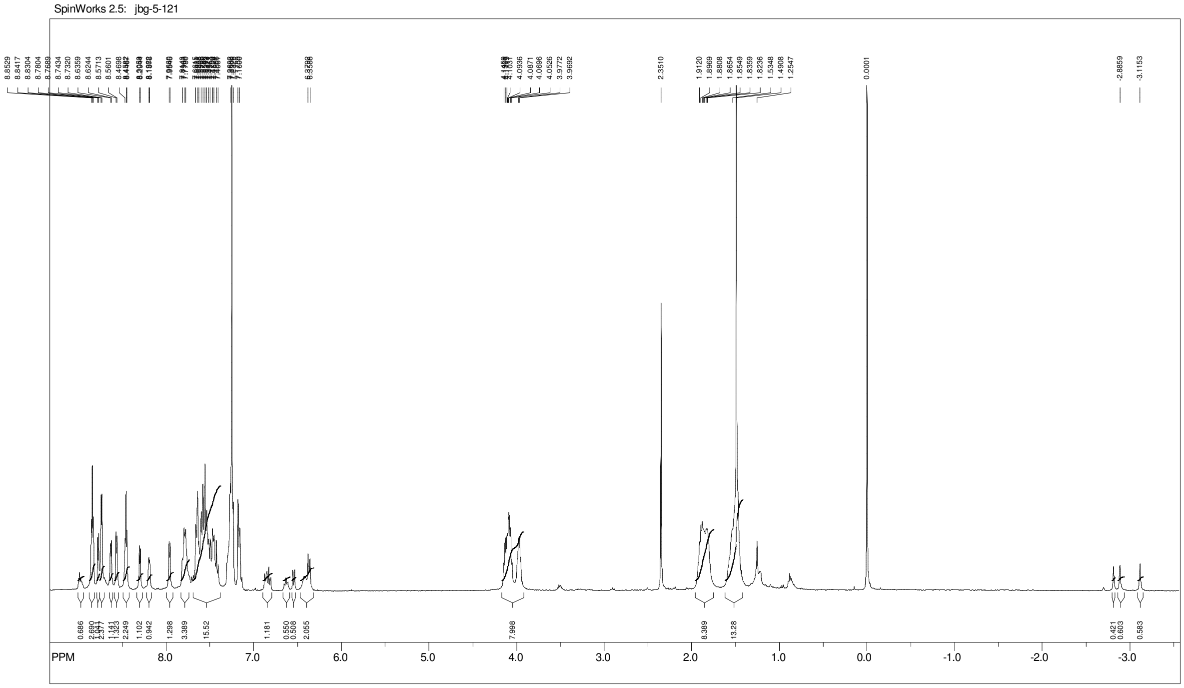


Synthesis of compound H6:

To a 100 mL round bottom flask equipped with a stir bar and sealed with a septum was added porphyrin **3** (90 mg, 0.077 mmol), free base porphyrin **2a** (60 mg, 0.077 mmol), K_2CO_3 (85 mg, 0.61 mmol), NaI (23 mg, 0.153 mmol) and DMF (40 mL). The reaction vessel put under a low vacuum and backfilled with nitrogen 4 times and heated to 80 °C overnight. Once cooled, the solvent was removed under reduced pressure and the residue was dissolved in toluene, filtered and the solvent evaporated. This residue was purified by two successive column chromatography on silica gel (eluent: toluene) to afford 17 mg (12% yield) of host **H6** as a red solid.

Note: Host ***H6*** *shows a complicated NMR spectrum due to the presence of conformational isomers*[2] *and the two different porphyrin moieties. The product was analytically pure on TLC and the HRMS spectrum was unambiguous.*

^{1}H NMR ($CDCl_3$, 400 MHz): 8.98 (m, 1H), 8.84 (t, 2H, *J* = 4.2 Hz), 8.77 (d, 1H, J = 4.8 Hz), 8.73 (d, 2H, J = 4.8 Hz), 8.63 (d, 1H, J = 4.8 Hz), 8.57 (d, 1H, J = 4.4 Hz), 8.46 (t, 2H, *J* = 4.5 Hz), 8.30 (d, 1H, J = 4.8 Hz), 8.19 (d, 1H, J = 4.0 Hz), 7.68 (d, 1H, J = 4.6 Hz), 7.82-7.76 (m, 3H), 7.68-7.40 (m, 15H), 6.84 (m, 1H), 6.64 (m, 0.5H), 6.55 (m, 0.5H), 6.44-6.35 (m, 2H), 4.15-3.94 (m, 8H), 1.96-1.78 (m, 8H), 1.58-1.46 (m, 8H), -2.81 (s, 0.5H), -2.88 (s, 0.5H), -3.11 (s, 0.5H). ^{13}C NMR: *Due to the presence of conformational isomers, a clear spectrum with significant resolution and S/N ratio could not be obtained.* HRMS (APPI$^+$): calcd. for $C_{100}H_{71}Cl_8N_8O_4Zn$: 1791.2392, found: 1791.2388 $(M+H)^+$.



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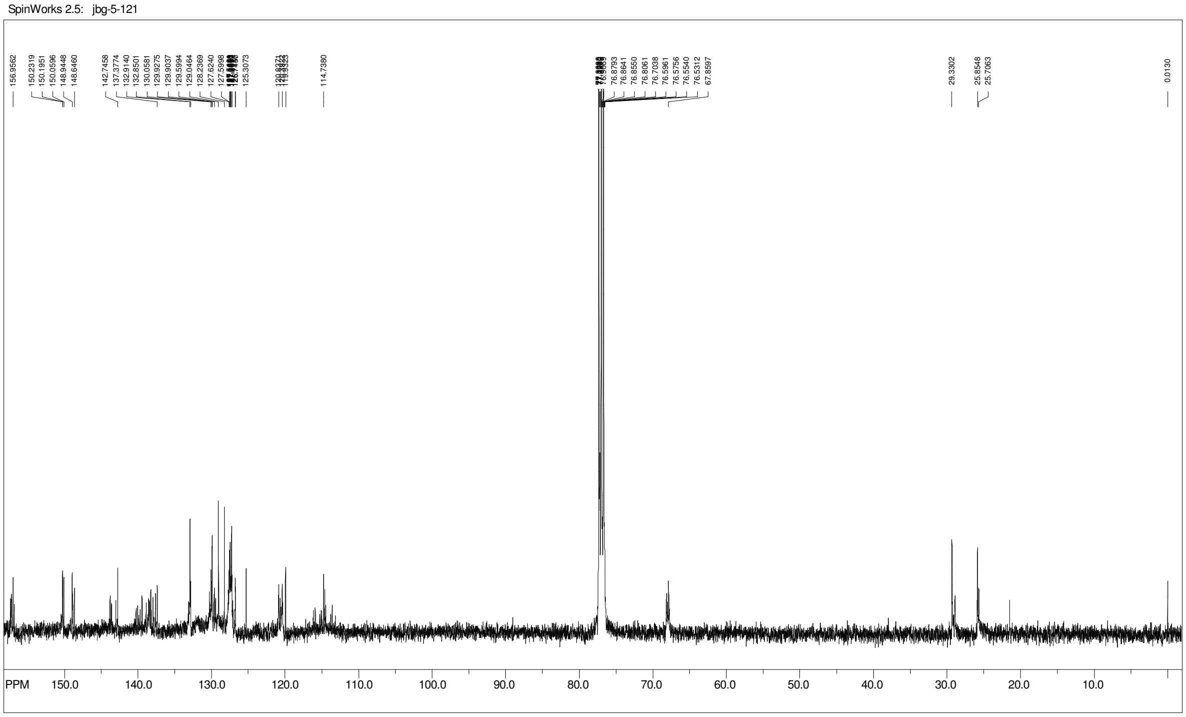

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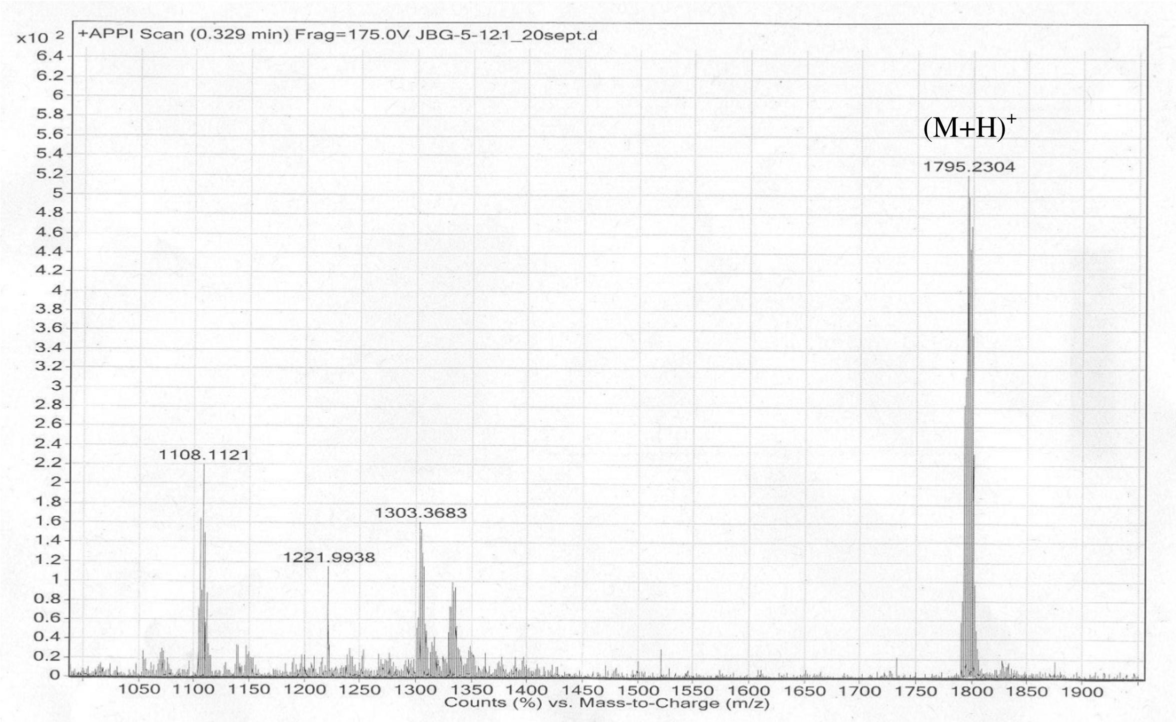
LB: 0.000 GB: 0.0000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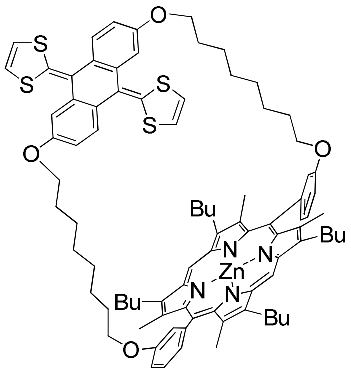


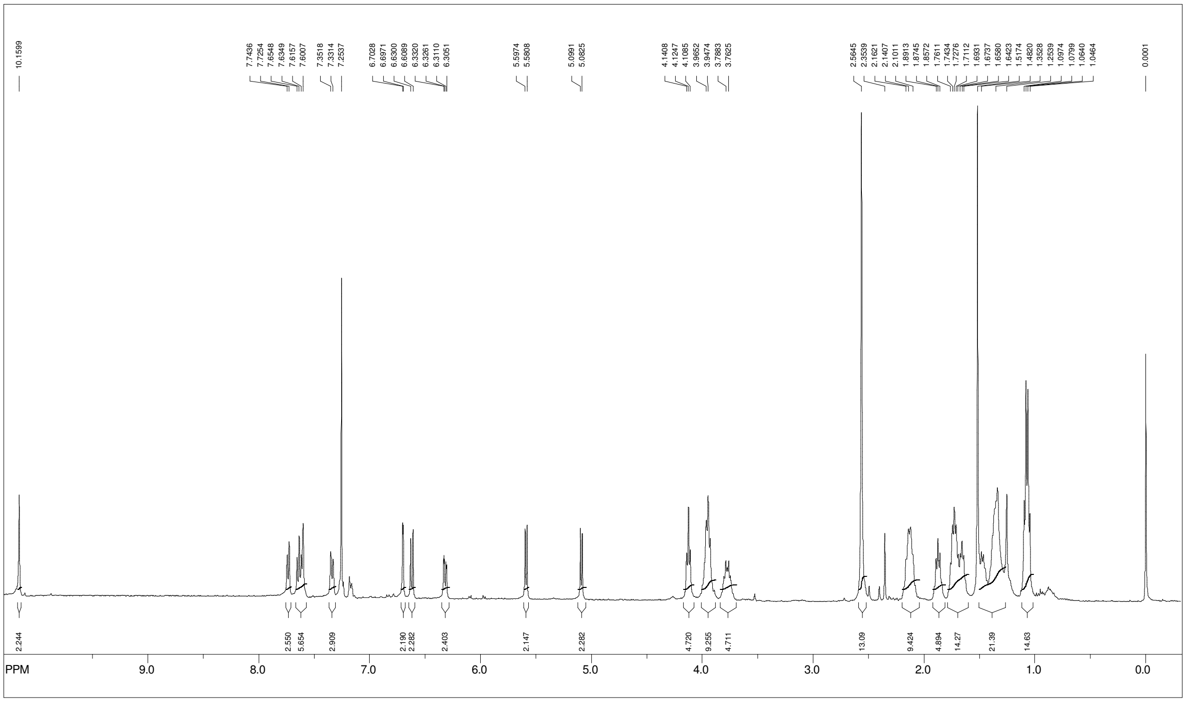
Synthesis of compound H7:

To a 100 mL round bottom flask equipped with a stir bar and sealed with a septum was added porphyrin **12** (94 mg, 0.081 mmol), K_2CO_3 (90 mg, 0.65 mmol) and DMF (40 mL). The reaction vessel was put under a low vacuum and backfilled with nitrogen 4 times and heated to 80 °C. The 2,6-dihydroxy-exTTF **10** (34 mg, 0.081 mmol) was dissolved in DMF (10 mL) under nitrogen and added to reaction vessel over 14 hours at a rate of 0.7 mL/h using a syringe pump. After the addition, the solution was heated for an additional 2 hours. Once cooled, the solvent was removed under reduced pressure and the residue dissolved in toluene, filtered and the solvent evaporated. This residue was purified by a column chromatography on silica gel (eluent gradient from 50% toluene/50% hexanes to 75% toluene/25% hexanes) to afforded 16 mg (13% yield) of host **H7** as a purple solid.

Note: This product is sensitive to acids and decomposes when kept in chloroform.

^{1}H NMR ($CDCl_3$, 400 MHz): 10.17 (s, 2H), 7.76 (d, 2H, J = 7.2 Hz), 7.68-7.60 (m, 4H), 7.36 (m, 2H), 6.71 (d, 2H, J = 2.0 Hz), 6.63 (d, 2H, J = 8.2 Hz), 6.33 (dd, 2H, J = 4.3 Hz, J = 2 Hz), 5.60 (d, 2H, J = 6.6 Hz), 5.10 (d, 2H, J = 6.6 Hz), 4.14 (t, 4H, J = 6.6 Hz), 3.96 (m, 8H), 3.79 (m, 4H), 2.58 (s, 12H), 2.14 (m, 8H), 1.89 (m, 4H), 1.78-1.65 (m, 12H), 1.45-1.30 (m, 16H), 1.10 (m, 12H). ^{13}C NMR: 158.83, 156.88, 147.91, 147.81, 146.59, 145.20, 143.651 138.41, 136.51, 132.85, 128.59, 127.83, 126.48, 125.76, 122.05, 121.62, 121.20, 120.16(2C), 119.48, 116.43, 116.33, 114.68, 112.04, 110.70, 97.80, 68.35, 67.99, 35.75, 29.97 (2C), 29.26, 28.86, 28.77, 28.70, 26.73, 25.67, 25.51, 23.64, 15.34, 14.49. HRMS (APPI$^+$): calcd. for $C_{88}H_{101}Cl_8N_8O_4Zn$: 1469.5992, found: 1469.5860 $(M+H)^+$.

SpinWorks 2.5: jbg-5-171



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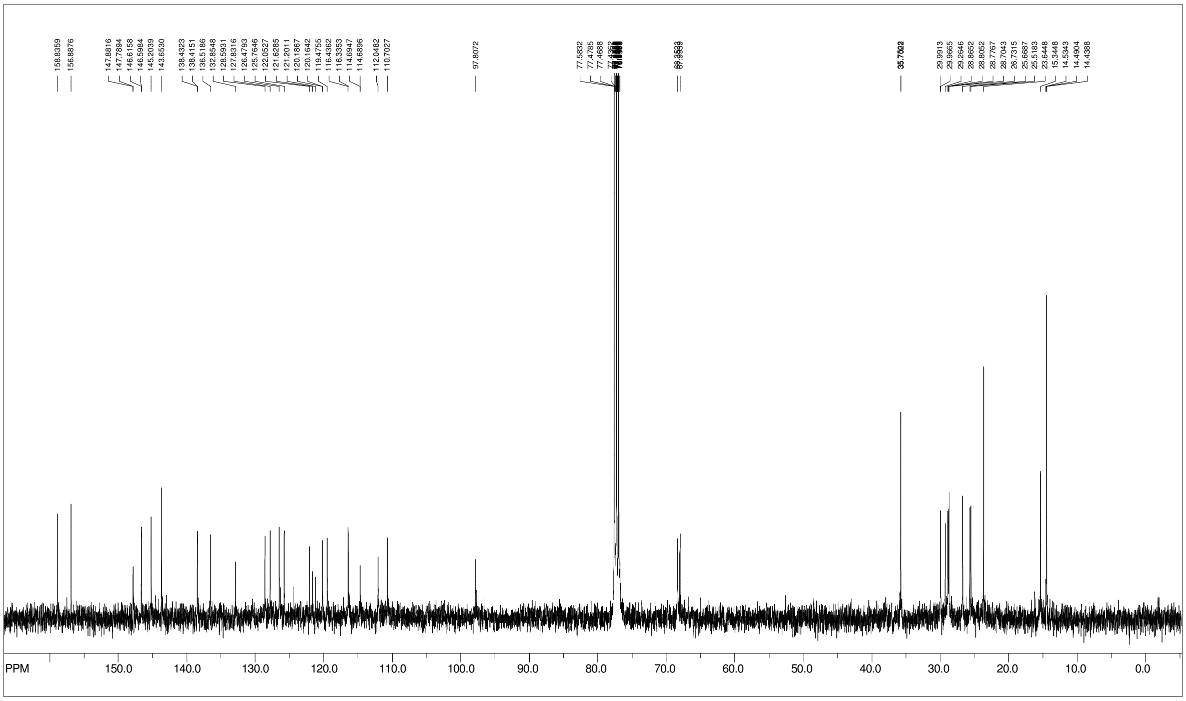
SpinWorks 2.5: jbg-5-171



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width: 25133.52 Hz = 249.999864 ppm = 0.416891 Hz/pt
number of scans: 1000

freq. of 0 ppm: 100.523085 MHz
processed size: 65536 complex points
LB: 1.000   GB: 0.0000

4. References

1. Conors, K. A., *Binding Constants: The Measurement of Molecular Complex Stability*. Wiley & Sons: New York, NY, **1987**.

2. Tashiro, K.; Aida, T.; Zheng, J.-Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K., *J. Am. Chem. Soc.* 1999, ***121*** (40), 9477-9478.