Liquid crystalline 21,23-dithiaporphyrins

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Contents:

Synthetic procedures and spectra.

All chemicals were purchased from Aldrich and used as received without further purification unless otherwise specified. Column chromatography was performed on SiliCycle SiliaFlash P60 silica gel (230-400 mesh). Thin-layer chromatography was carried out on Merck silica gel F-254 glass-backed TLC plates. Solvents were used as received or dried using an MBraun solvent purification system and reactions were typically carried out under N_2 atmosphere.

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Mass spectra were recorded with a Thermo Finnigan SSQ7000 spectrometer and UV/Vis spectra were recorded using a Cary 5000 spectrophotometer in dual beam mode. Thermograms were collected using a TA-Q200 DSC under N_2 atmosphere. Cross polarized optical microscopy was carried out on an Olympus BX-41 microscope equipped with a heating stage (Linkam T95). Powder X-Ray Diffraction experiments were conducted using a Bruker D8 Advance (40 kV, 40 mA) (Cu Kα) equipped with high temperature reactor chamber (Anton Paar XRK 900)

Cyclic voltammetry (CV) experiments were carried out on an CHI650 potentiostat that was controlled by a PC in a temperature-controlled, three-electrode cell (15 mL). The working electrode was a Glassy carbon disc with area of 0.28 cm^2 from BASi, which was polished after each use with 0.05 μm diamond slurry (Buehler) in an automated polisher (Buehler). The reference electrode was a silver wire in a 0.1 M $AgNO_3$ electrolyte dissolved in CH_3CN sealed in a glass tube separated by porous glass. The counter electrode was a Pt wire that was flame annealed prior to each use. All potentials were referenced to the ferrocene/ferricenium redox couple. Each CV experiment consisted of approximately 1-3 mM redox active species dissolved in 0.1 M tetrabutylammonium hexafluorophosphate in deoxygenated dichloromethane. All CV experiments were bubbled with Ar for 10 minutes prior to dissolving the redox active species and an Ar blanket was maintained during the entire experiment. Spectroelectrochemical spectra were generated with a Cary 5000 spectrophotometer linked with a CHI 650 potentiostat using a thin layer cell (ALS-Japan). The working electrode, in the beam path, was a Pt mesh, a Pt wire counter electrode and the same reference electrode, electrolyte and solvent as above were used.

4-Decyloxybenzaldehyde: Based on the procedure described by Geol and Jayakannan.[1] 4-hydroxybenzaldehyde (3.66 g, 30.0 mmol), KI (4.98 g, 30.0 mmol) and K_2CO_3 (8.28 g, 60.0 mmol) were added to acetone (70 mL) and refluxed for 2 h under nitrogen. To the hot solution, 1-bromodecane (6.8 mL, 33 mmol) was added slowly and refluxed for 24 h. Acetone was then removed under reduced pressure. The residue was dissolved in water (100 mL,) extracted with dichloromethane and washed with NaOH (150 mL, 2%). The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure to afford the crude compound. The crude compound was subjected to silica gel column chromatography using a mixture of hexanes and ethyl acetate (87:13) to afford the pure compound as an off-white oil (5.13 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H, Ar-C**H**O), 7.82 (d, *J* = 8.8 Hz, 2H, aryl), 6.98 (d, *J* = 8.7 Hz, 2H, aryl), 4.03 (t, *J* = 6.6 Hz, 2H, Ar-O-C**H$_2$**), 1.86 – 1.74 (m, 2H, Ar-O-CH_2C**H$_2$**), 1.51 – 1.41 (m, 2H, Ar-O-CH_2CH_2C**H$_2$**), 1.38 – 1.25 (m, 12H, aliphatic), 0.88 (t, *J* = 6.9 Hz, 3H, C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.77, 164.34, 132.01, 129.83, 114.81, 68.48, 31.96, 29.62, 29.41, 29.38, 29.13, 26.03, 22.75, 14.17.

4-Dodecyloxybenzaldehyde: Based on the procedure described by Geol and Jayakannan.[1] 4-hydroxybenzaldehyde (3.66 g, 30.0 mmol), KI (4.98 g, 30.0 mmol) and K_2CO_3 (8.28 g, 60.0 mmol) were added to acetone (70 mL) and refluxed for 2 h under nitrogen. To the hot solution, 1-bromododecane (7.9 mL, 33 mmol) was added slowly and refluxed for 24 h. Acetone was then removed under reduced pressure. The residue was dissolved in water (100 mL,) extracted with dichloromethane and washed with NaOH (150 mL, 2%). The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure to afford the crude compound. The crude compound was subjected to silica gel column chromatography using a mixture of hexanes and ethyl acetate (87:13) to afford the pure compound as an off-white oil (5.77 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H, Ar-C**H**O), 7.78 (d, *J* = 8.8 Hz, 2H, aryl), 6.95 (d, *J* = 8.7 Hz, 2H, aryl), 3.99 (t, *J* = 6.6 Hz, 2H, Ar-O-C**H$_2$**), 1.82 – 1.74 (m, 2H, Ar-O-CH_2C**H$_2$**), 1.48 – 1.39 (m, 2H, Ar-O-CH_2CH_2C**H$_2$**), 1.33 – 1.21 (m, 16H, aliphatic), 0.86 (t, *J* = 6.8 Hz, 3H, **CH$_3$**). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.68, 164.30, 131.97, 129.81, 114.77, 68.44, 31.97, 29.71, 29.69, 29.64, 29.61, 29.40, 29.11, 26.01, 22.74, 14.15.

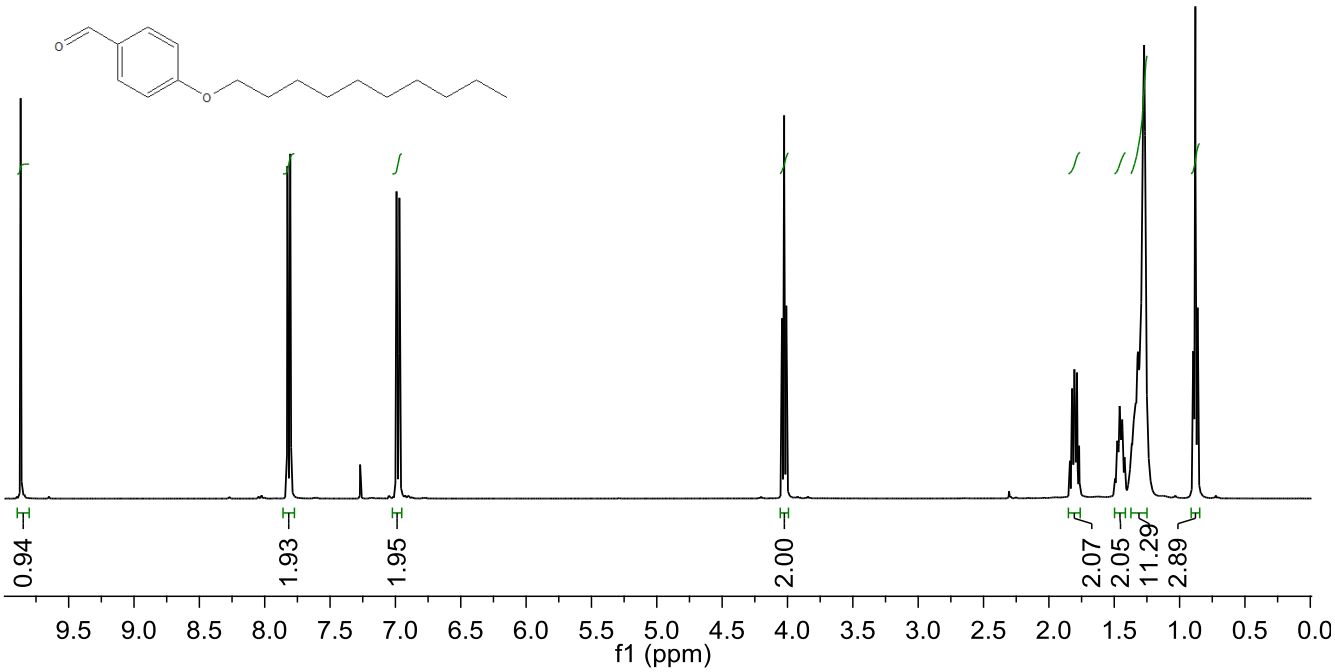
2,5-[(4-decyloxyphenyl)hydroxymethyl]-thiophene (1a): To a solution of diethylether (30 mL), thiophene (0.18 mL, 2.2 mmol) was added and the solution was cooled to 0 °C under a nitrogen atmosphere. To the ice-cold solution, *n*BuLi (1 mL of 2.5 M solution in hexane, 2.5 mmol) was added and the solution was stirred for 1 h. The 4-Decyloxybenzaldehyde (0.66 g, 2.5 mmol) was added and the solution was stirred for an additional hour at 0 °C. Another addition at 0 °C of *n*BuLi (1.2 mL of 2.5 M solution in hexane, 3.0 mmol) was followed by stirring for 1 h. The 4-Decyloxybenzaldehyde (0.66 g, 2.5 mmol) was added to the ice cold solution and let stir 1 h. The reaction was quenched with water (30 mL) and the aqueous layer was extracted with diethyl ether (100 mL). The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure to afford the crude compound. Silica gel column chromatography using hexanes and ethyl acetate (75:25) afforded **1a** as a pure yellow oil (0.61 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H, aryl), 6.86 (d, *J* = 8.6 Hz, 2H, aryl), 6.67 (d, *J* = 3.0 Hz, 1H, C**H**-OH), 5.89 (s, 1H, β-thiophene), 3.94 (t, *J* = 6.6 Hz, 2H, Ar-O-C**H$_2$**), 2.60 (s, 1H, CH-O**H**), 1.82 – 1.74 (m, 2H, Ar-O-CH$_2$C**H$_2$**), 1.49-1.41 (m, 2H, Ar-O-CH$_2$CH$_2$C**H$_2$**), 1.37-1.26 (m, 12H, aliphatic), 0.90 (t, *J* = 6.8 Hz, 3H, C**H$_3$**). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.80, 148.42, 135.17, 127.69, 124.20, 114.38, 72.05, 68.06, 31.98, 29.68, 29.66, 29.51, 29.41, 29.36, 26.14, 22.75, 14.18. HR-MS (ESI) calcd. for $C_{38}H_{55}O_3S$ $(M\text{-}OH)^+$: 591.387; found 591.388.

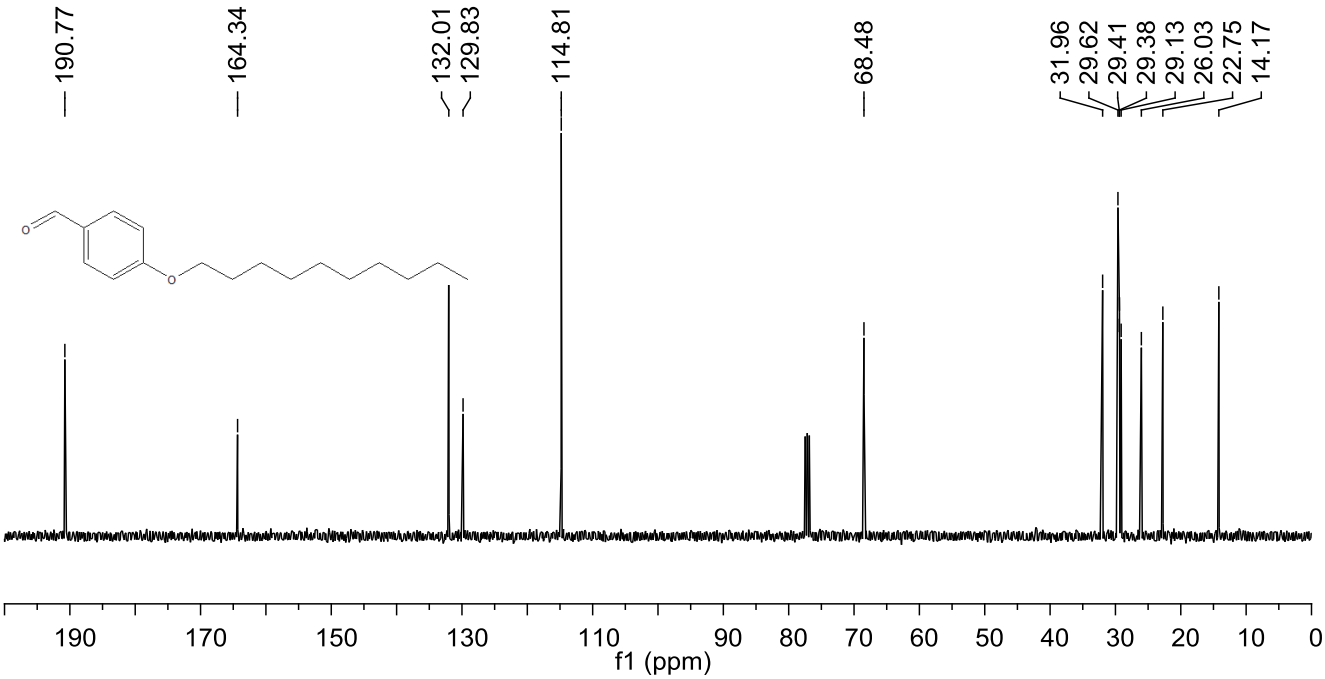
2,5-[(4-dodecyloxyphenyl)hydroxymethyl]-thiophene (1b): To a solution of hexanes (30 mL), *n*BuLi (3.9 mL of 1.4 M solution in hexane, 5.5 mmol) and TMEDA (0.8 mL, 5.4 mmol) were added and stirred under nitrogen. Thiophene (0.18 mL, 2.2 mmol) was added and the solution was refluxed for 1 h. The dilithiated species was allowed to cool to room temperature and then transferred to an ice cold solution of 4-Dodecyloxybenzaldehyde (1.58 g, 5.4 mmol).The reaction was quenched with water (30 mL) and the aqueous layer was extracted with diethyl ether (100 mL). The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure to afford the crude compound. Silica gel column chromatography using hexanes and ethyl acetate (75:25) afforded **1b** as a pure yellow oil (0.32 g, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H, aryl), 6.86 (d, *J* = 8.6 Hz, 2H, aryl), 6.68 (d, *J* = 2.7 Hz, 1H, C**H**-OH), 5.90 (s, 1H, β-thiophene), 3.94 (t, *J* = 6.6 Hz, 2H, Ar-O-C**H$_2$**), 2.38 (s, 1H), 1.85 – 1.68 (m, 2H, Ar-O-CH$_2$C**H$_2$**), 1.55 – 1.38 (m, 2H, Ar-O-CH$_2$CH$_2$C**H$_2$**), 1.29 – 1.21 (m, 16H, aliphatic), 0.89 (t, *J* = 6.8 Hz, 3H, C**H$_3$**). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.09, 148.52, 135.11, 127.72, 124.34, 114.58, 72.39, 68.19, 32.06, 29.80, 29.78, 29.75, 29.73, 29.55, 29.49, 29.41, 26.19, 22.83, 14.26. HR-MS (ESI) calcd. for $C_{42}H_{63}O_3S$ $(M\text{-}OH)^+$: 647.449; found: 647.449.

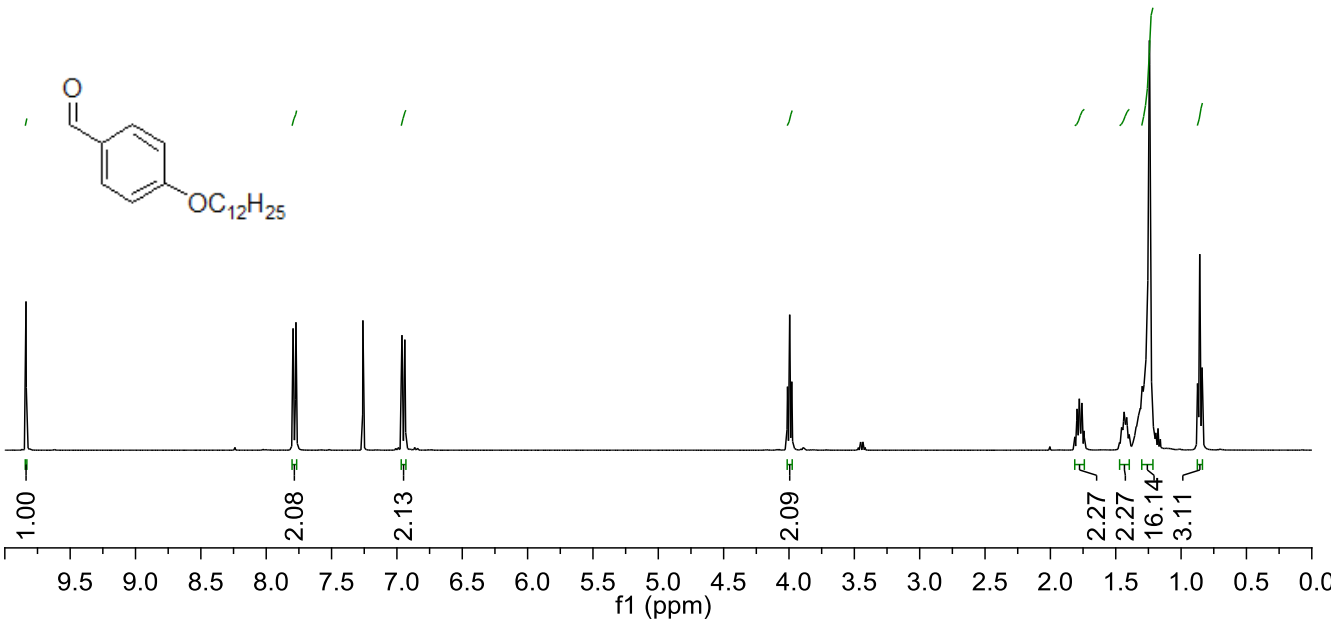
5, 10, 15, 20-Tetra(4-decyloxyphenyl)-21,23-dithiaporphyrin (2a): Pyrrole (0.10 mL, 1.4 mmol) was added to a solution of dichloromethane (70 mL) and diol **1a** (0.61 g, 1.0 mmol) and purged with nitrogen for 15 min. The condensation was initiated with a catalytic amount of $BF_3{\cdot}OEt_2$ (0.2 mL of a 2.5 M stock solution) and let stir for 1 h under nitrogen. The reaction was stirred in air for 1 additional hour upon the addition of DDQ (0.23 g, 1.0 mmol). The reaction solution was passed through an alumina slug using dichloromethane as eluent. The solvent was removed under reduced pressure and the crude compound was subjected to silica gel column chromatography using dichloromethane and hexanes (50:50). The desired compound **2a** was obtained as a purple solid (0.18 g, 14%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H, β-thiophene), 8.72 (s, 1H, β-pyrrole), 8.17 (d, *J* = 8.3 Hz, 2H, aryl), 7.34 (d, *J* = 8.4 Hz, 2H, aryl), 4.24 (t, *J* = 6.4 Hz, 2H, Ar-O-C**H$_2$**), 2.04 – 1.96 (m, 2H, Ar-O-CH$_2$C**H$_2$**), 1.68 – 1.60 (m, 2H, Ar-O-CH$_2$CH$_2$C**H$_2$**), 1.51 – 1.34 (m, 12H, aliphatic), 0.94 (t, *J* = 6.8 Hz, 3H, C**H$_3$**). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.41, 156.74, 148.13, 135.56, 135.41, 134.54, 133.95, 133.69, 113.64, 68.44, 32.12, 29.84, 29.81, 29.69, 29.63, 29.56, 26.39, 22.90, 14.32. HR-MS (ESI) calcd. for $C_{84}H_{109}O_4N_2S_2$ $(M+H)^+$: 1273.782; found: 1273.781. UV/Vis (toluene): λ_{max} nm (ε $M^{-1}cm^{-1}$) = 442 (3.0×10^5), 519 (2.5×10^4), 555 (1.4×10^4), 639 (1.9×10^3), 704 (7.3×10^3).

5, 10, 15, 20-Tetra(4-dodecyloxyphenyl)-21,23-dithiaporphyrin (2b): Pyrrole (0.03 mL, 0.4 mmol) was added to a solution of dichloromethane (30 mL) and diol **1b** (0.22 g, 0.3 mmol) and purged with nitrogen for 15 min. The condensation was initiated with a catalytic amount of $BF_3{\cdot}OEt_2$ (0.2 mL of a 2.5 M stock solution) and let stir for 1 h under nitrogen. The reaction was stirred in air for 1 additional hour upon the addition of DDQ (0.091 g, 0.4

mmol). The reaction solution was passed through an alumina slug using dichloromethane as eluent. The solvent was removed under reduced pressure and the crude compound was subjected to silica gel column chromatography using dichloromethane and hexanes (50:50). The desired compound **2b** was obtained as a purple solid (13.9 mg, 3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H, β-thiophene), 8.72 (s, 1H, β-pyrrole), 8.16 (d, *J* = 8.3 Hz, 2H, aryl), 7.32 (d, *J* = 8.2 Hz, 2H, aryl), 4.22 (t, *J* = 6.3 Hz, 2H, Ar-O-C**H$_2$**), 2.02 – 1.95 (m, 2H, Ar-O-CH_2C**H$_2$**), 1.61 (m, 2H, Ar-O-CH_2CH_2C**H$_2$**), 1.53 – 1.29 (m, 16H, aliphatic), 0.94 (t, *J* = 6.4 Hz, 3H, C**H$_3$**). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.40, 156.72, 148.11, 135.57, 135.42, 134.55, 133.93, 133.68, 113.63, 68.45, 32.12, 29.90, 29.85, 29.70, 29.63, 29.56, 26.39, 22.89, 14.32. HR-MS (ESI) calcd. for $C_{92}H_{125}O_4N_2S_2$ $(M+H)^+$: 1385.907; found: 1385.902. UV/Vis (toluene): λ_{max} nm (ε $M^{-1}cm^{-1}$) = 441 (5.1×10^5), 519 (4.5×10^4), 555 (2.5×10^4), 638 (3.2×10^3), 704 (1.3×10^4).



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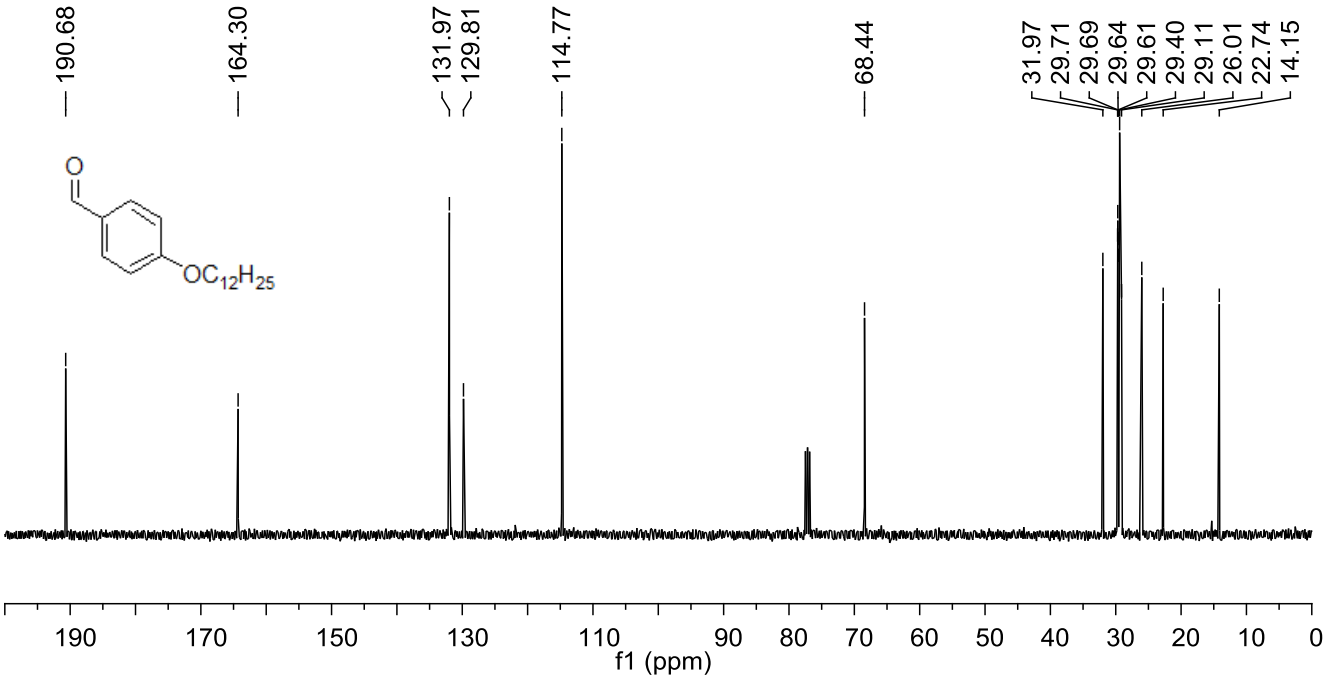
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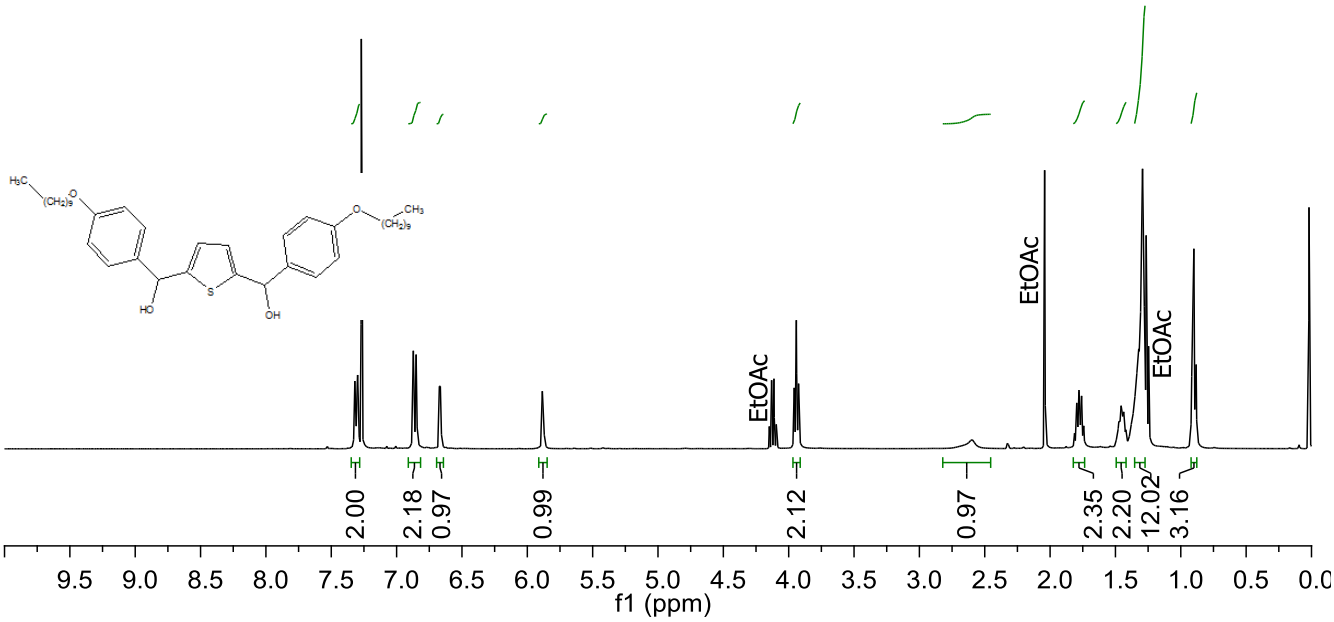
f1 (ppm)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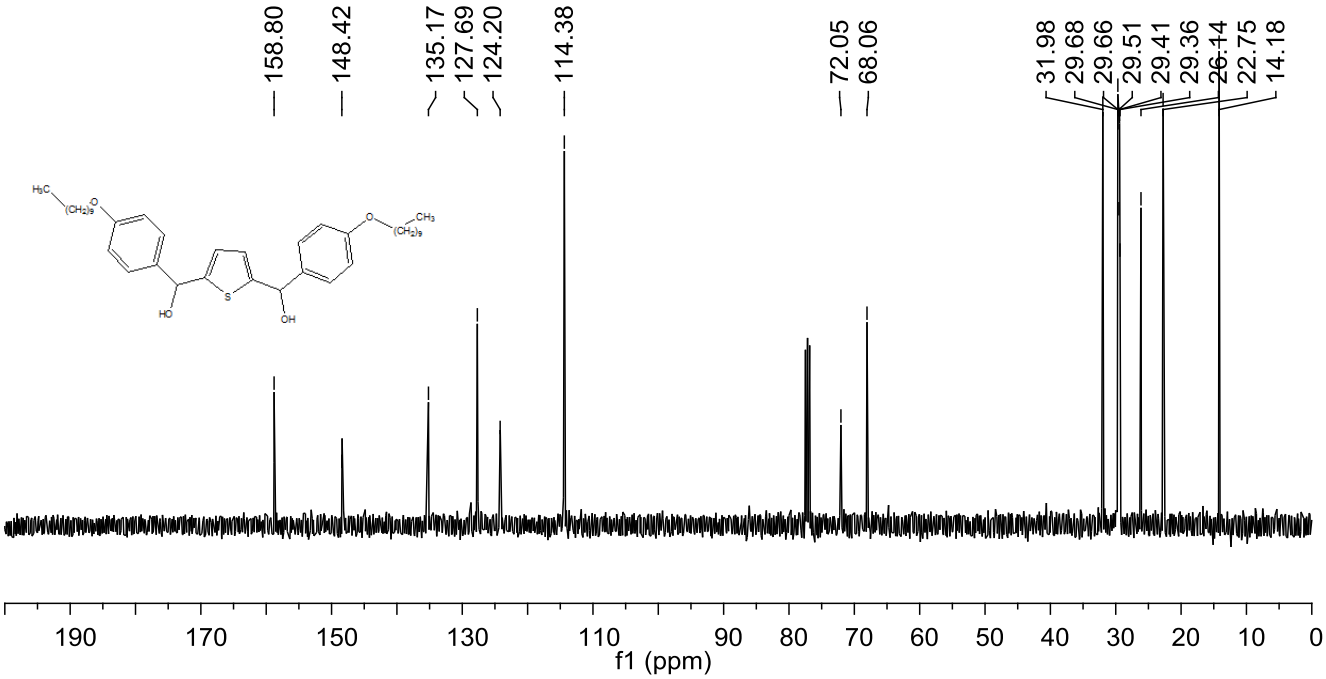
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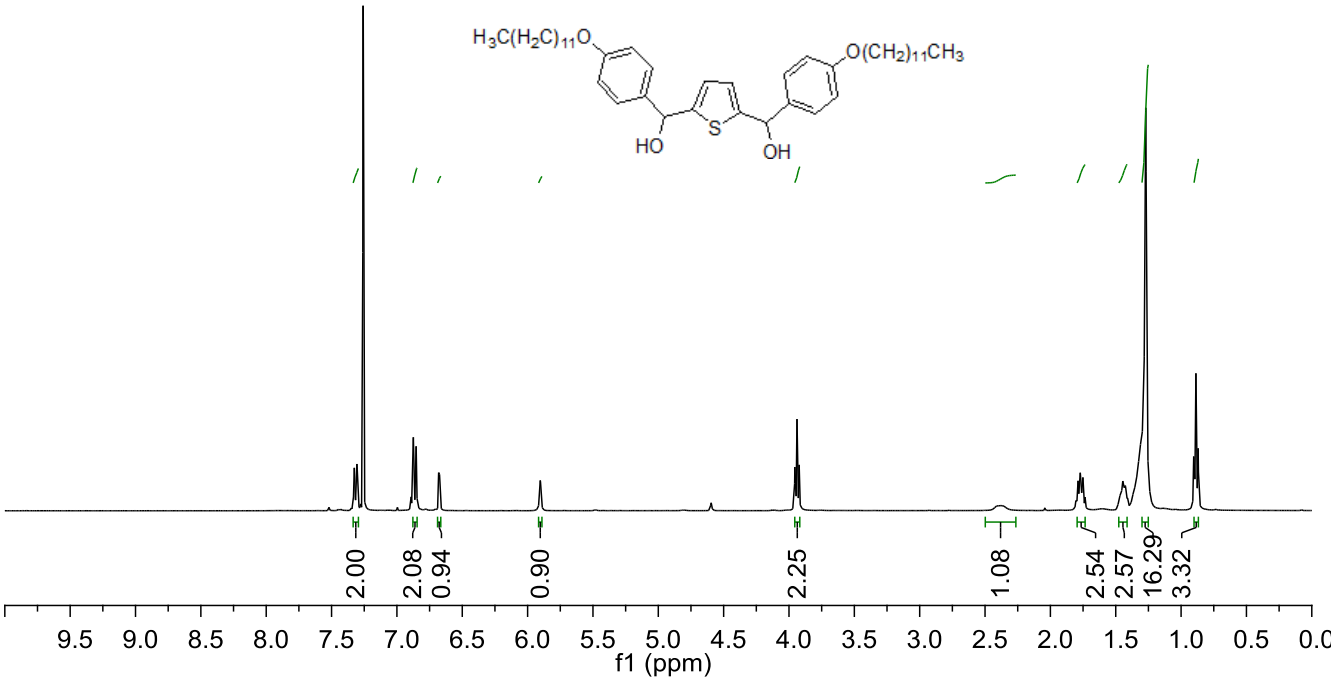
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16.29
3.32
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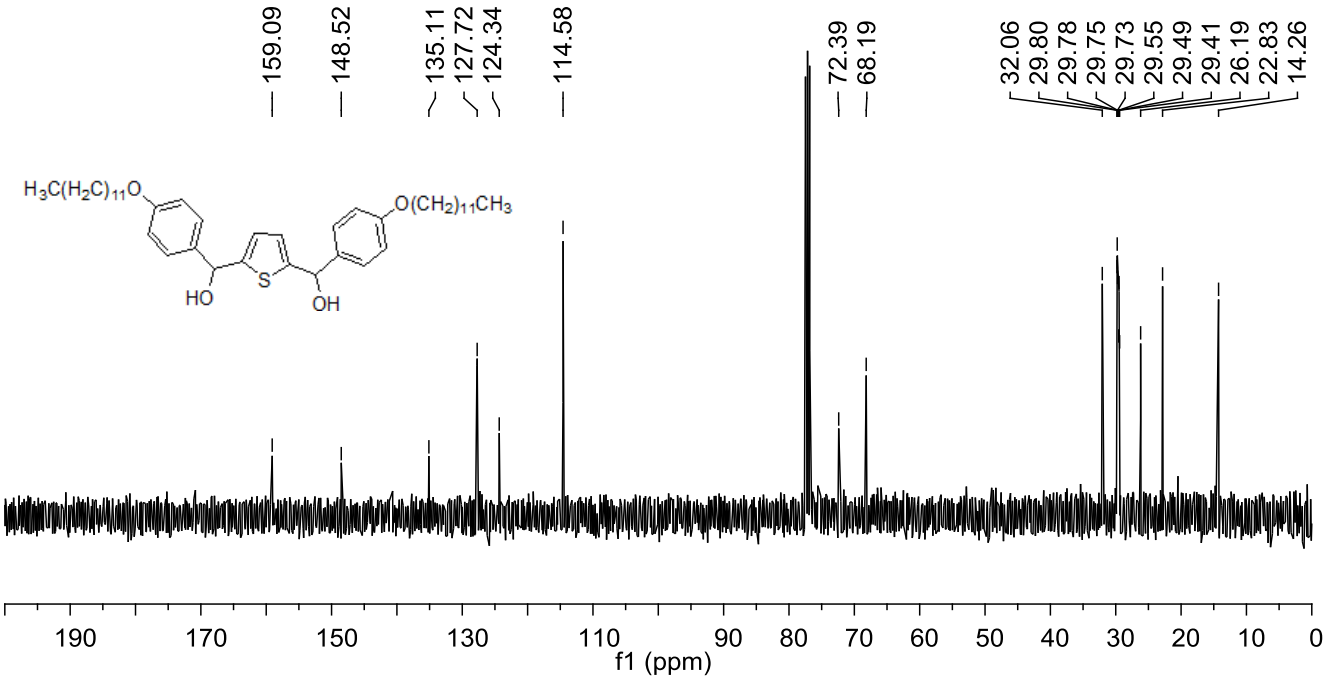
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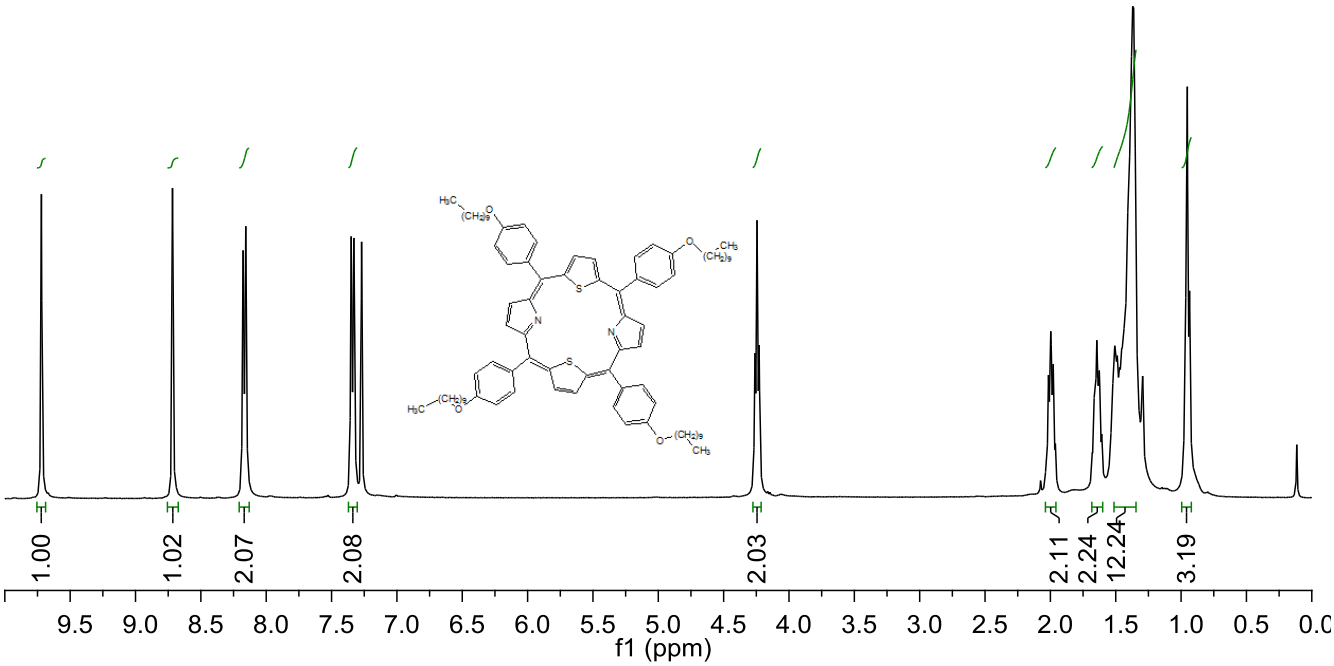
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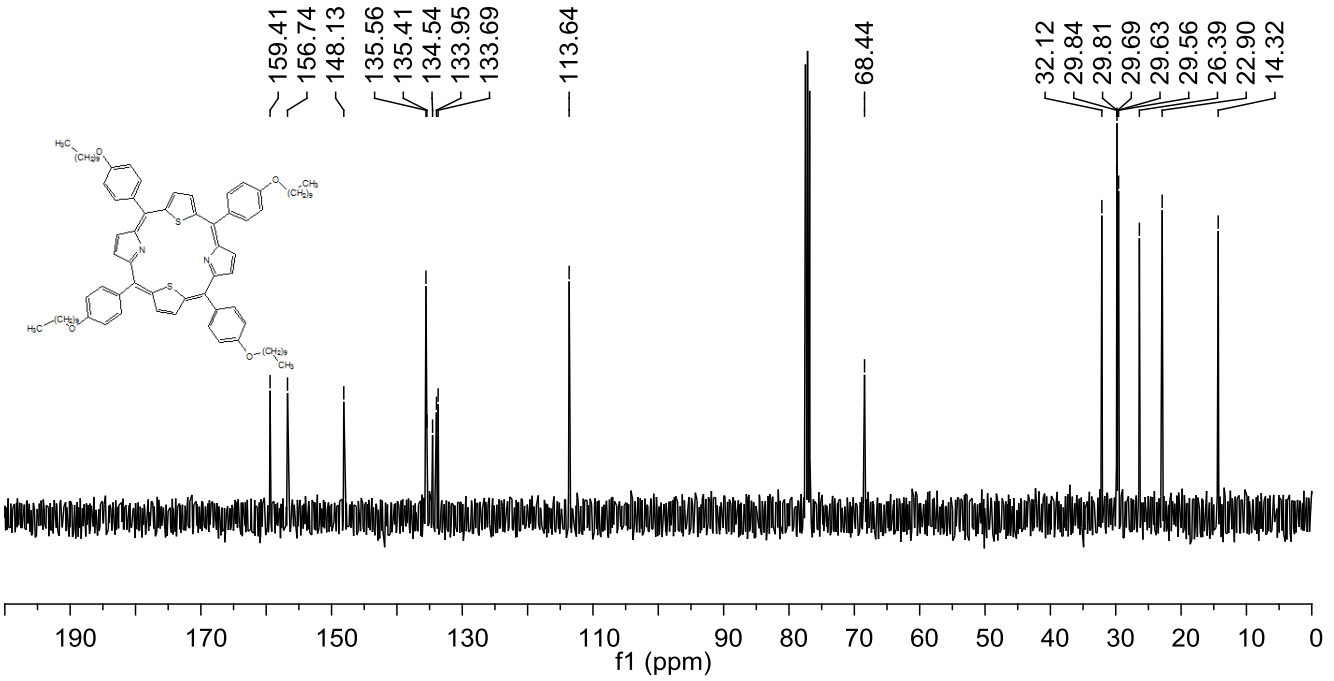
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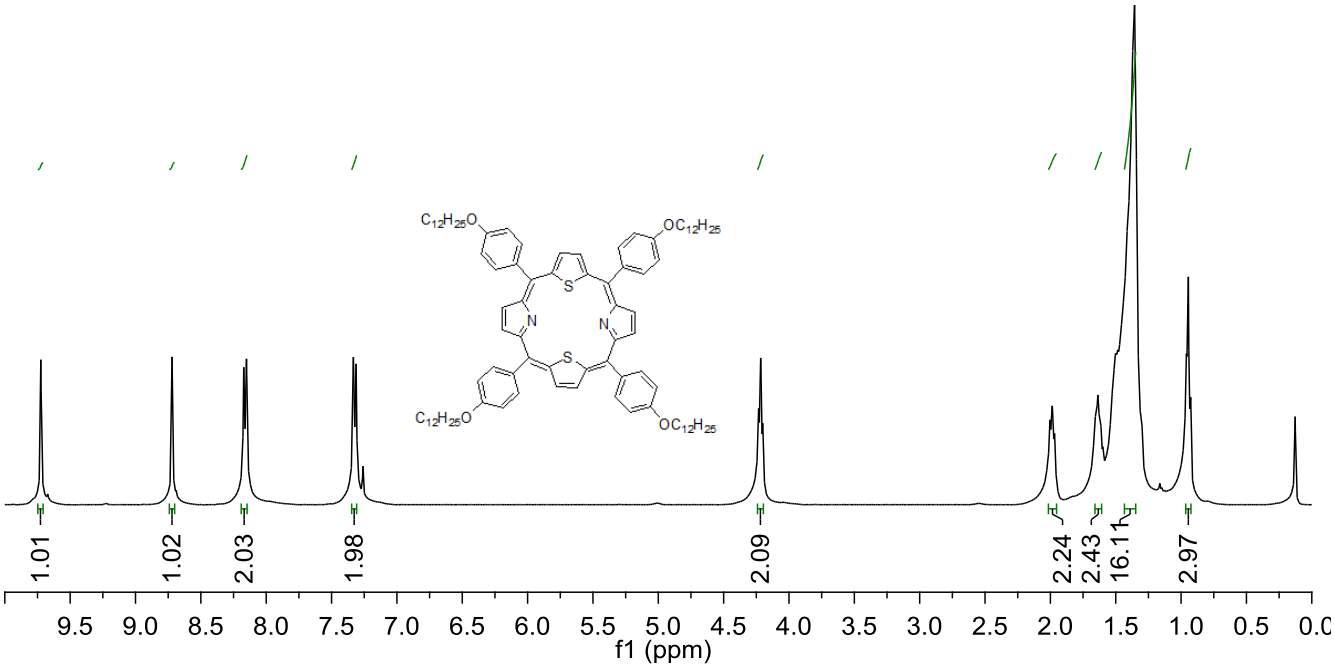
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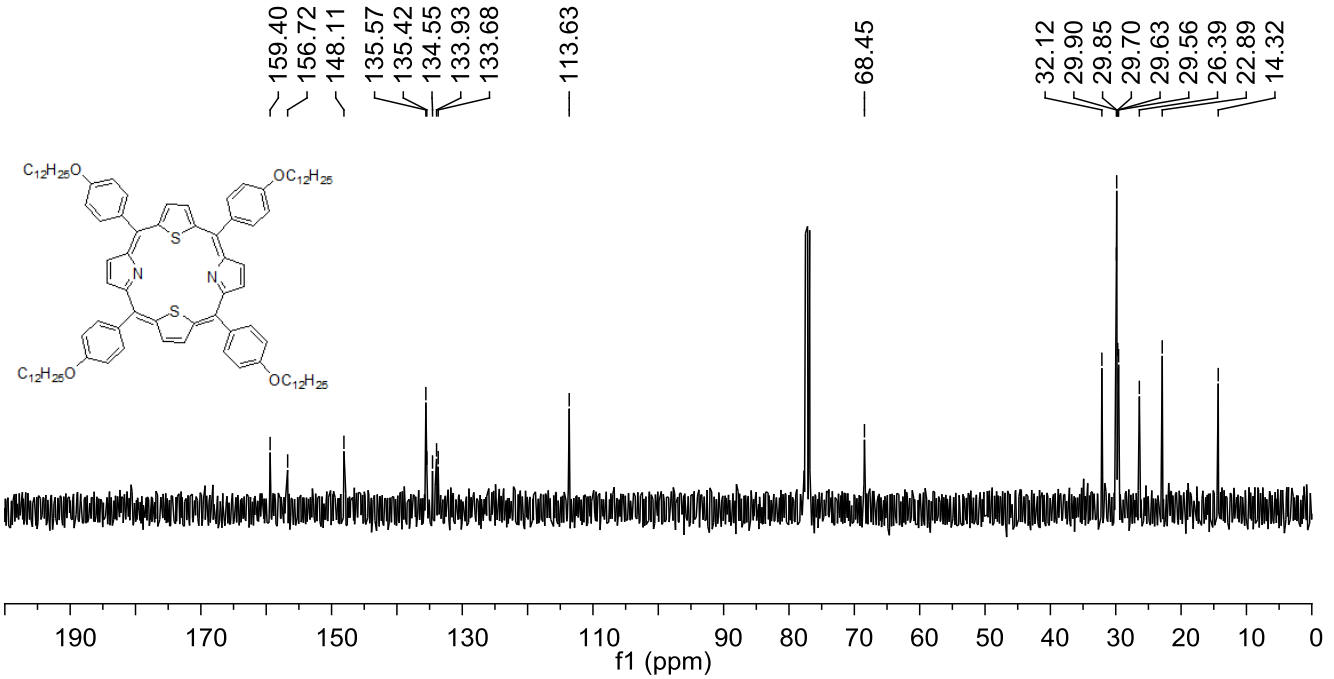
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29.63
29.56
26.39
22.89
14.32
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Table S1. Absorption peaks of **2a** and **2b** in toluene at room temperature.[a]

Compound	Soret	Q IV	Q III	Q II	Q I
2a	442 (300)	519 (25)	555 (14)	639 (1.4)	704 (7.3)
2b	441 (510)	519 (45)	555 (25)	638 (3.2)	704 (16)

[a] Absorption peaks are shown in nanometers followed by molar absorptivities in parentheses with units of 10^3 L mol^{-1} cm^{-1}.

Table S2. Electrochemical properties of **2a** and **2b**.

Compound	$E^{ox}_{1/2}(1)$ (mV)	$E^{ox}_{1/2}(2)$ (mV)	ΔE (mV)	$D_O(1)$ (10^{-6} cm^2 s^{-1})	$D_O(2)$ (10^{-6} cm^2 s^{-1})	$k_o(1)$ (10^{-4} cm s^{-1})	$k_o(2)$ (10^{-4} cm s^{-1})
2a	465	676	211	0.19	0.32	2.2	2.5
2b	467	668	201	0.14	0.31	2.5	2.7

Note: All electrochemical experiments were carried out in methylene chloride containing 0.1 M $(n\text{Bu})_4\text{NPF}_6$ with a glassy carbon working electrode, a Pt wire counter electrode and a Ag|0.1 M $AgNO_3$ reference electrode. All potentials are referenced to Fc/Fc^+. Diffusion coefficients of oxidized and reduced species were assumed to be the same and rate constants were calculated using Nicholson's method.[2]

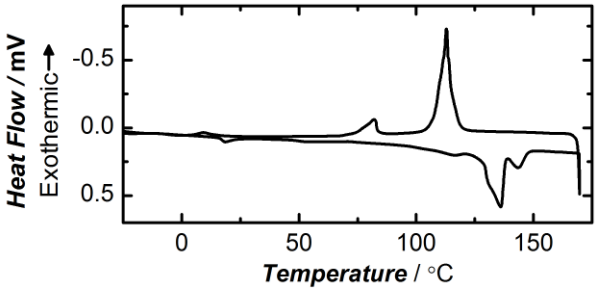

Fig. S1. DSC thermogram of dithiaporphyrin **2a** at 5 °C•min^{-1}.

Table S3. Differential scanning calorimetry phase transition temperatures (°C) and enthalpies (kJ·mol^{-1}, in parentheses) upon heating and cooling at 5 °C·min^{-1} for compounds **2a** and **2b**.

compound	peak 1 °C (kJ/mol)	peak 2 °C (kJ/mol)	peak 3 °C (kJ/mol)	peak 4 °C (kJ/mol)
2a (heating)	18.7 (1.2)	115.8 (1.9)	136.2 (15.5)	143.8 (1.6)
2a (cooling)	9.2 (0.9)	82.9 (6.4)	113.1 (26.6)	
2b (heating)	64.0 (0.5)	79.8 (0.7)	126.6 (36.8)	
2b (cooling)	52.8 (0.6)	69.3 (0.5)	88.3 (32.9)	

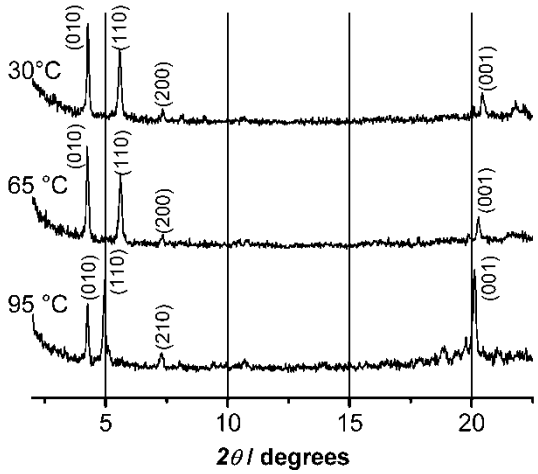

Fig. S2. XRD patterns of **2a** after melting at 150 °C for 10 minutes then cooling to: 95 °C, 65 °C and 30 °C.

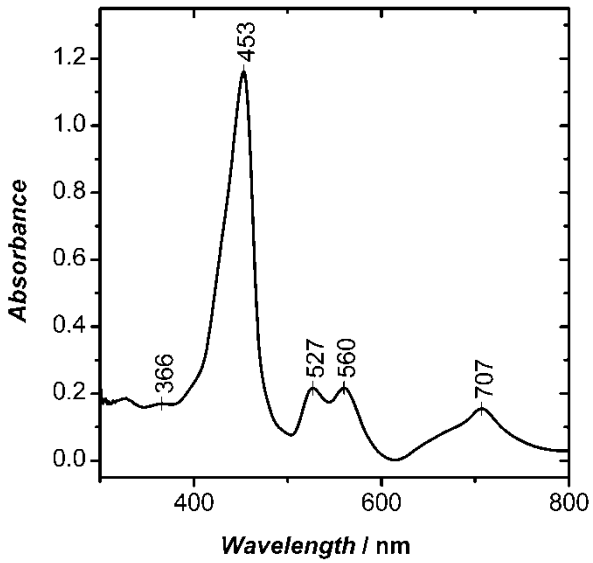

Fig. S3. UV-vis absorption spectrum of **2b** film on an ITO-coated glass slide.

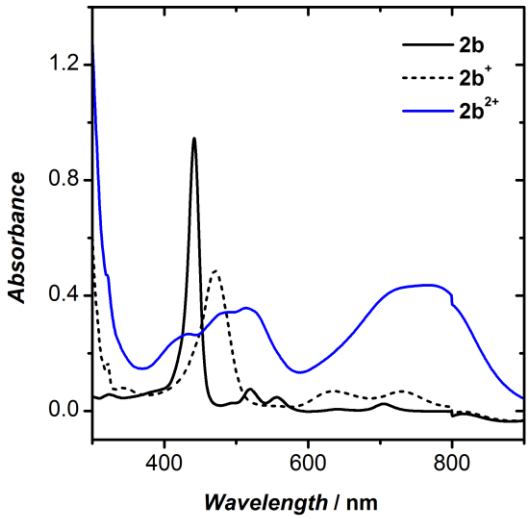

Figure S4. Spectroelectrochemical spectra of **2b** (black line), its monocation (dashed line) and dication (blue line).

Table S4. Variable temperature powder x-ray data analysis, including Miller indices and cell parameters. The following software was used to help assign cell parameters: Toolbar FullProf Suite Program (version 2.05, July 2011), WinPLOTR [April 2012], DicVol04[3] and TREOR.

Cmpd	Miller Index	d_{OBS} / Å	d_{CALCD} / Å	$d_{OBS} - d_{CALCD}$ / Å	Cell parameters / Å
2a-95 °C	(010)	20.8	21.4	0.6	*a* = 29(1)
	(110)	17.8	17.3	-0.5	*b* = 21(1)
	(210)	12.1	12.2	-0.1	*c* = 4.41(1)
	(001)	4.4	4.4	0.0	
2a-65 °C	(010)	20.8	21.0	0.2	*a* = 24.0(2)
	(110)	15.7	15.9	0.2	*b* = 21.0(3)
	(200)	12.0	12.0	0.0	*c* = 4.47(1)
	(001)	4.4	4.5	0.0	
2a-30 °C	(010)	20.7	21.0	0.3	*a* = 24.4(1)
	(110)	15.8	15.9	-0.1	*b* = 21.0(4)
	(200)	12.0	12.2	-0.2	*c* = 4.3(1)
	(520)	4.4	4.4	0.0	
	(001)	4.3	4.3	0.0	
2b – 82 °C	(100)	20.4	21.0	-0.6	*a* = 21(1)
	(200)	10.8	10.5	0.3	*c* = 4.4(1)
	(001)	4.4	4.4		
2b – 60 °C	(100)	20.3	20.4	-0.1	*a* = 19.8(1)
	(010)	19.1	18.8	0.3	*b* = 18.2(1)
	(200)	10.0	10.0	0.0	*c* = 4.5(1)
	(020)	9.2	9.2	0.0	
	(120)	8.4	8.4	0.0	
	(220)	6.8	6.8	0.0	
	(001)	4.4	4.4	0.0	
2b – 45 °C	(100)	20.2	20.1	0.1	*a* = 19.6(1)
	(010)	18.9	19.0	-0.1	*b* = 18.5(1)
	(200)	10.0	9.9	0.1	*c* = 4.4 (1)
	(220)	6.8	6.8	0.0	
	(130)	5.9	5.9	0.0	
	(040)	4.7	4.7	0.0	
	(001)	4.4	4.4	0.0	

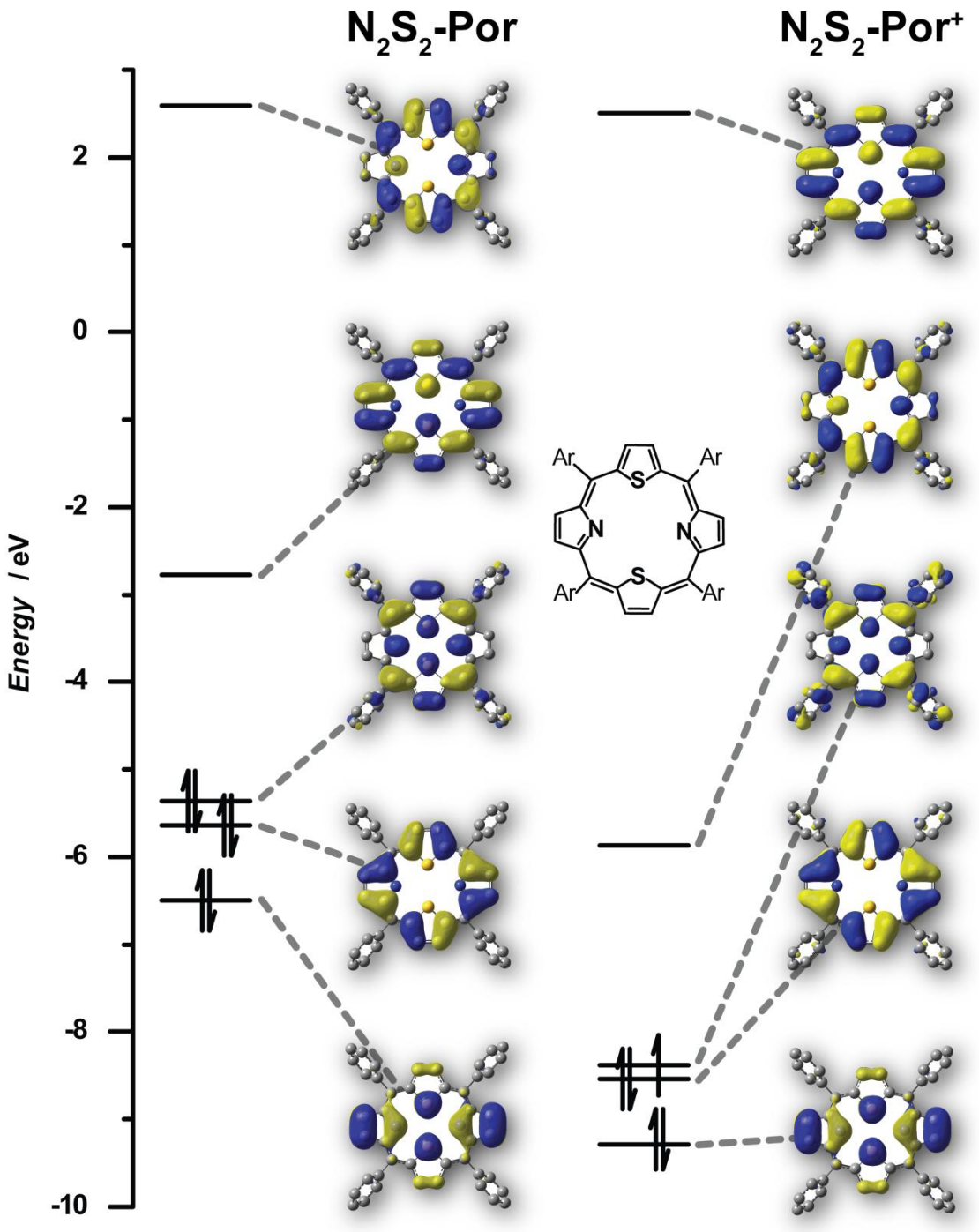

Figure S5. FMOs of N_2S_2 porphyrin and its radical cation calculated using DFT methods at the B3LYP-6-31G+(d) level.

References

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