

Electronic Supplementary Information

for

Facile Electrosynthesis of π -Extended Porphyrins

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Table S1. Half-wave or Peak Potentials (V vs SCE) in CH₂Cl₂, containing 0.1 M TBAP. Scan rate of 0.1 V/s.

M	Ring	Oxidation		Reduction		H-L gap (V)
		2 nd	1 st	1 st	2 nd	
H₂	TMP	1.46	1.03	-1.31	-1.68	2.34
	Open	1.27 ^b	1.02	-1.28	-1.67	2.30
	Fused	1.00	0.64	-1.10	-1.58	1.74
Zn	TMP	1.09	0.78	-1.47	-1.89	2.25
	Open	1.05	0.76	-1.44	-1.87	2.20
	Fused	0.79	0.52	-1.24	-1.72	1.76
Ni^a	TMP	1.38 ^b	1.02	-1.60 ^b	-	2.62
	Open	1.15	1.02	-1.47 ^b	-	2.49
	Fused	1.02	0.67	-1.24	-1.84 ^b	1.91
InCl	TMP	1.53	1.18	-1.19	-1.62	2.37
	Open	1.40 ^b	1.15	-1.15	-1.60	2.30
	Fused	1.13	0.79	-1.00	-1.48	1.79
IrCOCl	TMP	-	1.19	-1.32 ^c	-1.82	2.51
	Open	1.45 ^b	1.19	-1.29	-1.75	2.48
	Fused	0.77	0.51	-1.24	-1.73	1.75

^aData taken from ref 20, ^bpeak potential at a scan rate of 0.1 V/s. ^ccoupled with an oxidation process at $E_{1/2} = -1.49$ V

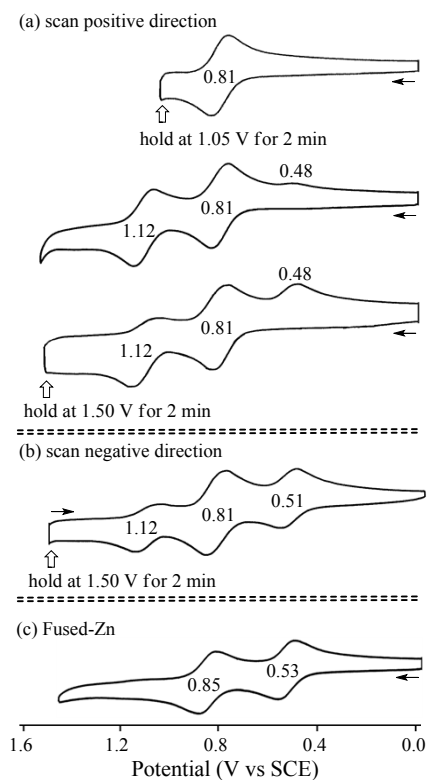


Figure S1 Cyclic voltammograms showing electrochemically induced generation of the fused Zn(II) complex from the porphyrin bis-radical of the related open macrocycle (a) after initial positive scans from 0.0 to 1.50 V and (b) after an initial negative scan from 1.50 to 0.0 V in PhCN, 0.1 M TBAP, scan rate = 0.1 V/s. For comparison, a cyclic voltammograms of the chemically generated Zn(II) porphyrin with the fused π -extended system is shown in part c.

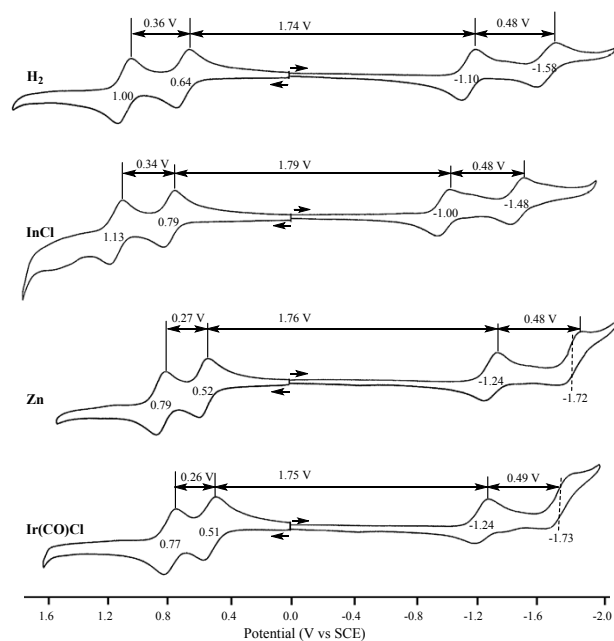


Figure S2. Cyclic voltammograms of the chemically synthesized π -extended porphyrins in CH_2Cl_2 , 0.1 M TBAP. The $\Delta E_{1/2}$ between the various redox progresses is also given in the figure.

Table S2. UV-vis spectral data of neutral investigated porphyrins in CH_2Cl_2 , 0.1 M TBAP.

Ring	M	Soret bands (nm)				Visible bands (nm)			
TMP	H ₂	400 ^{sh}	418			514	547	592	648
	Zn	400 ^{sh}	421			513	549	-	
	Ni	-	415			528	561		
	InCl	405 ^{sh}	425			561	599	-	
	Ir(CO)Cl	-	421			533	567	-	
Open	H ₂	400 ^{sh}	423			516	550	592	648
	Zn	400 ^{sh}	422			513	550	-	
	Ni		417			529	562		
	InCl	404 ^{sh}	428			562	601		
	Ir(CO)Cl	-	424			534	567		
Fused	H ₂	386	418	452	480	568	617	643	709
	Zn	380	421	463	488	556	622	-	672
	Ni	379	-	460	486	550	586		672
	InCl	383	426	469	495	564	606	-	688
	Ir(CO)Cl	378	-	464	489	555	595	-	672

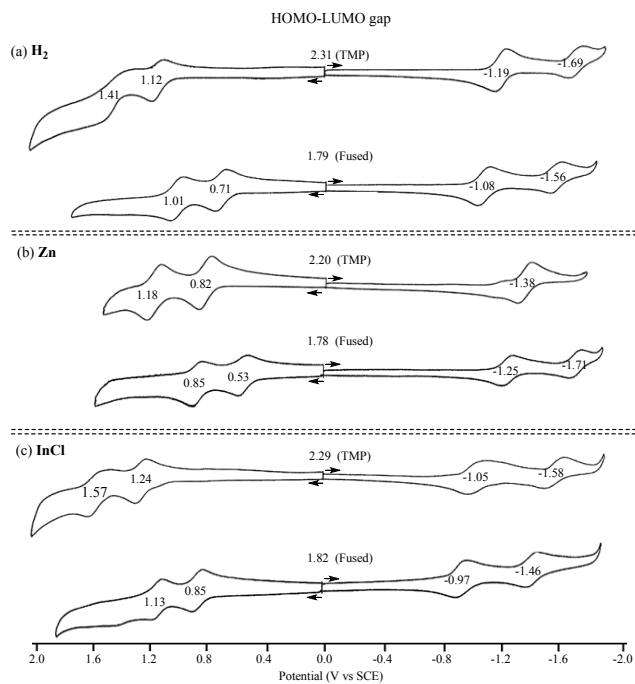


Figure S3. Cyclic voltammograms illustrating the reduction and oxidation of porphyrins with **TMP** and fused macrocycles in PhCN, 0.1 M TBAP. The $\Delta E_{1/2}$ between the two reversible redox progresses (the HOMO-LUMO gap) is also given in the figure.

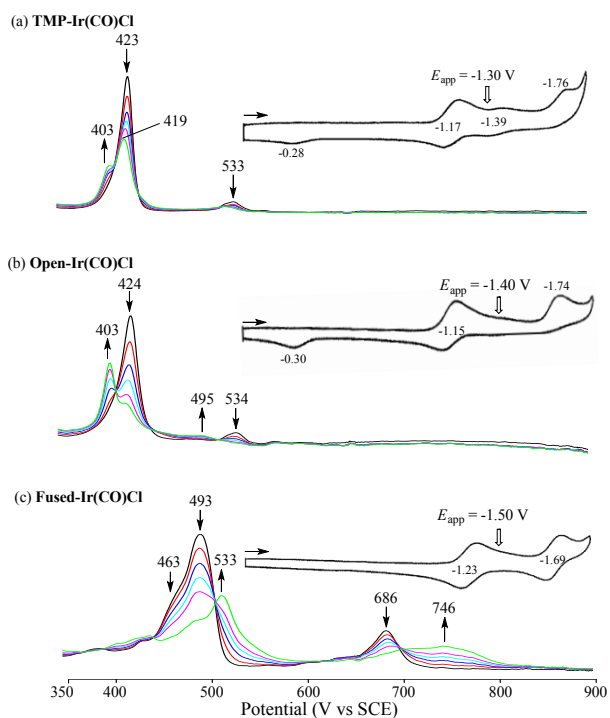


Figure S4. UV-visible spectral changes obtained during the first reduction of (a) **TMP-Ir(CO)Cl**, (b) **Open-Ir(CO)Cl** and (c) **Fused-Ir(CO)Cl** in PhCN, 0.1 M TBAP.

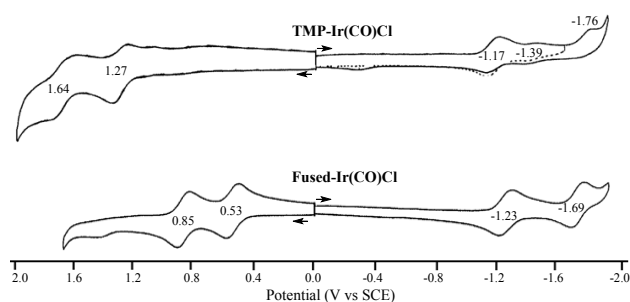


Figure S5. Cyclic voltammograms of **Ir(CO)Cl** centered orphyrins with **TMP** and **Fused** macrocycles in PhCN, 0.1 M TBAP.

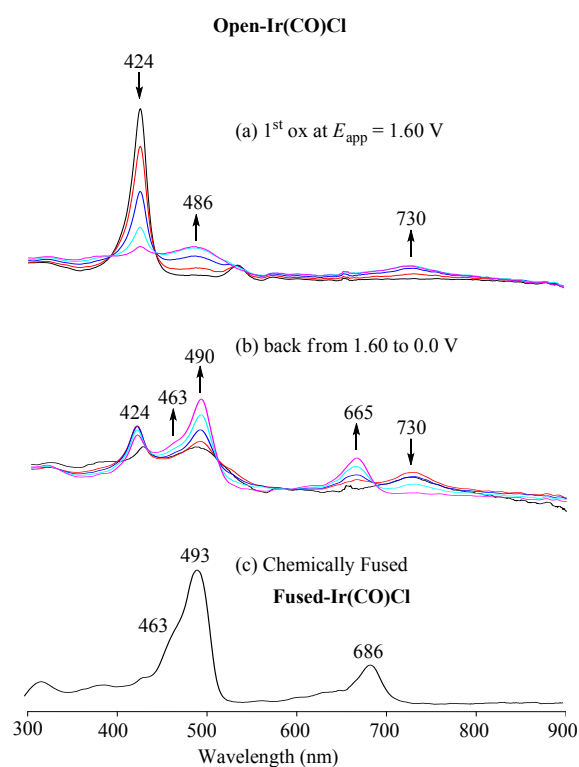


Figure S6. UV-visible spectral changes (a) during oxidation of **Open-Ir(CO)Cl** in a thin-layer cell at an applied potential of 1.60 V, (b) after re-reduction of the above compound at $E_{app} = 0.00$ V to electrogenerate the neutral fused compounds in PhCN, 0.1 M TBAP and (c) UV-vis spectra of the chemically synthesized **Fused-Ir(CO)Cl** under the same solution condition.

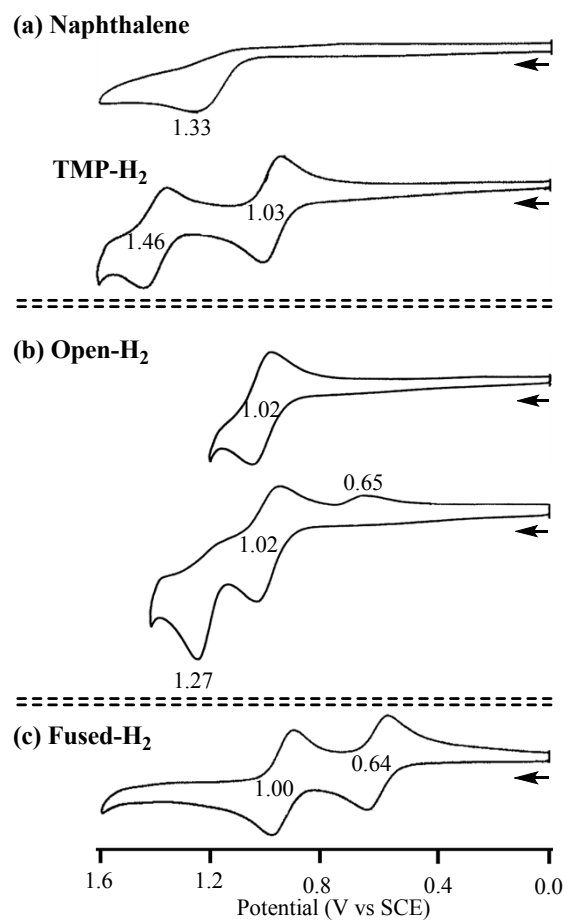


Figure S7. Cyclic voltammogram of (a) naphthalene and **TMP-H₂**, (b) **Open-H₂** and (c) **Fused-H₂** in CH₂Cl₂, 0.1 M TBAP.

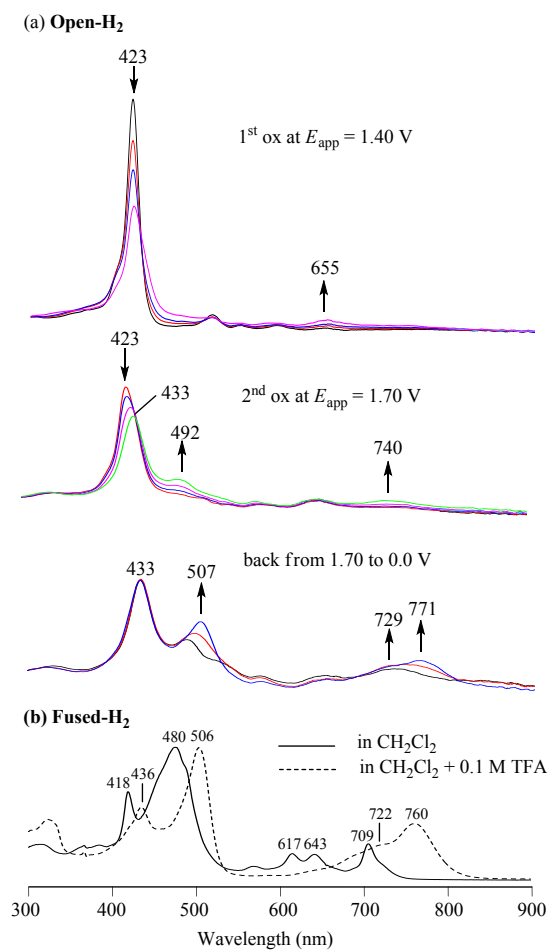


Figure S8. UV-visible spectrum of (a) **Open-H₂** during oxidation and rereduction in CH₂Cl₂, 0.1 M TBAP and (b) **Fused-H₂** before (—) and (-----) after addition of TFA in CH₂Cl₂.

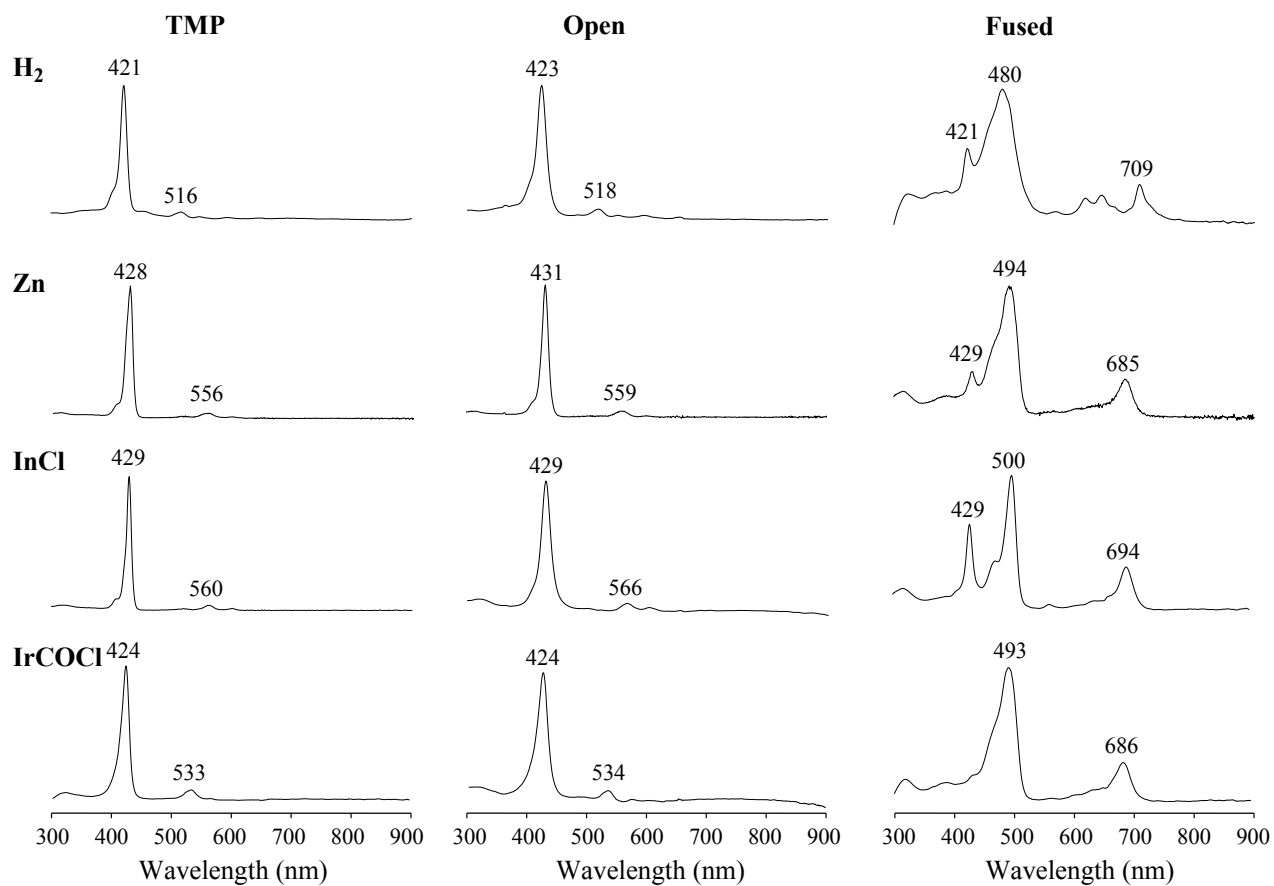
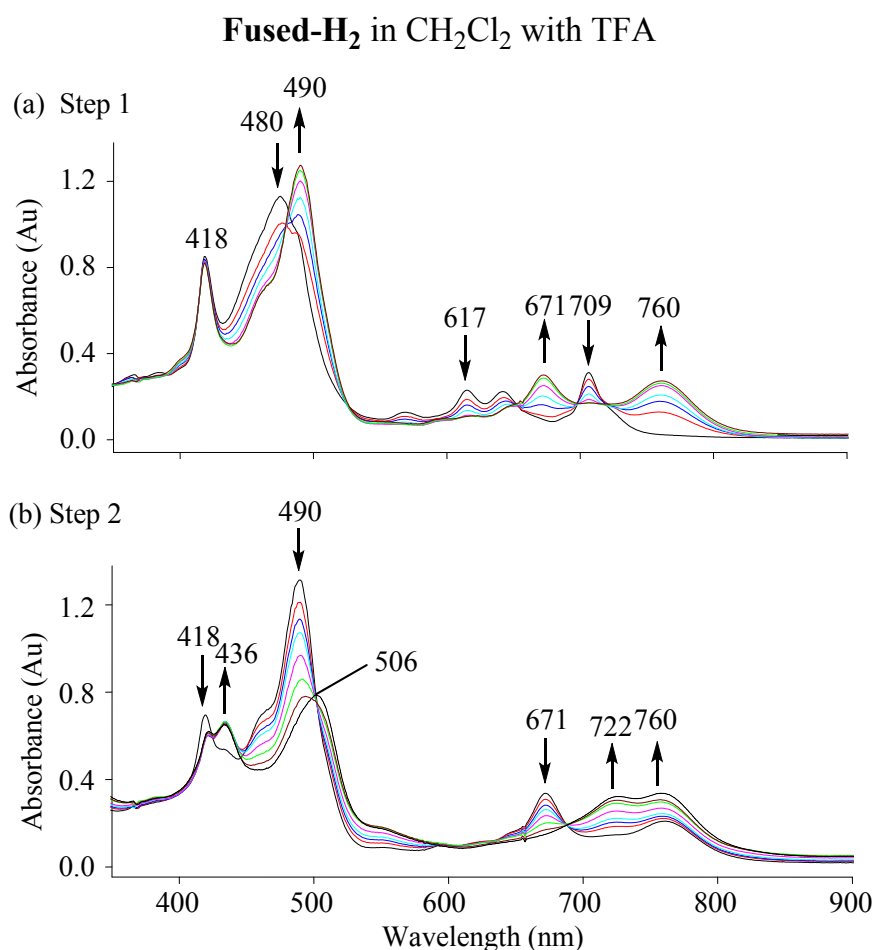


Figure S9. UV-vis spectra of investigated porphyrins in PhCN, 0.1 M TBAP.

Figure S10. UV-vis titration of Fused-H₂ in CH₂Cl₂ with TFA.



EXPERIMENTAL SECTION

Chemicals. TMP-H₂, Open-H₂, Open-Zn, were prepared according to published procedures.[1] 1,6-dimethoxynaphthalene is commercially available.

Absolute dichloromethane (CH₂Cl₂, 99.8%, EMD Chemicals Inc.) was used for electrochemistry without further purification. Benzonitrile (PhCN) was purchased from Aldrich Chemical Co. and distilled over P₂O₅ under vacuum prior to use. Tetra-*n*-butylammonium perchlorate (TBAP), used as supporting electrolyte, was purchased from Sigma Chemical or Fluka Chemika Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least one week prior to use.

All chemicals were purchased from Aldrich or Alfa Aesar and were used as received unless otherwise noted. Reagent grade solvents (CH₂Cl₂, hexanes) were distilled prior use. All reported NMR spectra were recorded on 400 or 500MHz spectrometer. UV-vis spectrum absorption were recorded in CH₂Cl₂. Chromatography was performed on silica (Kieselgel 60, 200 - 400 mesh). Dry column vacuum chromatography (DCVC) was performed on preparative thin-layer chromatography silica. Mass spectra were obtained via FD-MS or ESI-MS.

Fused-H₂. Method A: Open-Zn (46 mg, 0.05 mmol) was dissolved in dry CH₂Cl₂ (15 mL) and Fe(ClO₄)₃•H₂O (195 mg, 0.5 mmol) in MeNO₂ was added *via* syringe within 5 min. After 25 minutes CF₃OOH was added (2 mL) and stirred for additional 20 minutes. The reaction was filtered directly through a pad of silica. Additional DCVC (CH₂Cl₂:hexanes) gave pure product. Crystallization from CH₂Cl₂:hexanes afforded product as green crystals with 52% (22 mg); ¹H NMR (500 MHz, CDCl₃, Me₄Si): δH(ppm) = 9.37 (s, 1H), 9.02 (d, *J* = 3.8 Hz, 1H), 8.72 (d, *J* = 9.5 Hz, 1H), 8.63 (d, *J* = 4.5 Hz, 1H), 8.50 (d, *J* = 4.5 Hz, 1H), 8.48-8.46 (m, 2H), 8.42 (d, *J* = 4.5 Hz, 1H), 7.70 (d, *J* = 9.5 Hz, 1H), 7.42 (d, *J* = 9.5 Hz, 1H), 7.30-7.25 (m, 6H), 7.20-7.18 (m, 1H), 4.40 (s, 3H), 4.30 (s, 3H), 2.66 (s, 3H),

2.63 (s, 3H), 2.59 (s, 3H), 1.94 (s, 12H), 1.93 (s, 6H), -1.14 (br. s, 2H); UV-vis (CH₂Cl₂): λ_{\max} (ϵ) 475 (101 300), 570 (2 400), 615 (5 500), 641 nm (12 200); HRMS (ESI) [M+H]⁺ [C₅₉H₅₃N₄O₂]⁺: calcd 849.4169, found 849.4169. **Method B:** Controlled-potential bulk electrolysis was carried out in a 10 ml CH₂Cl₂ solution containing 0.1 M TBAP and **Open-H₂** (5.37 mg, 0.0064 mmol). The controlled oxidizing potential was set at +1.50 V which was sufficient to generate the species [**Open-H₂**]²⁺ which was converted to [**Fused-H₄**]⁴⁺ in solution. The potential was held at +1.50 V for two hours and then switched to +0.0 V, which resulted in a conversion of [**Fused-H₄**]⁴⁺ to [**Fused-H₄**]²⁺. The doubly protonated dication was converted to **Fused-H₂** by adding dry Et₃N (0.1 mL) in DCM (5 mL). After 15 min solvent was removed in vacuum and the residue was dissolved in CH₂Cl₂. The crude product was first purified by silica gel column chromatography, with a solvent mixture of hexanes and CH₂Cl₂ (3:2) as eluent. Additional DCVC (CH₂Cl₂:hexanes) gave pure green solid product with 53% yield. The spectral data of product correlated to data obtained in **Method A**.

TMP-Zn. TMP-H₂ (32 mg, 0.04 mmol), Zn(OAc)₂•H₂O (700 mg, 4.00 mmol), and chloroform (30 mL) were placed in a round bottomed flask, stirred for 8 hours. Upon completion reaction of the solvent was removed in vacuum and the residue was dissolved in CH₂Cl₂. The crude product was purified by silica gel column chromatography, with a solvent mixture of hexanes and CH₂Cl₂ (3:2) as eluent. Solvents were removed in vacuum to yield a red colored solid (33 mg, 98%); ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ H(ppm) = 8.67 (br s, 8H), 7.34 (s, 8H), 2.02 (s, 12H), 1.84 (s, 12H), 1.67 (s, 12H); UV-vis (CH₂Cl₂): λ_{\max} (ϵ) 371 (6, 000), 419 (67, 500), 514 (1, 800), 548 (2, 400), 649 nm (1, 700); LRMS (FD) calcd for C₅₆H₅₂N₄Zn: calcd 844.35, found 844.30, isotope profiles agree.

TMP-InCl. TMP-H₂ (32 mg, 0.04 mmol), InCl₃ (88 mg, 0.40 mmol), sodium acetate (298 mg, 4.25 mmol), and glacial acetic acid (15 mL) were placed in a round bottomed flask, heated to 110 °C for 30 hours. Upon reaction completion, the solvent was removed in vacuum and the residue was dissolved in CH₂Cl₂. The crude product was extracted from saturated NaHCO₃, organic phases washed with brine and dried over Na₂SO₄. Solvents were removed in vacuum to yield a green colored solid (15 mg, 48%); ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ H(ppm) = 8.82 (s, 8H), 7.28 (s, 8H), 2.65 (s, 12H), 1.99 (s, 12H), 1.73 (s, 12H); UV-vis (CH₂Cl₂): λ_{\max} (ϵ) 426 (445, 600), 561 (15, 900), 599 nm (5, 700); LRMS (FD) calcd for C₅₆H₅₂ClInN₄: calcd 930.29, found 930.30, isotope profiles agree.

TMP-Ir(CO)Cl. TMP-H₂ (32 mg, 0.04 mmol), [Ir(COD)Cl]₂ (52 mg, 0.08 mmol) were added into xylene (30 mL), and the solution was refluxed for 4 days. The solution changed color from purple to red. The crude mixture was dried under high vacuum and purified by silica gel column chromatography, with a solvent mixture of hexanes and CH₂Cl₂ (3:2) as eluent. A reddish purple solid (14 mg, 0.01 mmol, 62%) was obtained by recrystallization from CH₂Cl₂/CH₃OH; ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ H(ppm) = 8.68 (s, 8H), 7.28 (s, 8H), 2.62 (s, 12H), 1.92 (s, 12H), 1.83 (s, 12H); UV-vis (CH₂Cl₂): λ_{\max} (ϵ) 423 (255 300), 534 (22 800), 567 nm (3000); LRMS (FD) calcd for C₅₇H₅₂ClIrN₄O: calcd 1036.34, found 1036.30, isotope profiles agree.

Open-Ir(CO)Cl. Open-H₂ (20 mg, 0.02 mmol), [Ir(COD)Cl]₂ (26 mg, 0.04 mmol) were added into xylene (15 mL), and the solution was refluxed for 3 days. The solution changed color from purple to red. The crude mixture was dried under high vacuum and purified by silica gel column chromatography, with a solvent mixture of hexanes and CH₂Cl₂ (3:2) as eluent. A reddish purple solid (14 mg, 0.01 mmol, 62%) was obtained by recrystallization from CH₂Cl₂/CH₃OH; ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ H(ppm) = 8.60-8.71 (m, 8H), 8.52 (d, *J* = 7.6 Hz, 1H), 8.33 (d, *J* = 9.2 Hz, 1H), 7.20-7.35 (m, 8H), 6.01 (d, *J* = 2.8 Hz, 1H), 4.29 (s, 3H), 4.28 (s, 3H), 2.62 (s, 9H), 1.92 (s, 9H), 1.83 (s, 9H); UV-vis (CH₂Cl₂): λ_{\max} (ϵ) 421 (289 300), 533 (20 800), 563 nm (4100); LRMS (FD) calcd for C₆₀H₅₂ClIrN₄O₃: calcd 1104.33, found 1104.30, isotope profiles agree.

Open-InCl. Open-H₂ (24 mg, 0.04 mmol), InCl₃ (88 mg, 0.40 mmol), sodium acetate (298 mg, 4.25 mmol), and glacial acetic acid (15 mL) were placed in a round bottomed flask, heated to 110 °C for 24 hours. Upon reaction completion, the solvent was removed in vacuum and the residue was dissolved in CH₂Cl₂. The crude product was extracted from saturated NaHCO₃, organic phases washed with brine and dried over Na₂SO₄. Solvents were removed in vacuum to yield a greenish colored solid (25 mg, 62%); ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ H(ppm) = 8.84-8.85 (m, 8H), 8.41 (d, *J* = 9.2 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 7.28-7.30 (m, 6H), 7.10-7.15 (m, 2H), 6.08 (d, *J* = 2.8 Hz, 1H), 4.29 (s, 3H), 4.28 (s, 3H), 2.64 (s, 3H), 2.62 (s, 6H), 1.97 (s, 6H), 1.93 (s, 6H), 1.90 (s, 6H); UV-vis (CH₂Cl₂): λ_{\max}

(ϵ) 427 (287, 000), 561 (16, 600), 602 nm (5, 100); LRMS (FD) calcd for $C_{59}H_{52}ClInN_4O_2$: calcd 998.20, found 998.20, isotope profiles agree.

Fused-Zn. Fused- H_2 (24 mg, 0.04 mmol), $Zn(OAc)_2 \cdot H_2O$ (700 mg, 4.00 mmol), and chloroform (30 mL) were placed in a round bottomed flask, stirred for 8 hours. Upon reaction completion, the solvent was removed in vacuum and the residue was dissolved in CH_2Cl_2 . The crude product was purified by silica gel column chromatography, with a solvent mixture of hexanes and CH_2Cl_2 (3:2) as eluent. Solvents were removed in vacuum to yield a red colored solid (26 mg, 98%); 1H NMR (400 MHz, $CDCl_3$, Me_4Si): δH (ppm) = 9.42 (br s, 2H), 9.22 (d, $J = 4.4$ Hz, 1H), 8.62 (d, $J = 4.4$ Hz, 1H), 8.58 (d, $J = 9.2$ Hz, 1H), 8.52-8.60 (m, 4H), 7.61 (d, $J = 9.2$ Hz, 1H), 7.20-7.30 (m, 7H), 4.37 (s, 3H), 4.27 (s, 3H), 2.64 (s, 3H), 2.62 (s, 3H), 2.60 (s, 3H), 1.92 (br s, 12H), 1.89 (s, 6H); UV-vis (CH_2Cl_2): λ_{max} (ϵ) 383 (18, 800), 421 (39, 500), 487 (87, 300), 550 (11, 900), 617 (7, 900), 668 (21, 900), 718 nm (7, 400); LRMS (FD) calcd for $C_{59}H_{50}N_4O_2Zn$: calcd 910.30, found 910.30, isotope profiles agree.

Fused-InCl. Method C: Fused- H_2 (12 mg, 0.02 mmol), $InCl_3$ (44 mg, 0.20 mmol), sodium acetate (150 mg, 2.13 mmol), and glacial acetic acid (10 mL) were placed in a round bottomed flask, heated to 110 °C for 20 hours. Upon reaction completion, the solvent was removed in vacuum and the residue was dissolved in CH_2Cl_2 . The crude product was extracted from saturated $NaHCO_3$, organic phases washed with brine and dried over Na_2SO_4 . Solvents were removed in vacuum to yield a green colored solid (11 mg, 55%); 1H NMR (400 MHz, $CDCl_3$, Me_4Si): δH (ppm) = 9.45 (s, 2H), 9.10 (d, $J = 3.2$ Hz, 1H), 8.95 (d, $J = 4.4$ Hz, 1H), 8.70-8.78 (m, 4H), 8.58-8.65 (m, 2H), 7.72 (d, $J = 9.2$ Hz, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.40 (d, $J = 9.4$ Hz, 1H), 7.19-7.25 (m, 4H), 4.40 (s, 3H), 4.30 (s, 3H), 2.67 (s, 3H), 2.65 (s, 3H), 2.63 (s, 3H), 1.98 (s, 12H), 1.93 (s, 6H); UV-vis (DCM): λ_{max} (ϵ) 385 (11, 800) 427 (50, 800), 470 (28, 700), 493 (62, 500), 563 (3, 300), 605 (3, 300), 633 (4, 600), 686 nm (19, 600); LRMS (FD) calcd for $C_{59}H_{50}ClInN_4O_2$: calcd 996.26, found 996.20, isotope profiles agree. **Method D:** Controlled-potential bulk electrolysis was carried out in a 5 ml CH_2Cl_2 solution containing 0.1 M TBAP and **Open-InCl** (11.04 mg, 0.011 mmol). The controlled oxidizing potential was set at +1.60 V which was sufficient to generate the species which was converted to **Fused-InCl** in solution. The potential was held at +1.60 V for 2.5 hours and then switched to +0.0 V for two hours, which resulted in a conversion to **Fused-InCl**. The crude product was first purified by silica gel column chromatography, with a solvent mixture of hexanes and CH_2Cl_2 (3:2) as eluent. Additional SEC column (toluene) and DCVC (CH_2Cl_2 :hexanes) gave pure green solid product 5.2 mg with 47% yield. The spectral data of product correlated to data obtained in **Method C**.

Fused-Ir(CO)Cl. Fused- H_2 (12 mg, 0.02 mmol), $[Ir(COD)Cl]_2$ (26 mg, 0.04 mmol) were added into xylene (15 mL), and the solution was refluxed for 4 days. The solution changed color from purple to red. The crude mixture was dried under high vacuum and purified by silica gel column chromatography, with a solvent mixture of hexanes and CH_2Cl_2 (3:2) as eluent. A reddish solid (11 mg, 0.01 mmol, 52%) was obtained by recrystallization from CH_2Cl_2/CH_3OH ; 1H NMR (400 MHz, $CDCl_3$, Me_4Si): δH (ppm) = 9.41 (s, 2H), 9.32 (d, $J = 5.2$ Hz, 1H), 9.20 (d, $J = 5.2$ Hz, 1H), 8.75 (d, $J = 8.4$ Hz, 1H), 8.67 (d, $J = 8.2$ Hz, 1H), 8.52-8.57 (m, 4H), 7.71 (d, $J = 9.2$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.35 (d, $J = 3.6$ Hz, 1H), 7.21-7.28 (m, 4H), 4.37 (s, 3H), 4.28 (s, 3H), 2.65 (s, 3H), 2.63 (s, 3H), 2.61 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 1.93 (s, 3H), 1.86 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H); UV-vis (CH_2Cl_2): λ_{max} (ϵ) 312 (25 400), 337 (17 200), 484 (123 600), 546 (6000), 583 (9000), 607 (1 200), 656 nm (4 500); LRMS (FD) calcd for $C_{60}H_{50}ClIrN_4O_3$: calcd 1102.32, found 1102.30, isotope profiles agree.

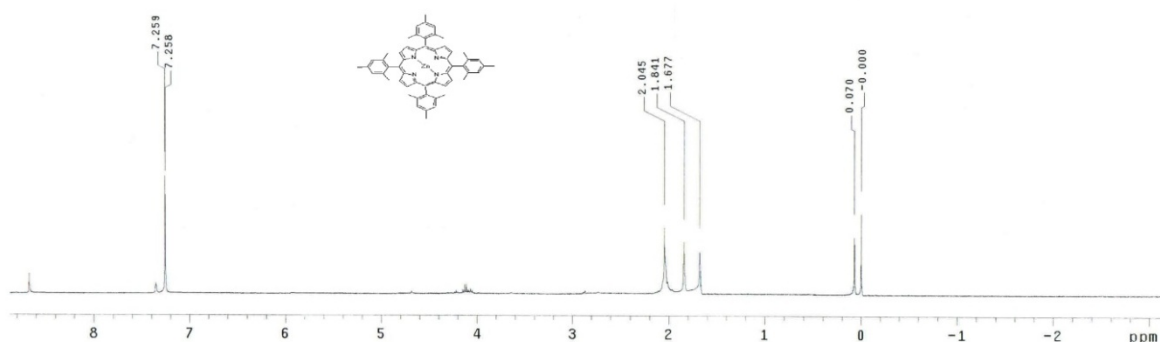
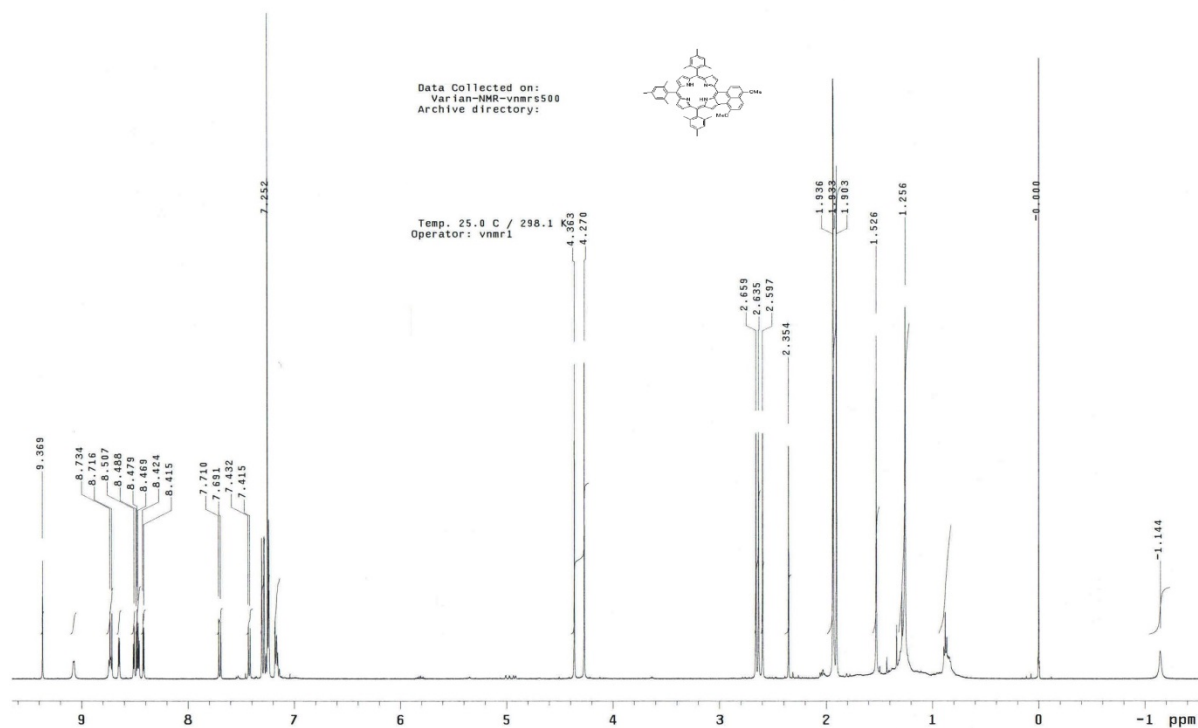
INSTRUMENTATION

Cyclic voltammetry was carried out with an EG&G Model 173 potentiostat/galvanostat at room temperature. A homemade three-electrode electrochemistry cell was used and consisted of a platinum button or glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE.

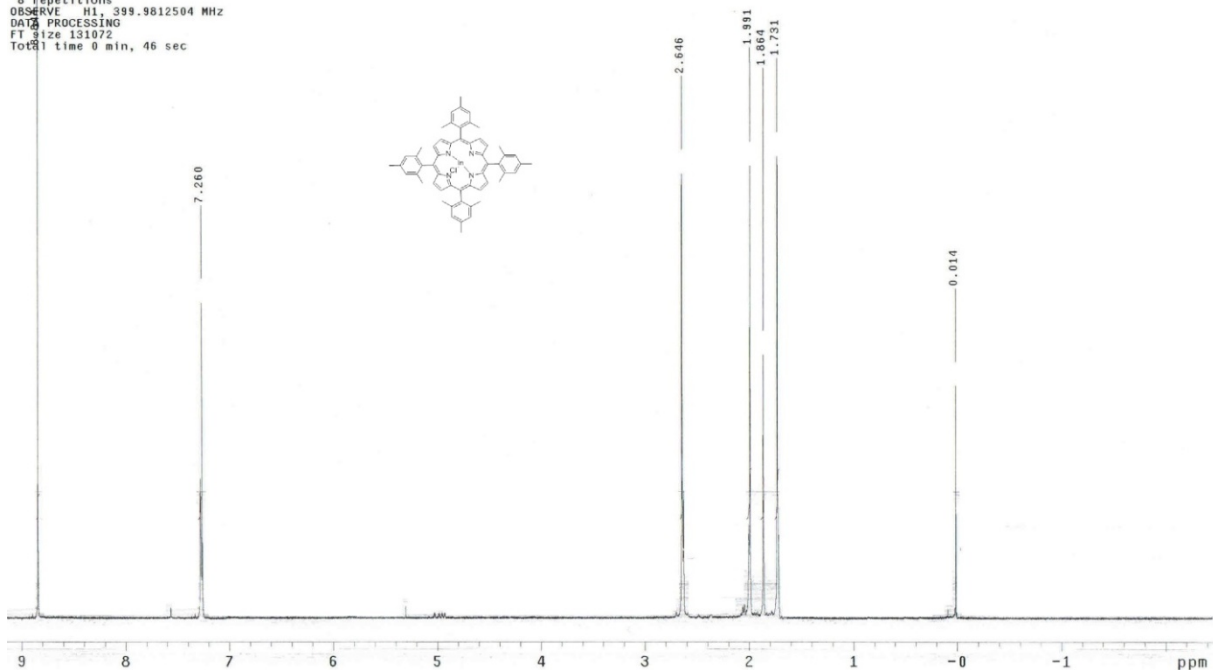
Thin-layer UV-visible spectroelectrochemical experiments were performed with a home-built thin-layer cell which has a light transparent platinum net working electrode. Potentials were applied and

monitored with an EG&G PAR Model 173 potentiostat. Time-resolved UV-visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High purity N₂ from Trigas was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment.

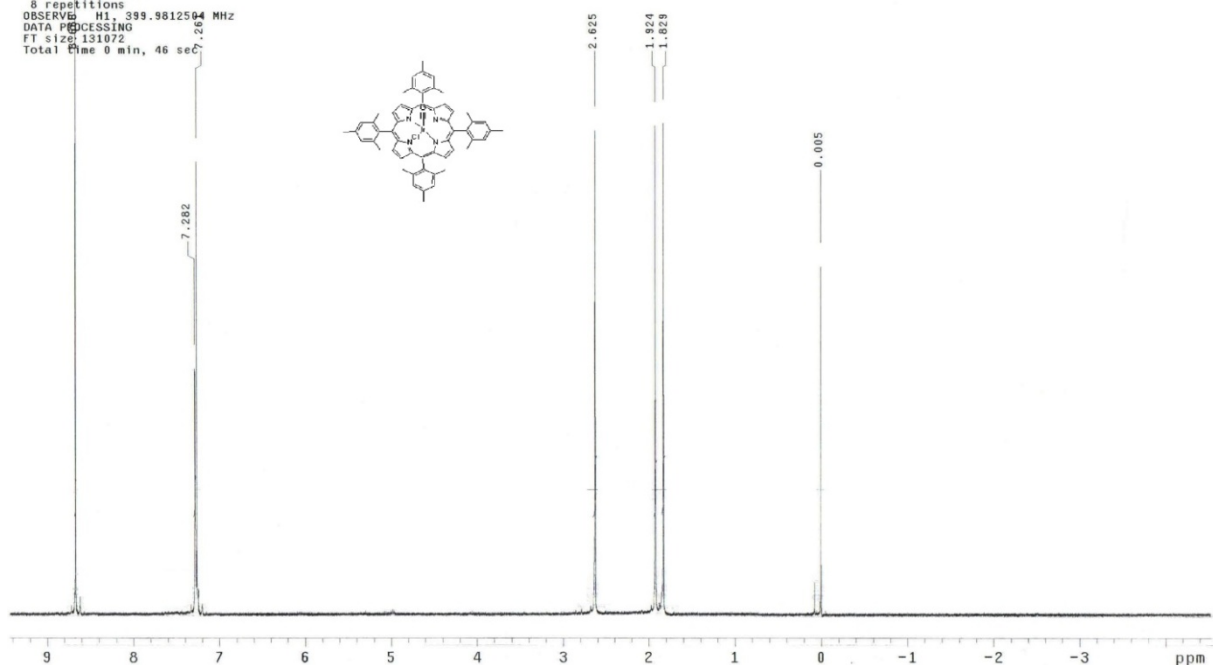
Controlled potential electrolysis was performed with an EG&G PAR 173 Potential/Galvanostat. An "H" type cell with a fritted glass junction to separate the cathodic and anodic portions of the cell was used for bulk electrolysis. The working and counter electrodes were made from platinum gauze. The reference electrode was an SCE. The sample and solvent were transferred into the electrolysis cell under nitrogen. The solution was stirred during electrolysis using a Fisher magnetic stirrer.



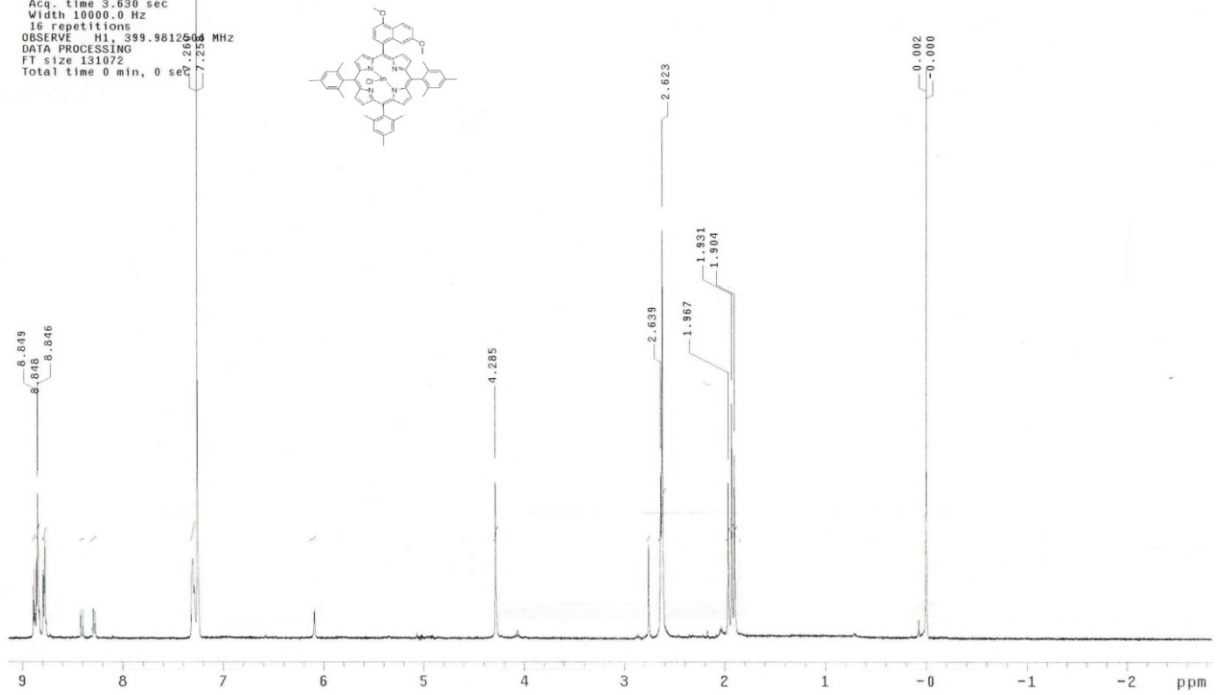
DK165
Pulse Sequence: s2pu1
Solvent: CDC13
Ambient temperature
Mercury-400BB "SchilfSUN"
Relax. delay 1.000 sec
Pulse 48.6 degrees
Acq. time 3.630 sec
Width 10000.0 Hz
8 repetitions
OBSERVE H1, 399.9812504 MHz
DATA PROCESSING
F1 size 131072
Total time 0 min, 46 sec



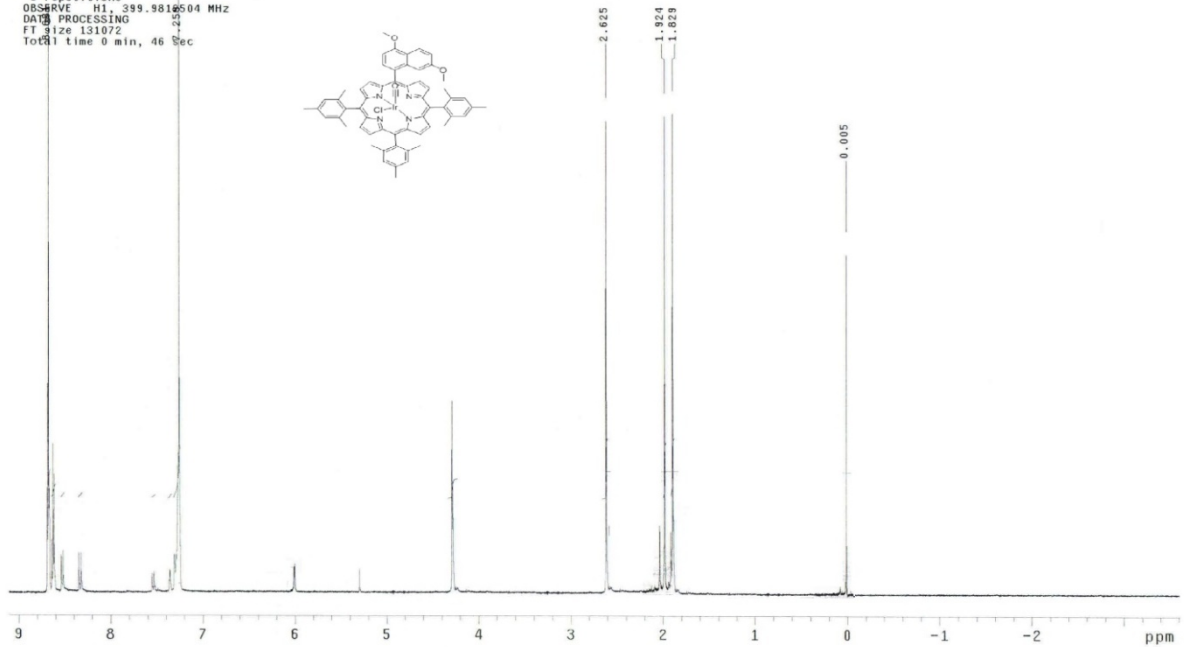
Solvent: CDC13
Ambient temperature
Mercury-400BB "SchilfSUN"
Relax. delay 1.000 sec
Pulse 48.6 degrees
Acq. time 3.630 sec
Width 10000.0 Hz
8 repetitions
OBSERVE H1, 399.9812504 MHz
DATA PROCESSING
F1 size 131072
Total time 0 min, 46 sec

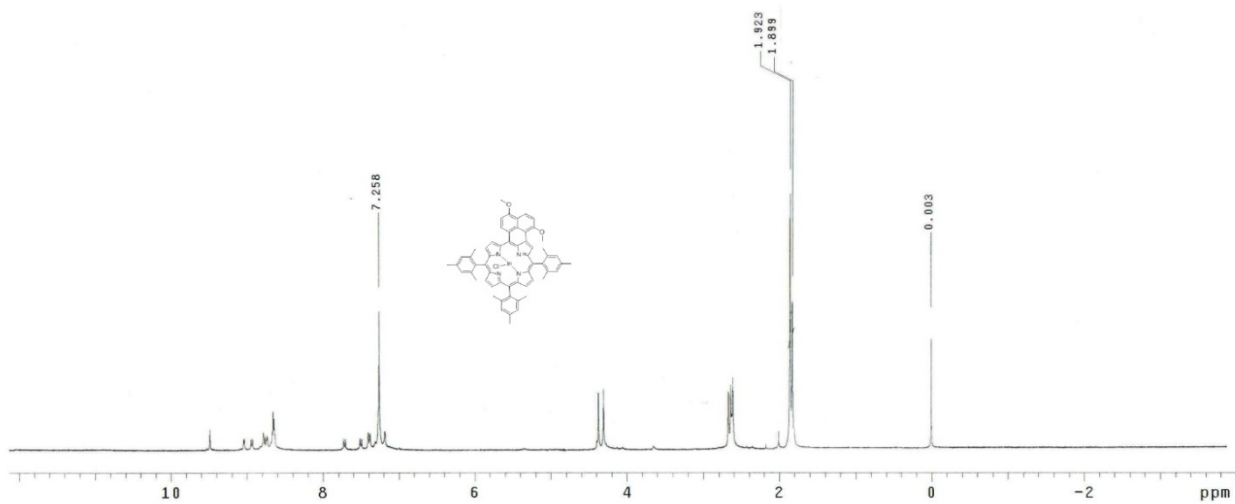
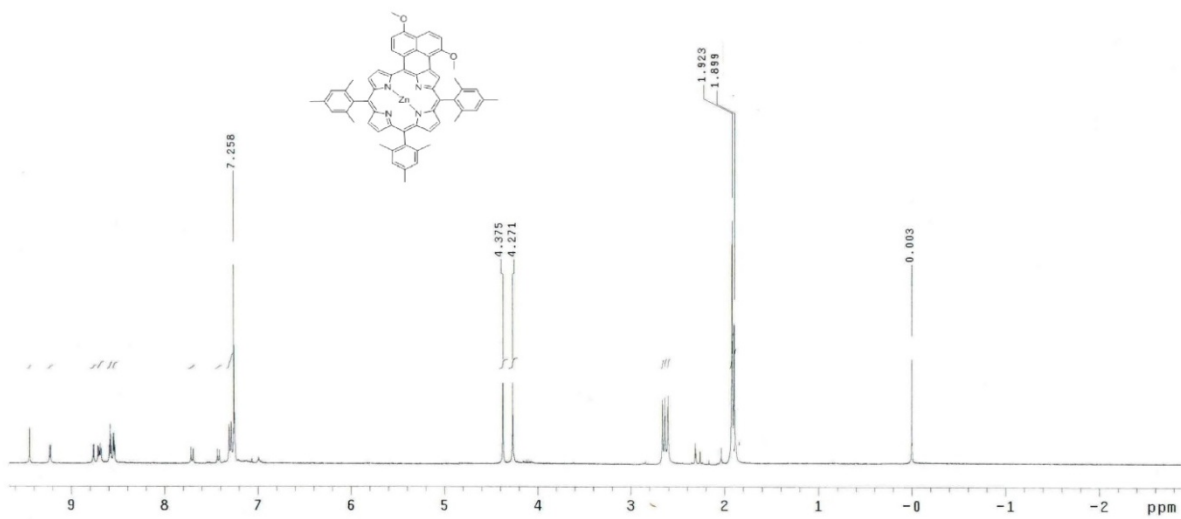


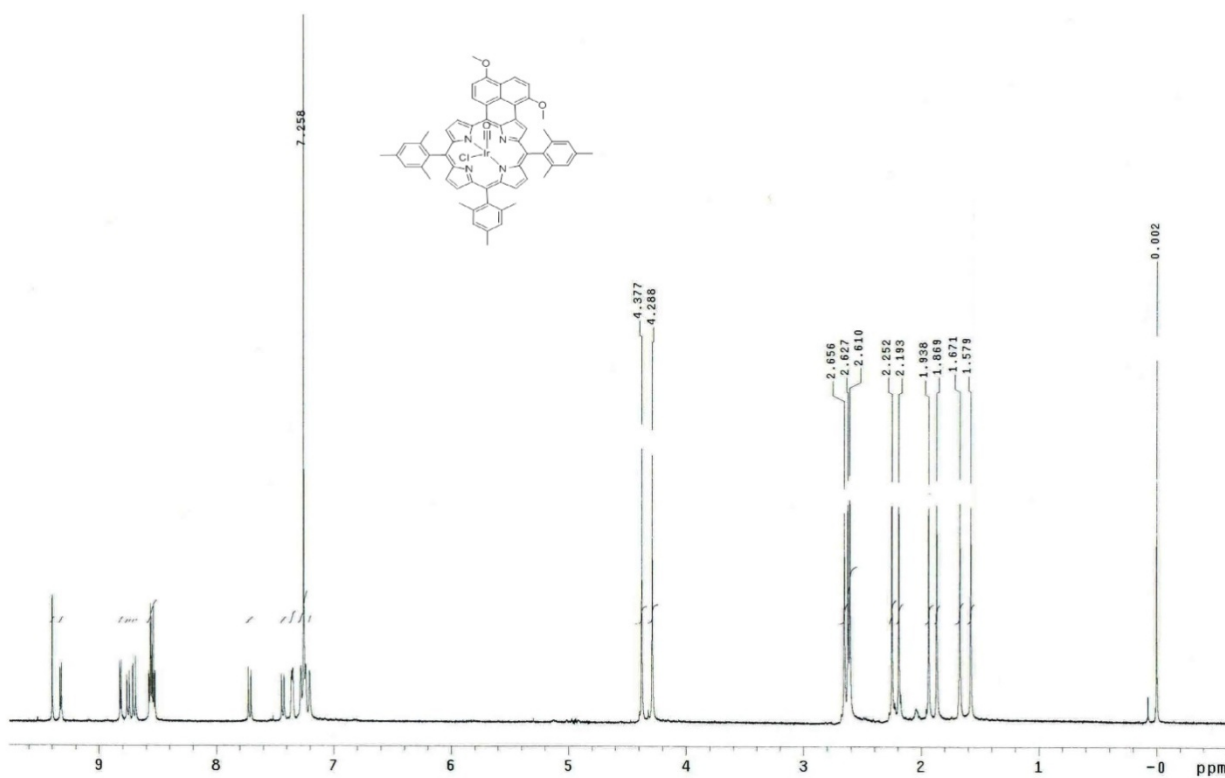
Solvent: CDCl3
Ambient temperature
Mercury-400BB "SchiffSUN"
Relax. delay 1.000 sec
Pulse 48.6 degrees
Acq. time 3.550 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1: 399.9812504 MHz
DATA PROCESSING
FT size 131072
Total time 0 min, 0 sec



Solvent: CDCl3
Ambient temperature
Mercury-400BB "SchiffSUN"
Relax. delay 1.000 sec
Pulse 48.6 degrees
Acq. time 3.630 sec
Width 10000.0 Hz
8 repetitions
OBSERVE H1: 399.9816504 MHz
DATA PROCESSING
FT size 131072
Total time 0 min, 46 sec







LITERATURE

- [1] Lewtak, J. P.; Gryko, D.; Bao, D.; Sebai, E.; Vakuliuk, O.; Scigaj, M.; Gryko, D. T. *Org. Biomol. Chem.* 2011, **9**, 8178.