



**Journal Name**

COMMUNICATION

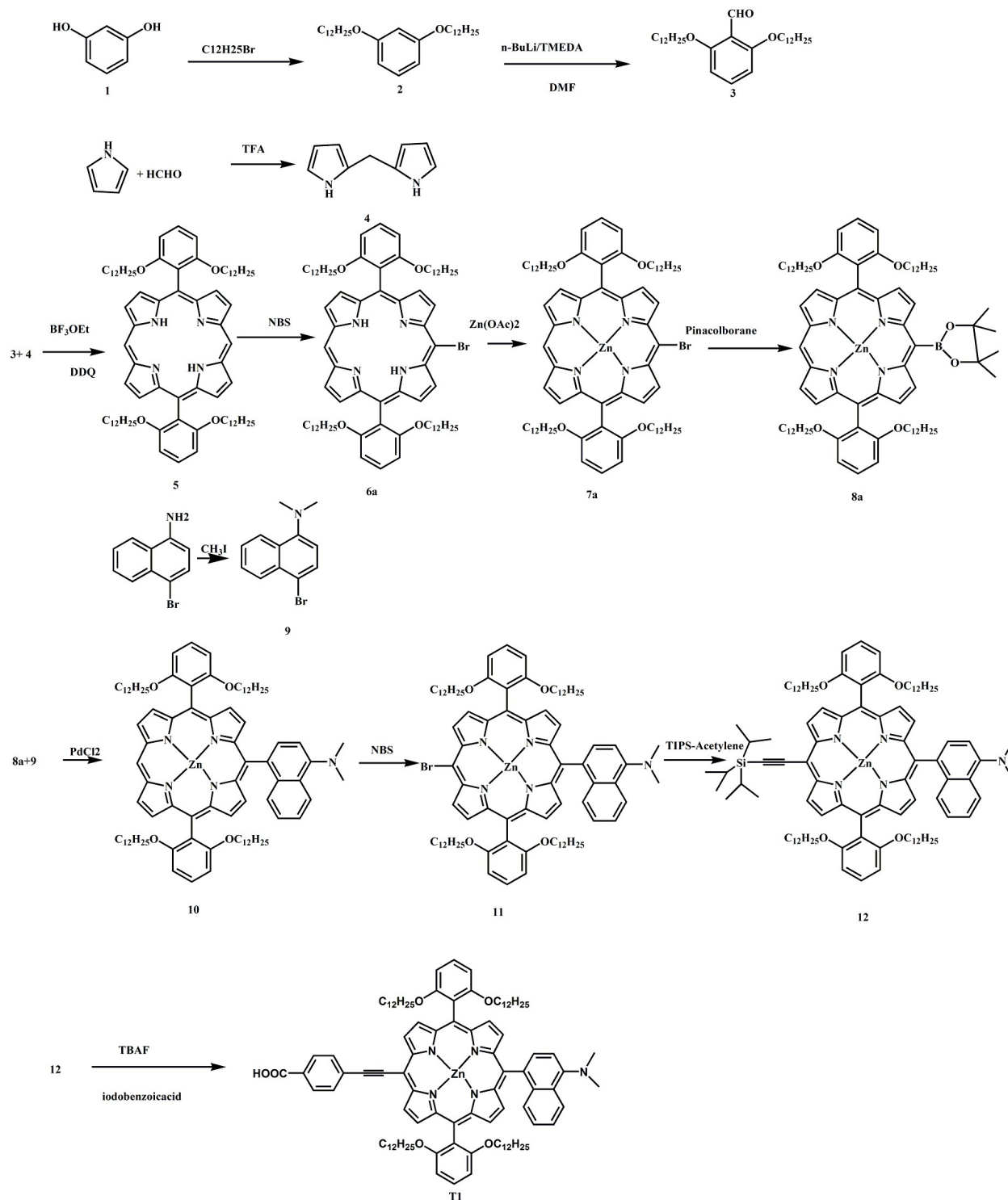
**Electronic Synthesis of push–pull porphyrin dyes with Supporting information**

**dimethylaminonaphthalene electron-donating groups and their application to dye-sensitized solar cell**

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The T1 and T2 porphyrins were achieved with a multi steps synthesis route (Scheme 1 and 2).

### Synthetic Route to T1



**schemeS1 T1 synthetic route**

**1,3-Di(n-dodecaoxy)benzene (2).** Resorcinol (10 g, 0.0908 mol) and n-bromohexane (60 mL) were successively added to a stirred suspension of potassium hydroxide (40 g, 0.713 mol) in 160 mL of dimethyl formamide (DMF). The reaction was allowed to stir overnight at room temperature and was then quenched with 150 mL of water. The product was extracted with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), dried over magnesium sulfate (Mg<sub>2</sub>SO<sub>4</sub>), and concentrated under reduced pressure. The product was purified using column chromatography (silica, n-hexane) to yield colorless oil (with solid after cooling) (92% yield).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.16 (1H, t), 6.50 (3H, d), 3.94 (4H, t), 1.78 (4H, m), 1.46 (4H, m), 1.28 (32H, m), 0.9 (6H, t)

**2,6-Didodecaoxybenzaldehyde (3).** 2,6-Didodecaoxybenzaldehyde was synthesized according to previously reported method [1]. To a stirred solution of 1,3-Di(n-dodecaoxy)benzene (10 mmol) or in dry THF (60 mL) at 0 °C, was added dropwise n-BuLi (8 mL, 1.5 M in hexanes). The mixture was stirred at rt for 3 h and then DMF (1.83 g, 25 mmol) was added. After 2 h, the mixture was poured into water and was extracted with ether (3 × 30 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent in vacuo, the product was purified by column chromatography with hexanes/EtOAc (9:1) as an eluent to afford yellowish white solid (75% yield).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 10.55 (1H, s), 7.39 (1H, t), 6.54 (2H, d), 4.04 (4H, t), 1.84 (4H, m), 1.46 (4H, m), 1.28 (32H, m), 0.9 (6H, t)

**2,2-dipyrromethane (4).** 1.2 mL formaldehyde 40% solution was added to 30 mL of pyrrole. 25 μL trifluoroacetic acid (TFA) was added and the reaction was stirred for 30 min at 50 °C. Crushed NaOH (1 g) was added, and stirring was continued for an additional 10 min. The pyrrole was removed in vacuo and the residue was purified by column chromatography (silica, 50:50 n-hexane/dichloromethane) to yield a white solid (32% yield).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 8.00 (2H, s), 6.78 (2H, m), 6.17 (2H, m), 6.06 (2H, m), 4.01 (2H, s)

**5,15-Bis(2,6-didodecaoxyphenyl)porphyrin (5)** To a degassed solution of dipyrromethane (1.46 g, 10 mmol) and compound 3 (4.75 g, 10 mmol) in DCM (1 L) was added BF<sub>3</sub>-OEt

(1mmol). After the solution was stirred at 25 °C under dinitrogen for 6 h, DDQ (2.3 g, 10mmol) was added and the mixture was stirred for an additional 1 h. Et<sub>3</sub>N (1 mL) was added to the mixture. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using DCM as eluent. The product was collected as a purple powder (yield 40%).

<sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): 10.15(2H,s), 9.27(4H,d), 8.98(4H,d), 7.70(2H,t), 7.04(4H,d) 3.84(8H,t) -3.00(2H,s)

**5-Bromo-10,20-bis(2,6-didodecaoxyphenyl)porphyrin(6a)** To a stirred solution of porphyrin 5 (2.4 g, 2mmol) in chloroform (150 mL) in a crushed ice bath was slowly added NBS (0.37g, 2.1mmol). The reaction was followed by TLC, after the reaction was completed, acetone (30 mL) was added to quench and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using DCM/hexanes = 1/3 as eluent to gain a purple powder (yield 60%).

<sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): 10.03(1H,s), 9.64(2H,d), 9.19(2H,d), 8.91(4H,d), 7.73(2H,t), 7.02(4H,d) 3.866(8H,t) -2.84(2H,s)

**[5-Bromo-10,20-bis(2,6-di-dodecaoxyphenyl)porphinato] zinc(II) (7a)** A solution of 6a porphyrin (1.5 g, 1.2mmol) and Zn(OAc)<sub>2</sub>•2 H<sub>2</sub>O (3.4 g, 12mmol) in a mixture of chloroform (50 mL) and MeOH (2mL) was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure the residue was purified by column chromatography (silica gel) using DCM as eluent to give the product (yield 98%).

<sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): 10.08(1H,s), 9.71(2H,d), 9.26(2H,d), 8.98(4H,d), 7.72(2H,t), 7.03(4H,d) 3.84(8H,t)

**[5,15-bis(2,6-di-dodecaoxyphenyl)10-(4,4,5,5-tetramethyl[1,2,3]dioxaborolan-2-yl)porphinato] zinc(II) (8a)**. 8a was synthesized according to previously reported method[2]. A 100 ml two neck flask was charged with 7a (420 mg, 0.3mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (7mg, 0.01mmol), triethylamine (560 μl), pinacolborane (365 μl, 2.4mmol) and dichloromethane (50ml) under inert atmosphere. The mixture was refluxed and stirred for 3 hours. The reaction was quenched with aqKCl, washed with water and dried over MgSO<sub>4</sub>. The solvent was evaporated

and product was purified by silica gel chromatography using 2:1 ratio of hexane:DCM as eluant. The first band was isolated corresponded to 5,15-Bis(2,6-didodecaoxyphenyl)porphyrinato zinc(II) while the second band contained the porphyrinboronate complex.

$^1\text{Hnmr}$ (300MHz,  $\text{CDCl}_3$ ): 10.17(1H,s), 9.86(2H,d), 9.31(2H,d), 9.06(2H,d), 9.01(2H,d), 7.72(2H,t), 7.03(4H,d) 3.80(8H,t ) 1.85(12H,s) FAB-MS: m/z calcd for  $\text{C}_{86}\text{H}_{127}\text{BN}_4\text{O}_6\text{Zn}$  1389.15; found 1389.1 [M]<sup>+</sup>.

**1-bromo4-(N,N-dimethylamino)naphthalene(9).** To a solution of 1-amino4-bromo naphthlene(1g, 4.5mmol) and  $\text{K}_2\text{CO}_3$ (1g) in dry dmf, methyl iodide (3ml, 45mmol) was added at 60 °C. The reaction mixture was stirred for 24 h. The mixture was extracted with DCM and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduce pressure the residue was purified by column chromatography (silica gel) using hexane/ethyl acetate 1:3 as eluent to give the red oil.

$^1\text{Hnmr}$ (300MHz,  $\text{CDCl}_3$ ): 8.29(2H,m), 7.69(1H,d), 7.60(2H,m), 6.95(1H,d), 2.90(6H,s)

**5,15-bis(2,6-di-dodecaoxyphenyl)10-(4-dimemethylaminonaphth-1-yl)porphinato] zinc(II) (10)** A 100 ml two neck flask was charged with 8a(380mg, 0.27mmol),  $\text{Pd}(\text{PPh}_3)_4$ (16mg, 0.013mmol) , 1-bromo4-(N,N-dimethylamino)naphthalene (100mg, 0.4mmol) and THF (50ml) under inert atmosphere. The solution was degassed and 3ml of 2M  $\text{K}_2\text{CO}_3$  aquasolution was added to the mixture. The mixture was refluxed and stirred for 8 hours. The reaction was quenched with water, extracted with DCM and dried over  $\text{MgSO}_4$ . The solvent was evaporated and product was purified by silica gel chromatography using 3:1 ratio of hexane:DCM as eluant. The first band was isolated corresponded to 5,15-Bis(2,6-didodecaoxyphenyl)porphyrinato zinc(II) while the second band contained the product.

$^1\text{Hnmr}$ (300MHz,  $\text{CDCl}_3$ ): 10.10(1H,s), 9.26(2H,d), 9.02(2H,d), 8.80(2H,d), 8.63(2H,d), 8.51(1H,d), 8.18(1H,d), 7.70(2H,t), 7.45(2H,m), 7.16(1H,d), 6.95(5H,d) 3.83(8H,t ) , 3.20(6H,s) FAB-MS: m/z calcd for  $\text{C}_{92}\text{H}_{127}\text{N}_5\text{O}_4\text{Zn}$  1432.4; found 1432.1 [M]<sup>+</sup>.

**5-bromo 10,15 -bis(2,6-di-dodecaoxyphenyl)20-(4-dimemethylaminonaphth-1-yl)porphinato] zinc(II) (11)** To a stirred solution of porphyrin 10 (300mg, 0.2mmol) in DCM

(150 mL) was slowly added NBS (45mg, 0.24mmol) of 2 h at 0 °C. After the reaction was quenched with acetone (30 mL), the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using DCM:hexanes = 1:3 as eluent

<sup>1</sup>Hnmr(300MHz, CDCl<sub>3</sub>): 9.69(2H,d), 8.93(2H,d), 8.73(2H,d), 8.57(2H,d), 8.51(1H,d),8.12(1H,d),7.70(2H,t), 7.45(2H,m), 7.17(1H,d), 6.98(5H,d) 3.84(8H,t ) 3.20(6H,s)

**[5,15-Bis(2,6-di-dodecaoxyphenyl)-10-(4-dimethylaminonaphth-1-yl)-20-(triisopropylsilyl)ethynyl-porphinato] zinc(II) (12)** A mixture of the zinc complex of 11 (270mg, 0.18mmol), triisopropylacetylene (890μl, 4mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (30mg, 0.03mmol), CuI (6mg, 0.03mmol), PPh<sub>3</sub>(40mg, 0.15mmol), THF(30 mL) and NEt<sub>3</sub> (5 mL) was gently refluxed for 4 h under dinitrogen. The solvent was removed under vacuum. The residue was purified by column chromatography(silica gel) using DCM:hexanes = 1:4 to as eluent to give the product (0.82 g, 83%) as a purple solid.

<sup>1</sup>Hnmr(300MHz, CDCl<sub>3</sub>): 9.70(2H,d), 8.94(2H,d), 8.57(2H,d), 8.55(3H,m), 8.34(1H,d),7.67(2H,t), 7.49(2H,m), 7.15(1H,m), 6.96(5H,m) 3.83(8H,t ), 3.33(6H,s), 1.22(21H,m) FABMS: m/z calcd for C<sub>103</sub>H<sub>147</sub>N<sub>5</sub>O<sub>4</sub>SiZn 1612.7; found 1612.1 [M]<sup>+</sup>.

**[5,15-Bis(2,6-di-dodecaoxyphenyl)-10-(4-dimethylaminonaphth-1-yl)-20-(4-carboxyphenyl ethynyl)-porphinato] zinc(II) (T1)** T1 was synthesized according to previously reported method[3]. To a solution of porphyrin 12 (100 mg, 0.06mmol) in dry THF (10 mL) was added TBAF (1 mL, 1M in THF). The solution was stirred at 25°C for 30 min under dinitrogen. The mixture was quenched with water and then extracted with DCM. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The residue and 4-iodobenzoic acid (25 mg, 0.1mmol) were dissolved in a mixture of dry THF (20 mL) and NEt<sub>3</sub> (3.5 mL) and the solution was degassed with dinitrogen for 10 min; Pd<sub>2</sub>(dba)<sub>3</sub> (20 mg, 0.022mmol) and AsPh<sub>3</sub> (46mg, 0.15 mmol) were added to the mixture. The solution was refluxed for 4 h under dinitrogen. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using DCM:CH<sub>3</sub>OH = 50:1 as eluent to give the green solid.

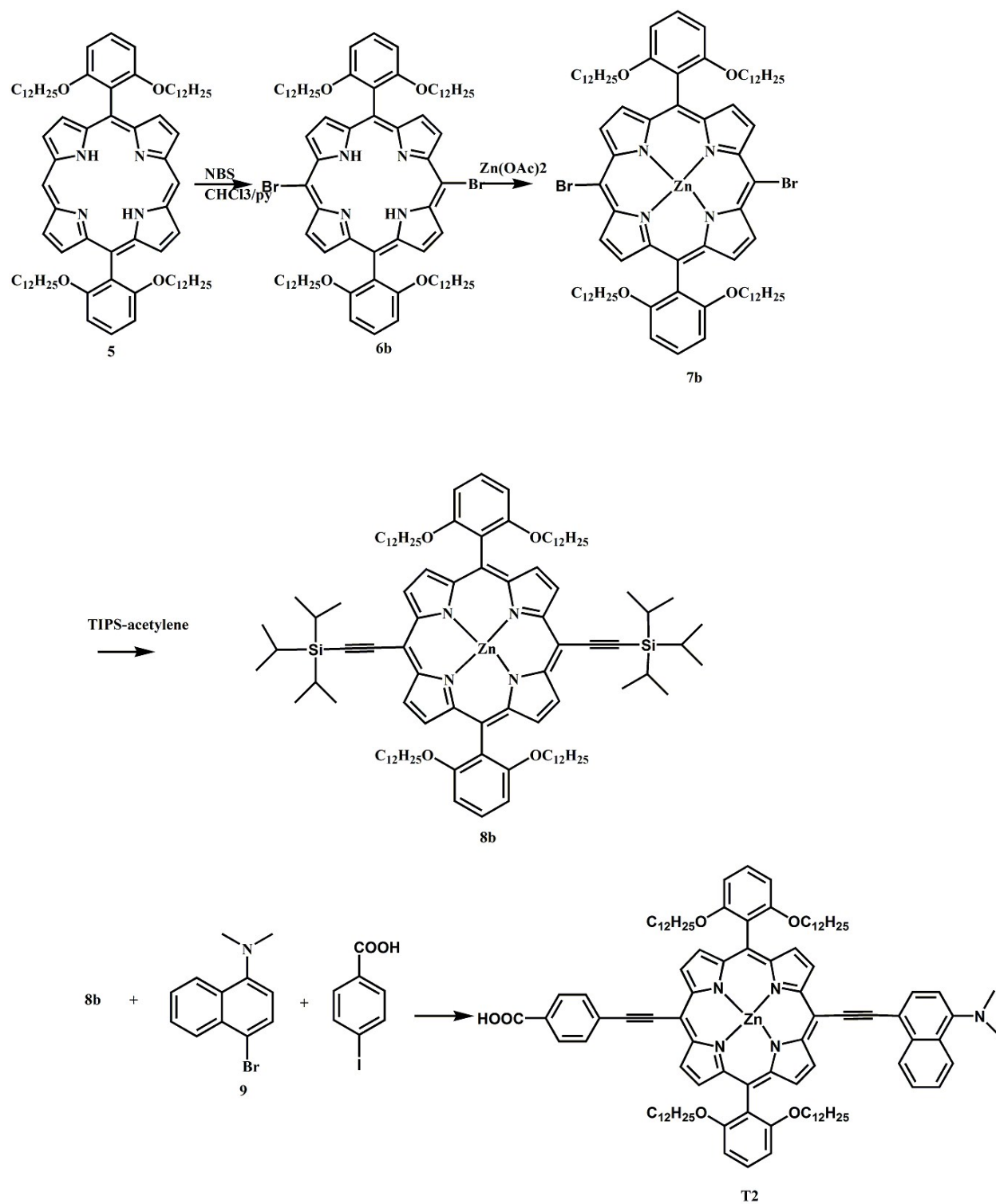
<sup>1</sup>Hnmr(300MHz, CDCl<sub>3</sub>): 9.73(2H,d), 8.94(2H,d), 8.68(2H,d), 8.53(2H,d), 8.49(1H,d),8.25(2H,m), 8.12(3H,m), 7.71(2H,t), 7.66(2H,m), 7.15(1H,m), 6.97(5H,m) 3.83(8H,t

),3.19(6H,s)  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ ) 159.9,151.8, 151.1, 150.9, 150.6, 150.3, 138.0,134.8, 132.2, 131.9, 131.2, 131.1, 130.3,130.0, 129.6, 127.8, 125.4, 123.8, 121.0, 119.6, 114.6, 112.2, 105.2, 97.5, 77.9, 68.5, 45.5, 31.8, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 25.4, 22.6, 14.0.FAB-MS: m/z calcd for  $\text{C}_{10}\text{H}_{13}\text{N}_5\text{O}_6\text{Zn}$  1578.5; found 1580.1  $[\text{M}]^+$ .

FT-IR:( $\nu\text{-cm}^{-1}$ ):

3548,3435,3060,2920,2851,2558,2191,2050,1685,1589,1503,1455,1382,1338,1285,1203,1173,1095,1018,997,942,920,881,855,792,738,692,666.

## Synthetic Route to T2



schemeS2 T2 synthetic route



**5,15-diBromo-10,20-bis(2,6-didodecaoxyphenyl)porphyrin (6b)** To a stirred solution of porphyrin5 (1.2 g, 1mmol) and pyridine(50 $\mu$ l) in chloroform (150 mL) in a crushed ice bath was slowly added NBS (445mg, 2.5mmol). The reaction was followed by TLC, after the reaction was completed, acetone (30 mL)was added to quench and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using DCM/hexanes = 1/3 as eluent to gain a purple powder (yield 80%).

<sup>1</sup>HNMR (300MHz, CDCl<sub>3</sub>): 9.64(2H,d), 9.19(2H,d), 8.91(4H,d), 7.73(2H,t),7.02(4H,d) 3.866(8H,t) -2.84(2H,s)

**[5,15-diBromo-10,20-bis(2,6-di-dodecaoxyphenyl)porphinato] zinc(II) (7b)** A solution of 6b porphyrin (1.36 g, 1 mmol) and Zn(OAc)<sub>2</sub>·2 H<sub>2</sub>O (2.9 g, 10mmol) in a mixture of chloroform (50 mL) and MeOH (2mL) was stirred at 60 °C for 2 h. The solvent was removed under reduce pressure the residue was purified by column chromatography (silica gel) using DCM as eluent to give the product (yield 98%).

<sup>1</sup>HNMR (300MHz, CDCl<sub>3</sub>): 10.08(1H,s), 9.71(2H,d), 9.26(2H,d), 8.98(4H,d), 7.72(2H,t),7.03(4H,d) 3.84(8H,t)

**[5,15-Bis(2,6-di-dodecaoxyphenyl)- 10,20-bis-(triisopropylsilyl)ethynyl-porphinato] zinc(II) (8b)**A mixture of the zinc complex of 7b (0.91 g, 0.81 mmol), triisopropylacetylene (370 $\mu$ l, 2.04 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.11 g, 0.16 mmol), CuI (0.047 g, 0.24 mmol), THF(30 mL) and NEt<sub>3</sub> (5 ml) was gently refluxed for 4 h under dinitrogen. The solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) using DCM:hexanes = 1:4 to as eluent to give the product asa green solid.

**[5,15-Bis(2,6-di-dodecaoxyphenyl)- 10-(4-dimemethylaminonaphth-1-yl- ethynyl)-20-(4-carboxyphenyl ethynyl)-porphinato] zinc(II) (T2)**

To a solution of porphyrin8b (95 mg, 0.06 mmol) in dry THF (10 mL) was added TBAF (1 ml, 1M in THF). The solution was stirred at 25 °C for 30 min under dinitrogen. The mixture was quenched with water and then extracted with DCM. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The residue with 4-iodobenzoic acid (25 mg, 0.1 mmol) and 1-bromo4-(N,N-dimethylamino)naphthalene (25mg, 0.1mmol)were

dissolved in a mixture of dry THF (18 mL) and NEt<sub>3</sub> (3.5 mL) and the solution was degassed with dinitrogen for 10 min; Pd<sub>2</sub>(dba)<sub>3</sub> (20 mg, 0.022 mmol) and AsPh<sub>3</sub> (46 mg, 0.15 mmol) were added to the mixture. The solution was refluxed for 4 h under dinitrogen. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using DCM: CH<sub>3</sub>OH = 50:1 as eluent to give the green solid.

<sup>1</sup>Hnmr(300MHz, CDCl<sub>3</sub>): 9.73(2H,d), 8.95(2H,d), 8.68(2H,d), 8.54(2H,d), 8.48(1H,d), 8.25(2H,m), 8.12(3H,m), 7.78(2H,t), 7.72(2H,m), 7.24(1H,m), 7.15 (5H,m) 3.84(8H,t), 3.20(6H,s)

FT-IR:

3518,3463,3060,2955,2919,2849,2550,2331,2190,2051,1827,1685,1598,1500,1455,1388,1310,1254,1206,1186,1159,1094,1062,1018,997,942,876,852,791,767,751,709,682.

### **Device fabrication and Characterizations:**

#### **Preparation of nanoporous TiO<sub>2</sub> paste**

Two kinds of TiO<sub>2</sub> paste containing nanocrystalline TiO<sub>2</sub> (20 nm, paste A) and submicroparticle TiO<sub>2</sub> (350 nm, paste B) were prepared by a previously reported procedure [4, 5]. 3 g of TiO<sub>2</sub> nanopowder was added to mortar and grinded with gradual addition of 0.5 ml of acetic acid, 2.5 ml of deionized water and 15 ml of ethanol. The TiO<sub>2</sub> dispersion was transferred with 50 ml of ethanol to a round bottom flask and homogenized by an ultrasonic bath for 30 min. 10 g of terpineol was added to the dispersion and sonication was resumed for another 30 min. Alternating stirring and sonication were used three consecutive times after adding 1.5 g of ethyl cellulose (10% solution in ethanol) to the TiO<sub>2</sub> dispersion. Finally ethanol was removed by a rotary evaporator. The resulting screen-printing paste corresponds to 21 wt.% TiO<sub>2</sub>, 10 wt.% ethyl cellulose and 69 wt.% terpineol (paste A).

Paste B which was used in the light-scattering layers was prepared with the same method using 350 nm TiO<sub>2</sub> nanoparticles.

#### **Fabrication of porous-TiO<sub>2</sub> electrodes**

The FTO glass was first cleaned with detergent solution, distilled water and methanol using an ultrasonic bath (10 min for each solution), and then rinsed with methanol. After treatment in 40

mM aqueous  $\text{TiCl}_4$  solution at 70 °C for 30 min, the FTO glass was again washed with water and methanol. Paste A was screen printed (manual screen printer, 90T, Estal Mono, Schweiz. Seidengazefabrik, AG, Thal) on the FTO glass and kept in a clean box for 10 min to let the paste relax and reduce the surface irregularity. After that, FTO glasses were dried for 10 min at 125 °C. This screen printing procedure with paste A (coating, storing and drying) was repeated to get an appropriate thickness of 10–12  $\mu\text{m}$  for the working electrode. After drying the (paste A) films at 125 °C, one layer of paste B was deposited by the screen-printing method, resulting in a light-scattering  $\text{TiO}_2$  film containing 350 nm anatase  $\text{TiO}_2$  particles. The electrodes coated with the  $\text{TiO}_2$  pastes were gradually heated under airflow at 325 °C for 5 min, at 375 °C for 5 min, and at 450 °C for 15 min, and finally, at 500 °C for 15 min.

The  $\text{TiO}_2$  films were once again treated with 40 mM  $\text{TiCl}_4$  solution, as previously described, then rinsed with water and methanol and heated at 450 °C for 15 min and 500 °C for 15 min. After cooling to 80 °C, the  $\text{TiO}_2$  electrodes were immersed into 0.1 mM dye solution with 35 mM 4-tert-Butylpyridine as additive in a mixture of ethanol and THF (volume ratio, 4:1) and kept at room temperature for 2 h to uptake the dye.

### **Preparation of counter Pt-electrodes and DSSC assemblage**

FTO glasses were washed with the same method as used for the working electrode. 0.05 M  $\text{H}_2\text{PtCl}_6$  solution was spin-coated on the FTO glass substrate at 2000 rpm for 15 s. The formed film was annealed at 450 °C for 1 hour in atmosphere.

Clamps assembled the dye-adsorbed  $\text{TiO}_2$  electrode and counter electrode into a sandwich-type cell. Finally a drop of electrolyte solution (0.10 M lithium iodide, 0.60 M butylmethylimidazolium iodide, 0.03 M  $\text{I}_2$ , and 0.05 M 4-tert-butylpyridine in acetonitrile/valeronitrile 75:25) was introduced into the clamped electrodes.

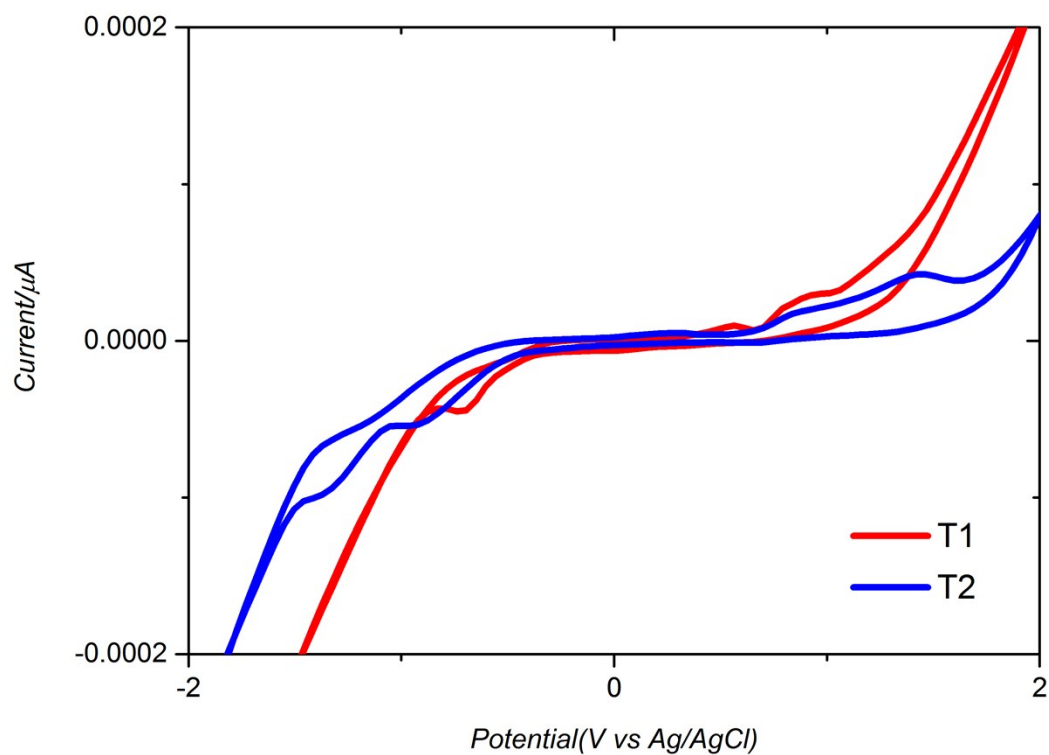


Figure S 1. Cyclic voltammograms of T12 and T2 in THF containing TBAClO<sub>4</sub> (0.1 M)

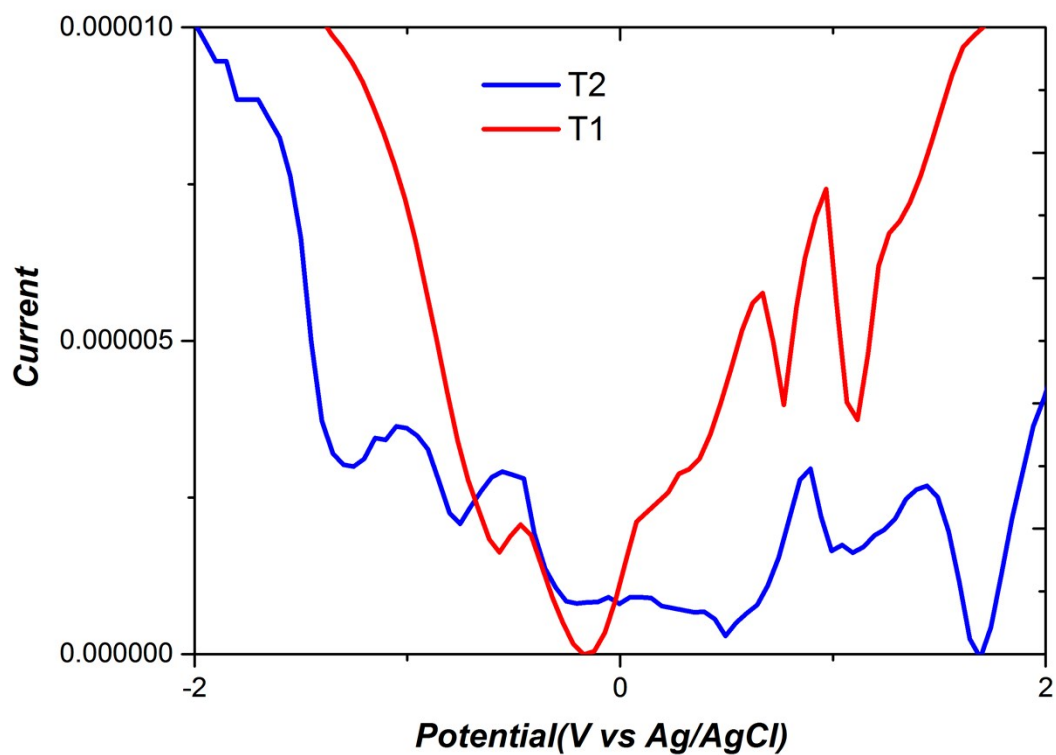
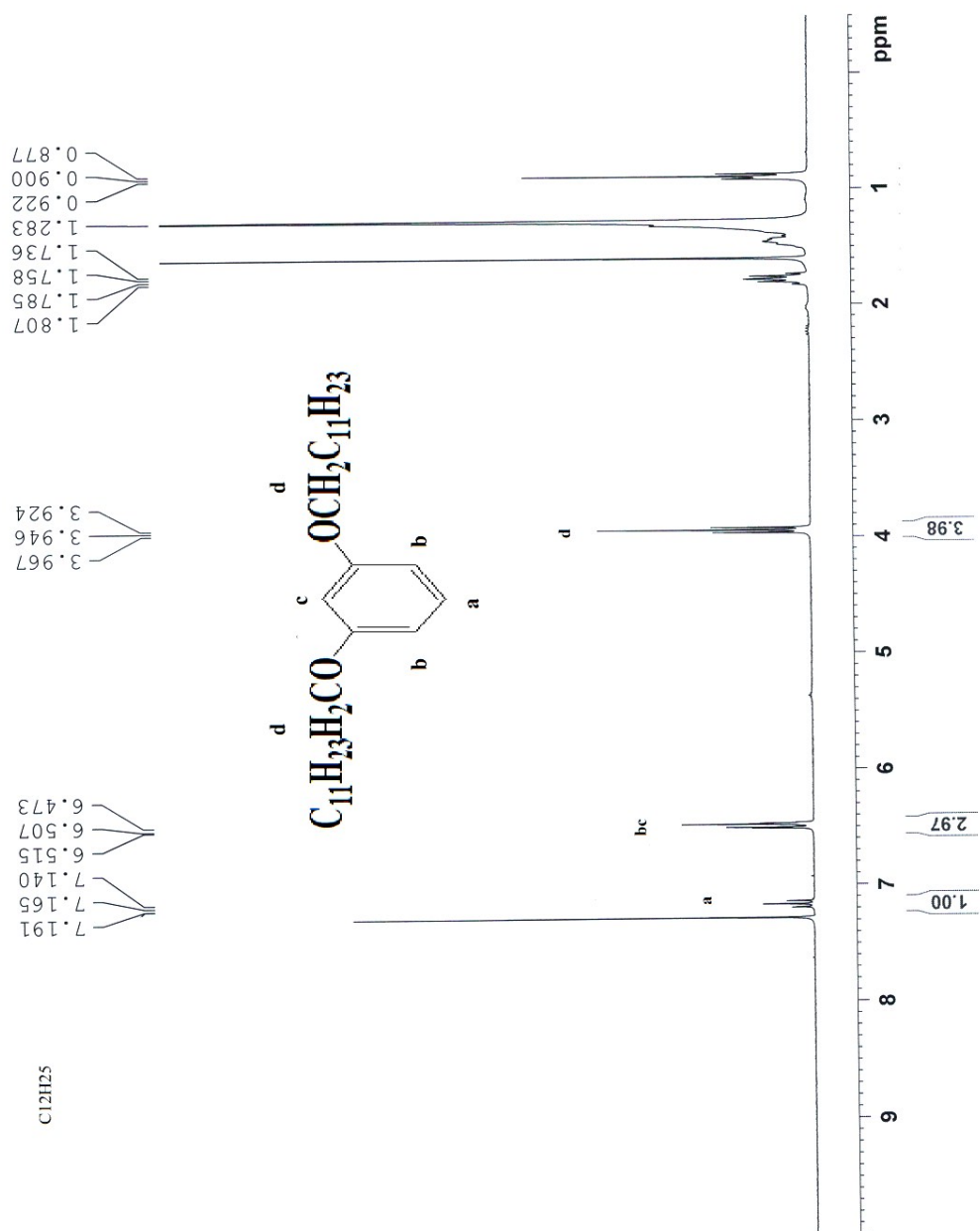
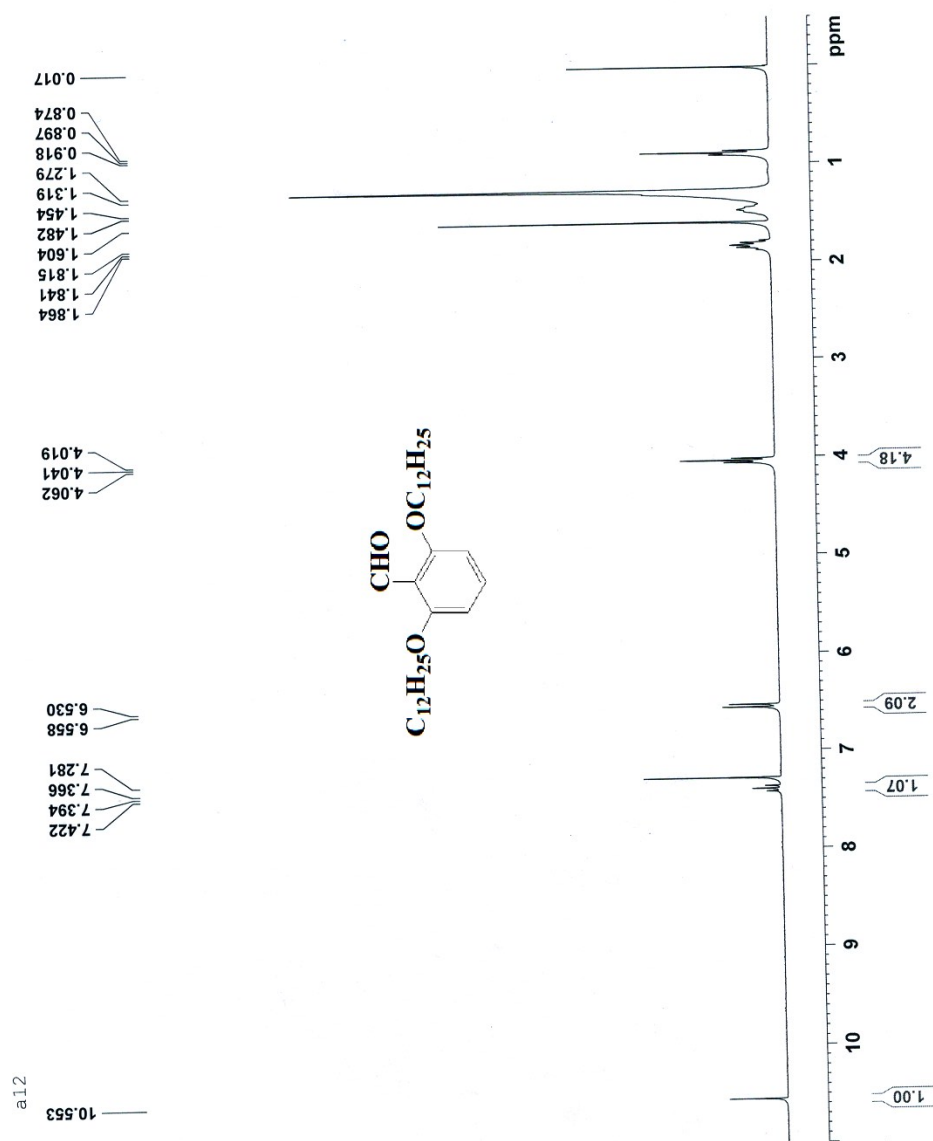
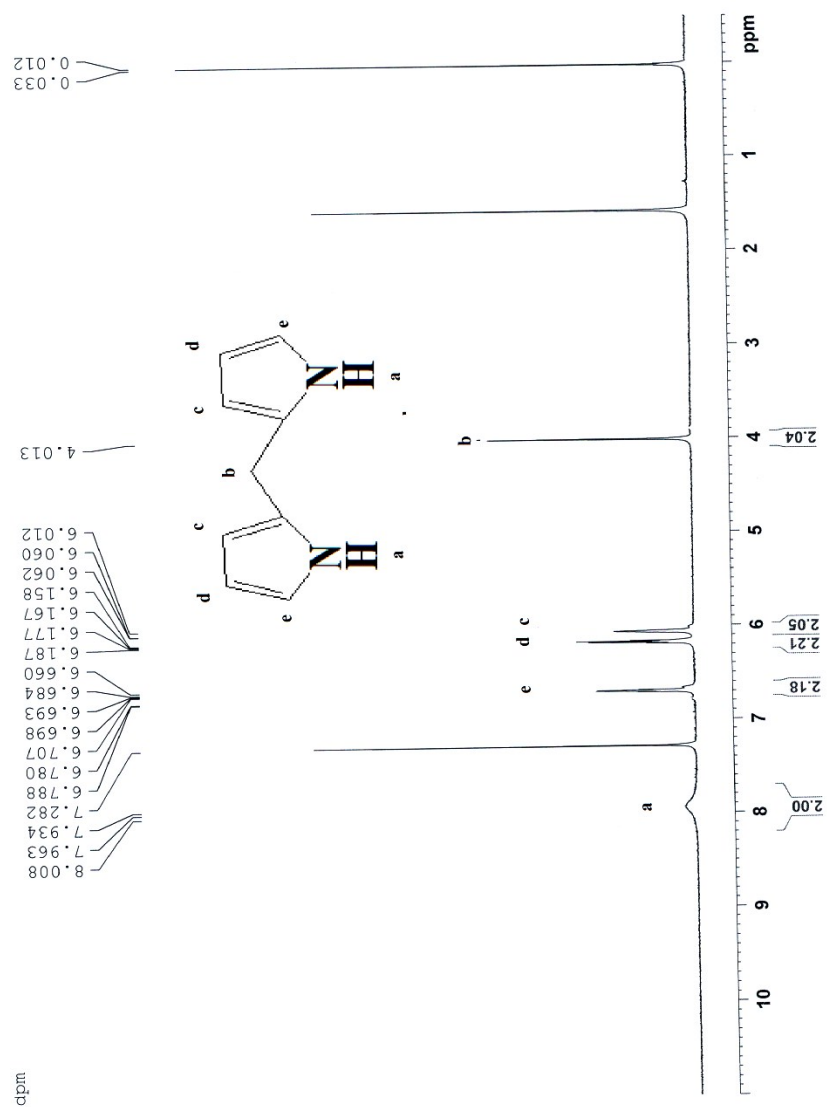


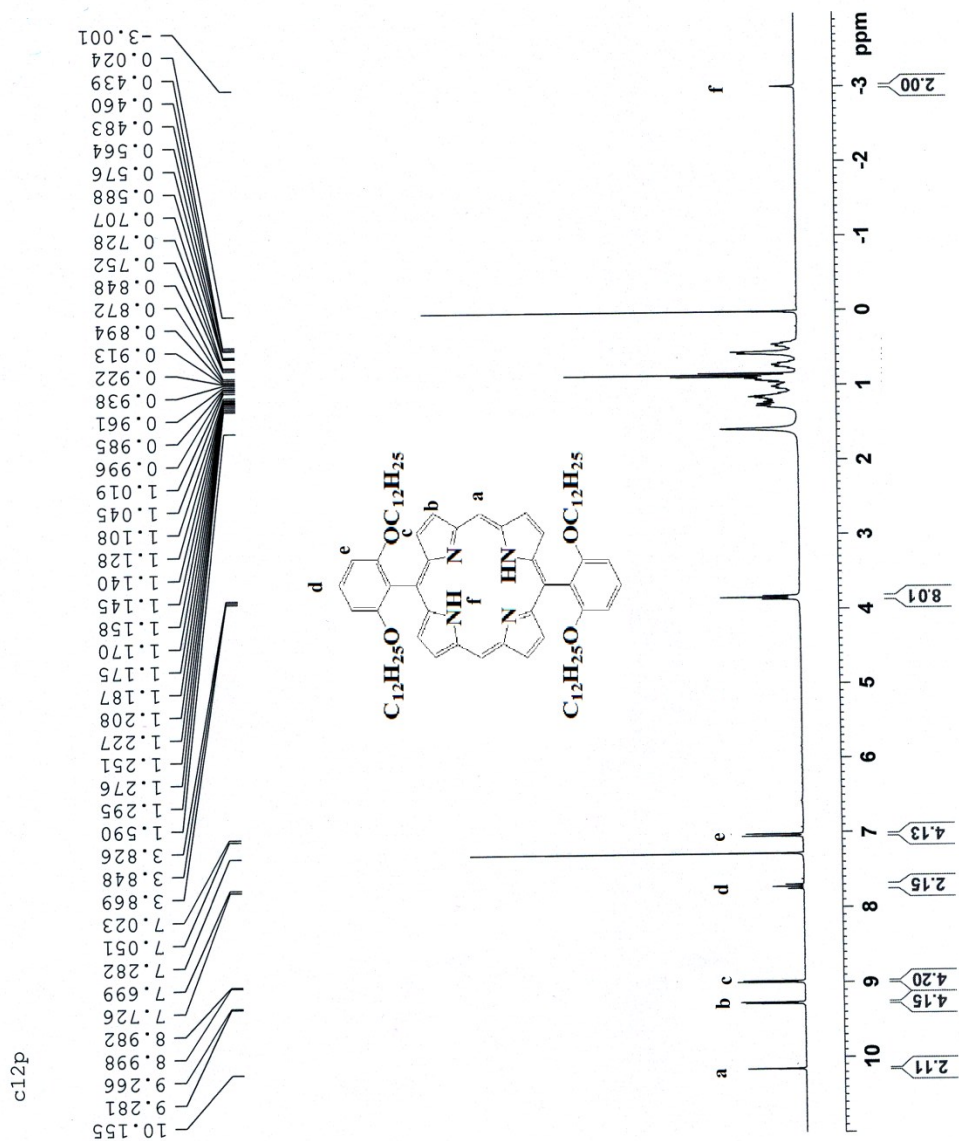
Figure S 2. Differential Puls voltammograms of T12 and T2 in THF containing TBAClO<sub>4</sub> (0.1 M)

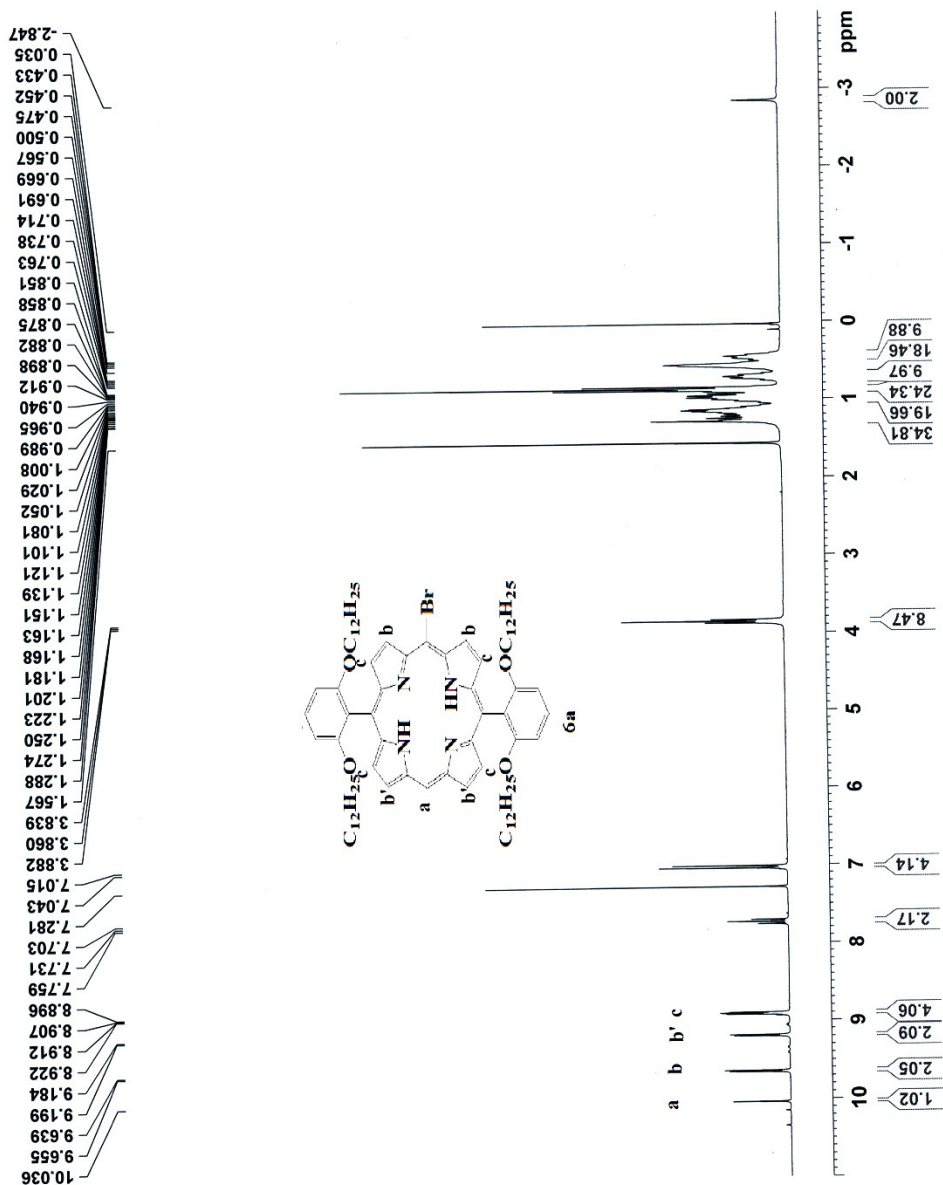


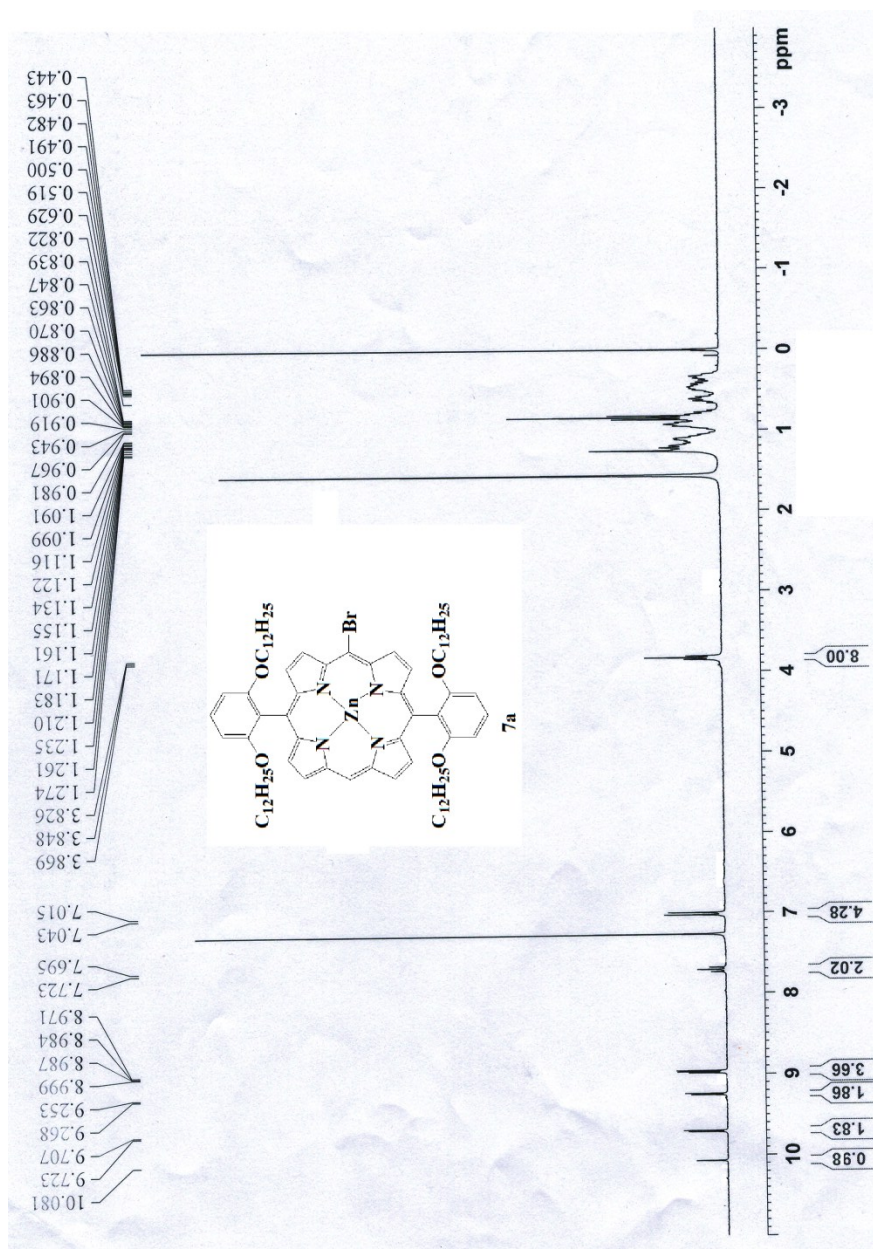


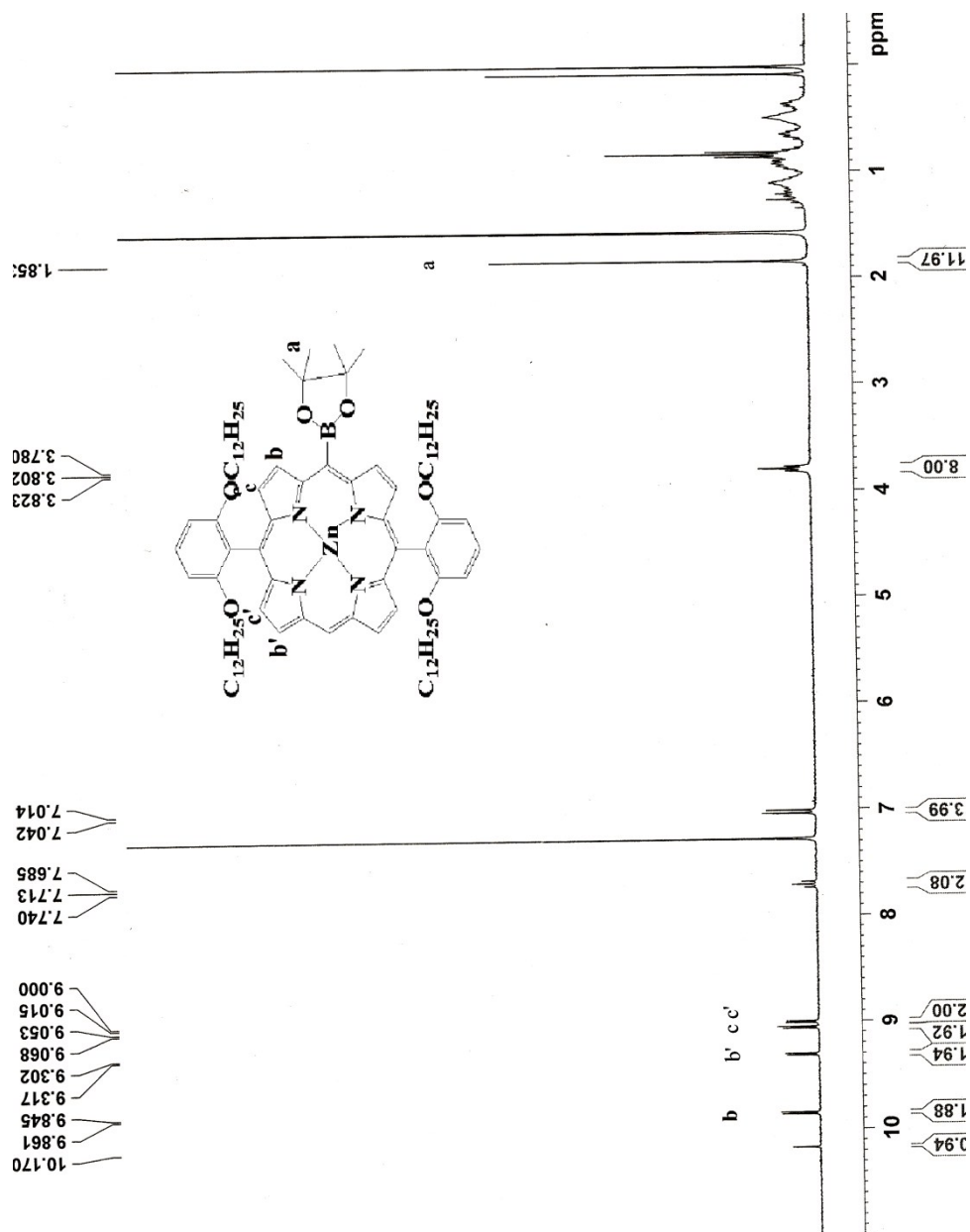


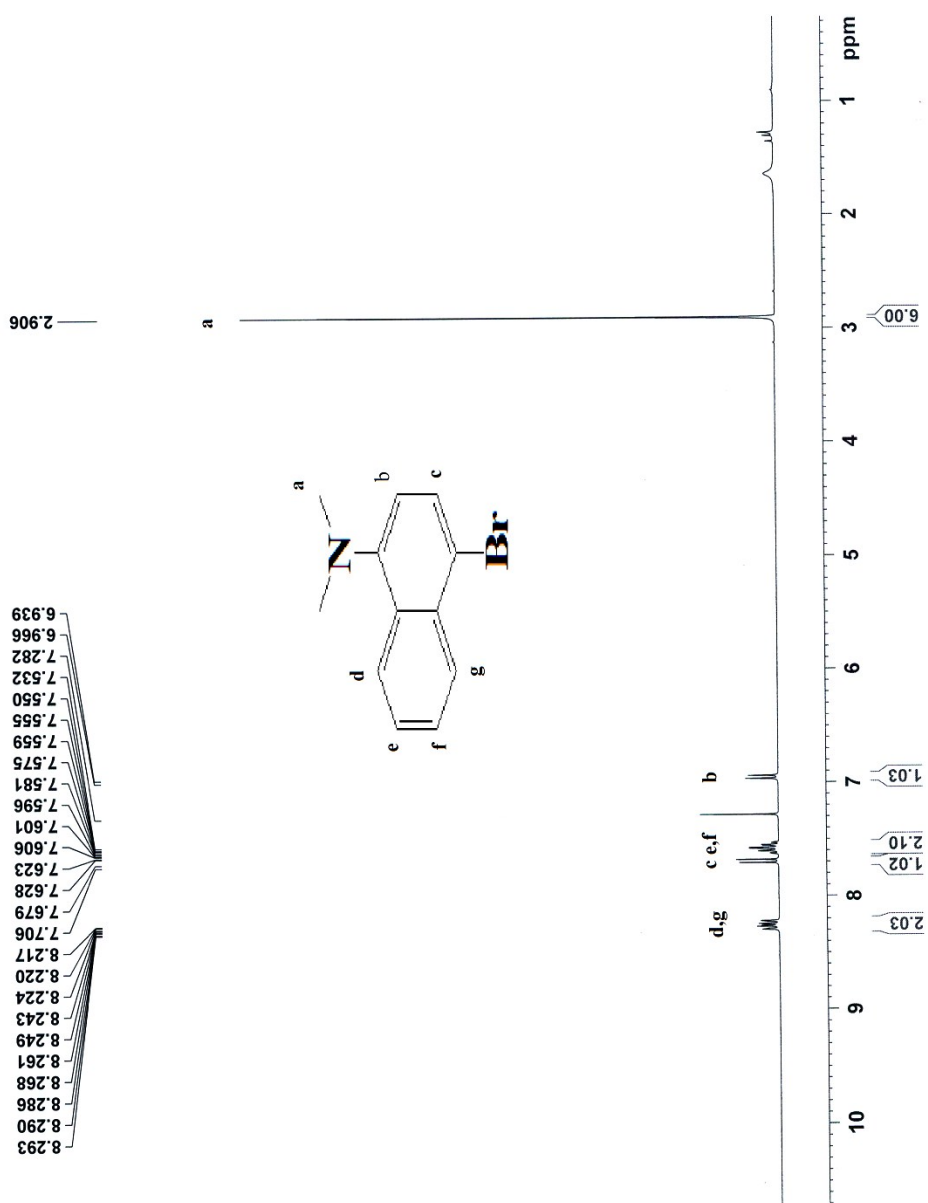


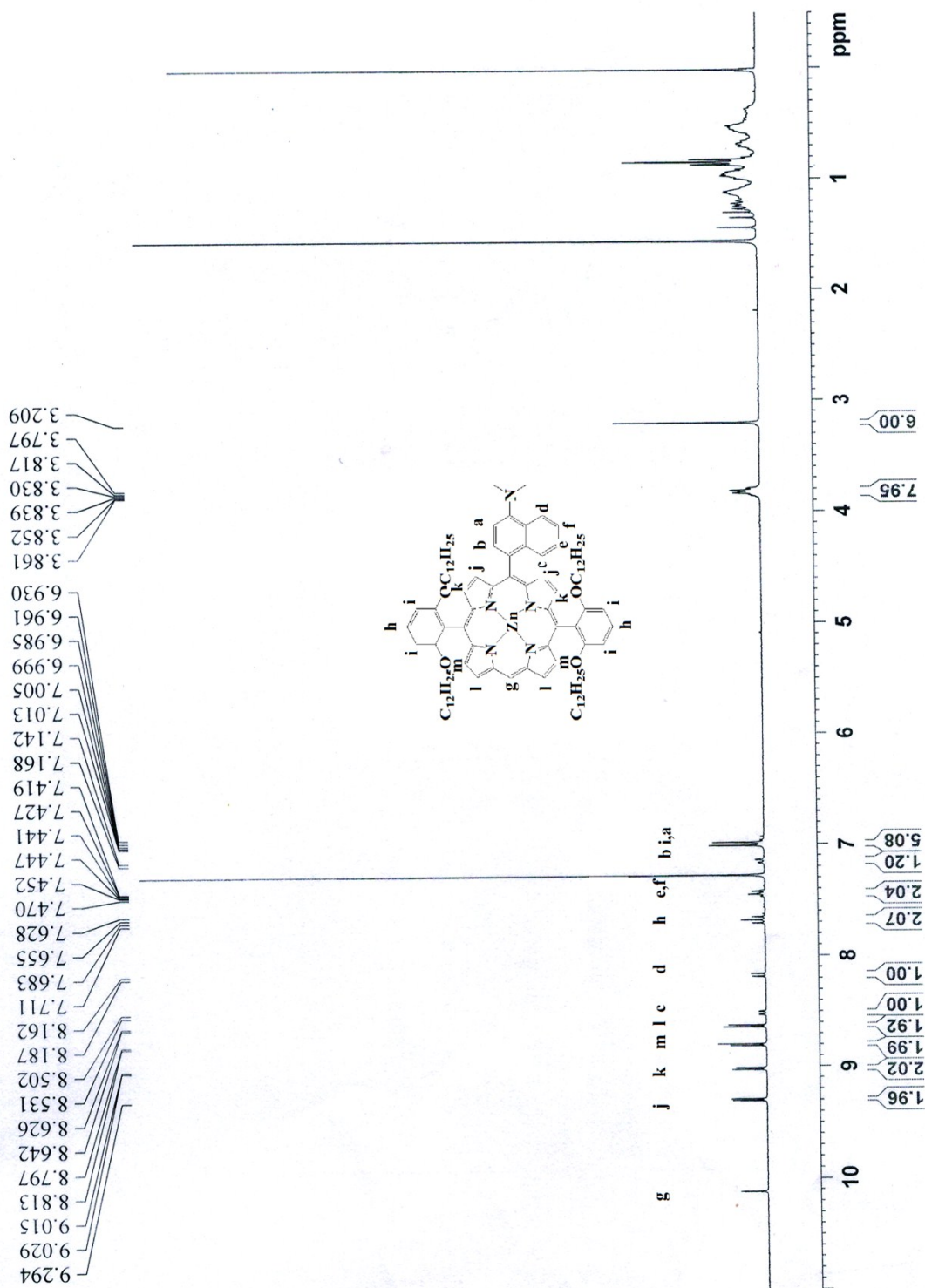


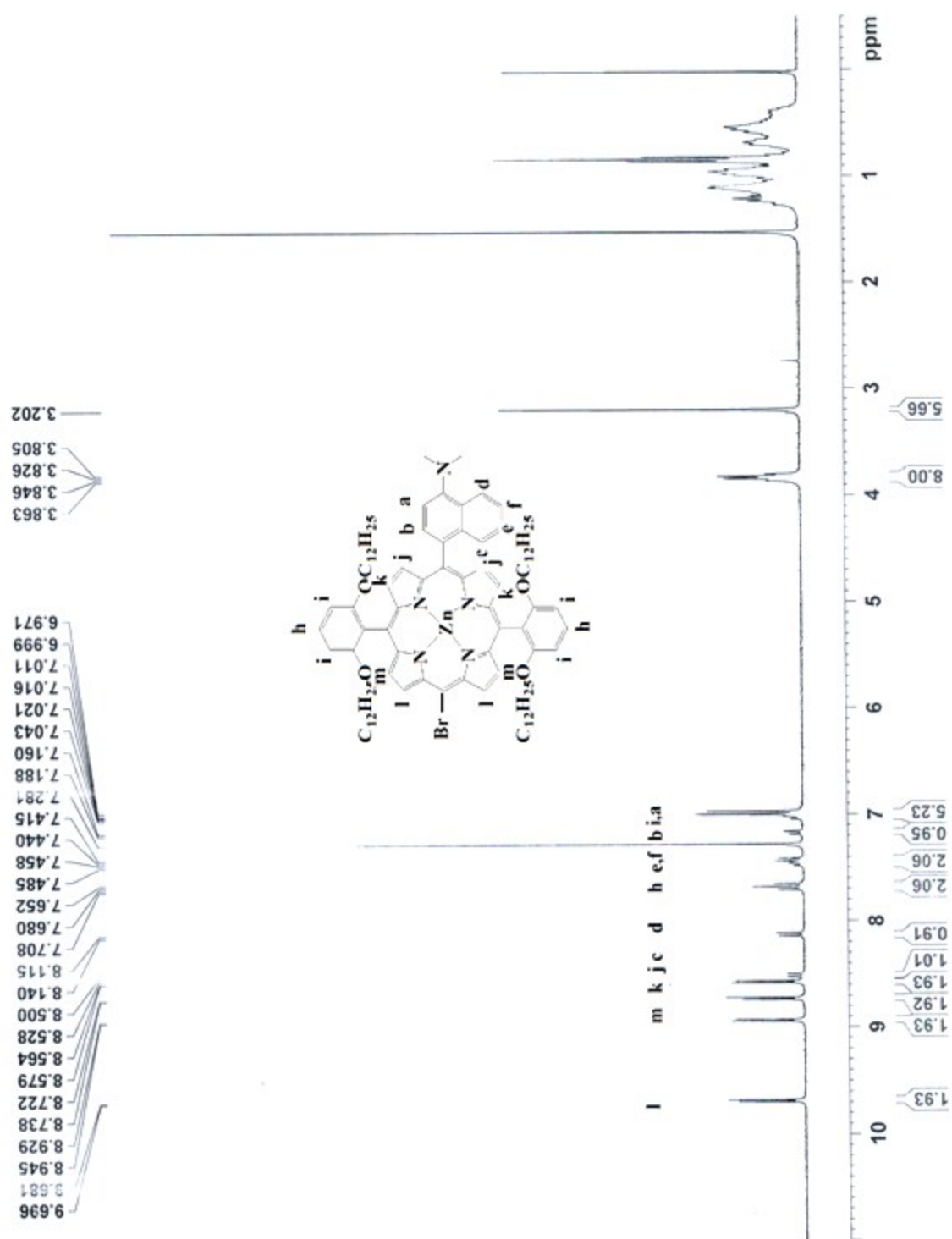


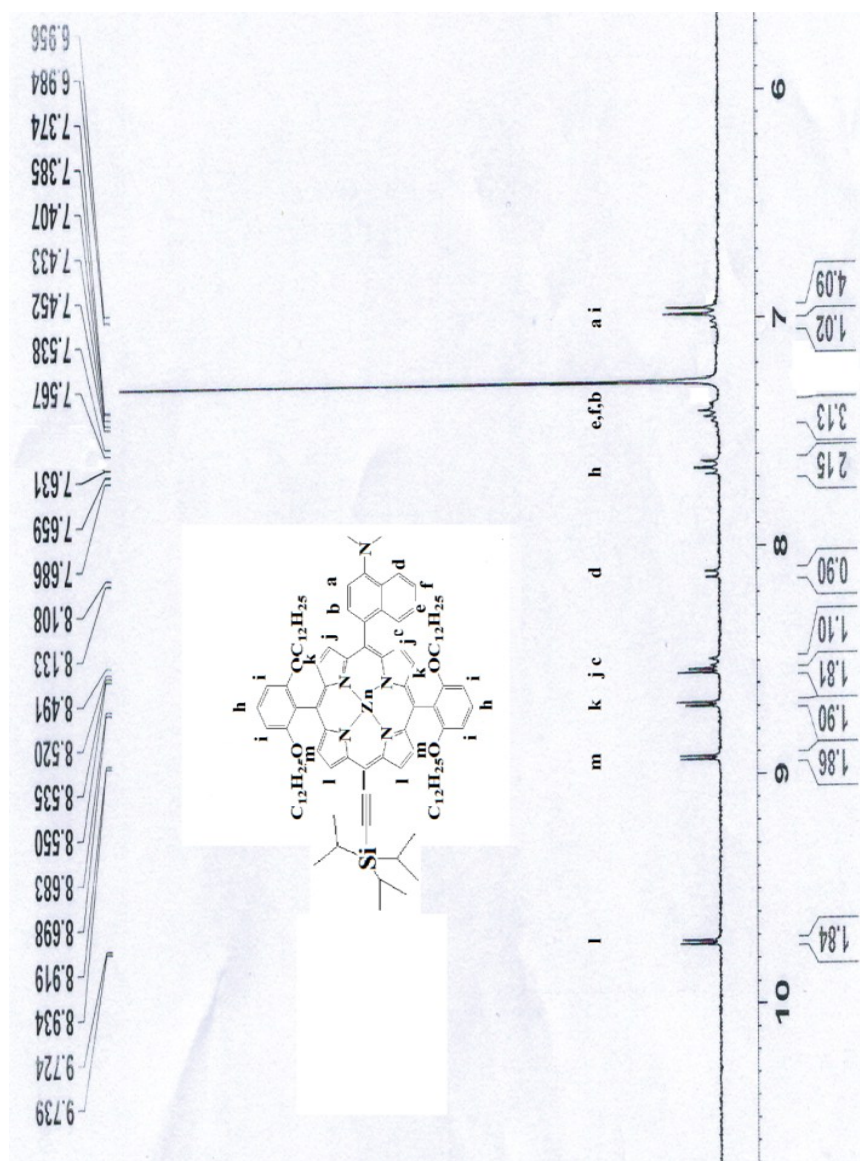




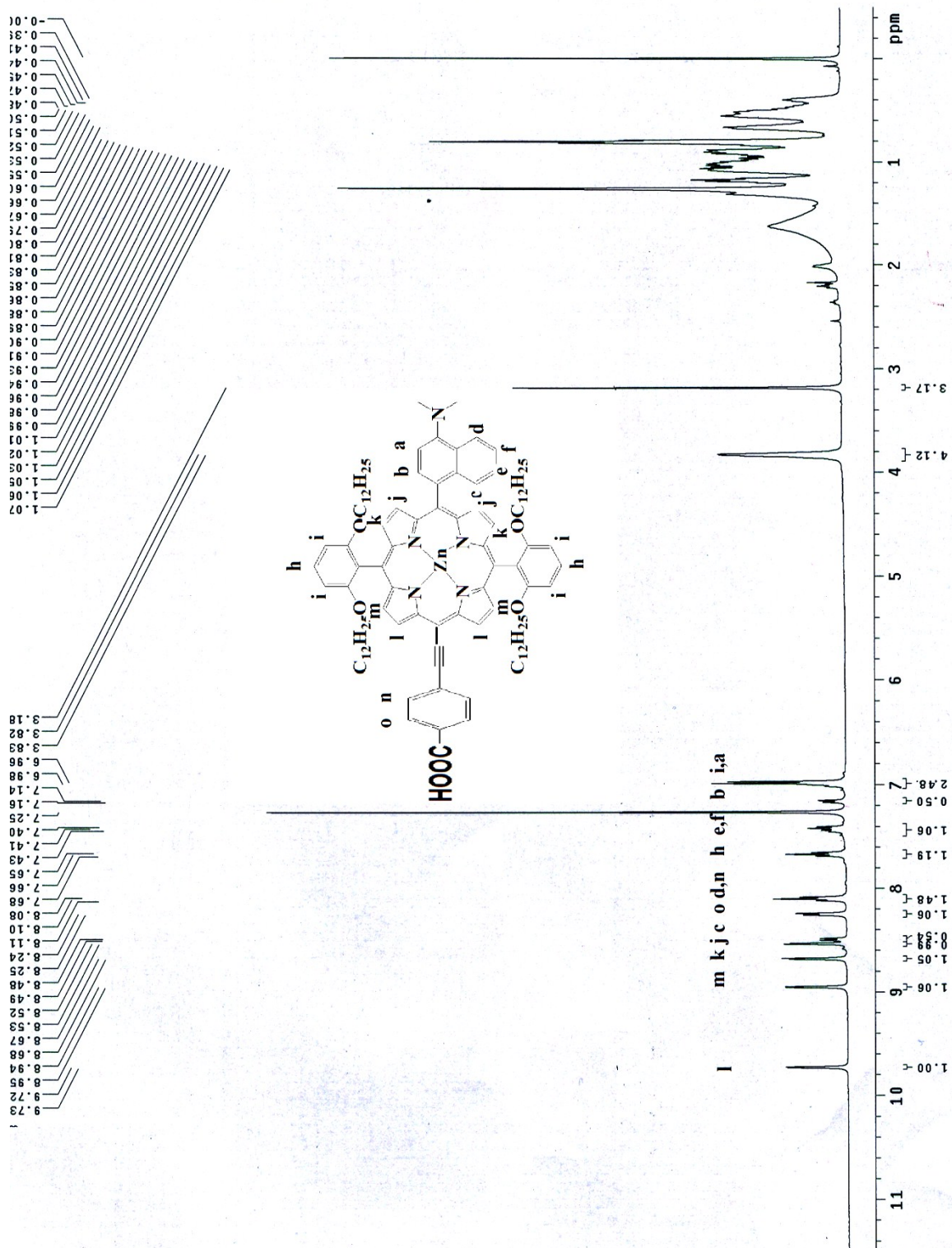


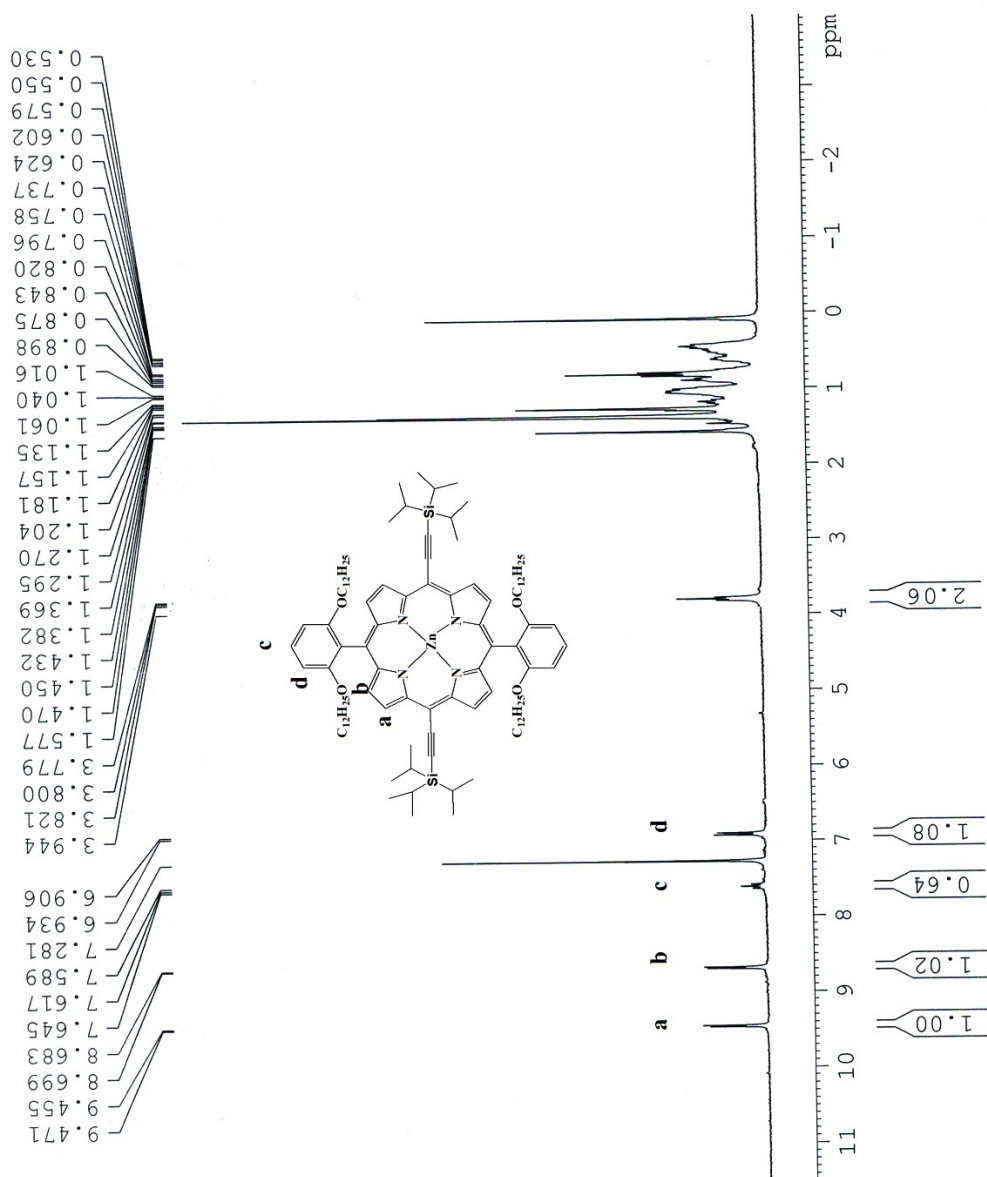












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