Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Porphyrin Based Push-Pull Conjugates as Donors for Solution-processed Bulk Heterojunction Solar Cells: A Case of Metal-dependent Power Conversion Efficiency

Ruchika Mishra,[a] Ramprasad Regar,[a] Rahul Singhal,[b] Piyush Panini,[a] Ganesh D. Sharma[c]* and Jeyaraman Sankar[a]*

[a]Department of Chemistry, Indian Institute of Science Education and Research (IISER) Bhopal, Bhopal Bypass Road, Bhauri, Bhopal, Madhya Pradesh , India - 462066

[b]Department of Physics, Malviya National Institute of Technology, Jaipur , Rajasthan, India - 302031

[c]Department of Physics, The LNM Institute of Information Technology (A Deemed University), Jamdoil, Jaipur, Rajasthan, India - 302031

E-mail: sankar@iiserb.ac.in; gdsharma273@gmail.com

Contents

Materials and Reagents: All reactions were carried out either under argon or nitrogen atmosphere. Solvents were dried according to routine procedures. Spectroscopic grade solvents were used for measuring electrochemical and optical properties. Unless otherwise noted, the chemicals received from Sigma Aldrich and Alfa Aesar were used without further purification. Samples synthesized were purified by column chromatography followed by recrystallization.

NMR and Mass Spectra Measurements: ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz, 500 MHz and 700 MHz spectrometer in $CDCl_3$.The chemical shift values have been referenced to the residual solvent signals. HRMS measurements were recorded on a microTOF-QII high resolution mass spectrometer from Bruker Daltonics coupled to a Waters Acquity UPLC system. MALDI-TOF spectra were obtained from Bruker UltraFLEXtreme instrument.

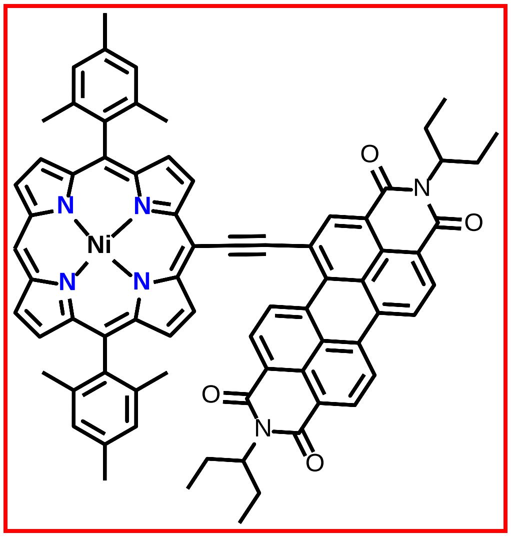
Electrochemical Measurements: Cyclic voltammetric measurements were carried out using CH potentiostat from CHI Instruments. CV experiments were done under continuous argon flow and a conventional three-electrode electrochemical cell was used. A glassy carbon working, a platinum counter and SCE reference electrodes were used. All the measurements were done in dichloromethane solution with 0.1 M TBAP as supporting electrolyte. All the spectra were recorded at a scan rate of 0.1 V/s.

Steady State Absorption Measurements: Steady state absorption measurements were done on carry 5000 UV/VIS/NIR spectrophotometer.

Single Crystal XRD Measurement: Single crystal X-ray diffraction measurements were done on a Bruker Apex diffractometer with a CCD detector with Mo-Kα radiation.

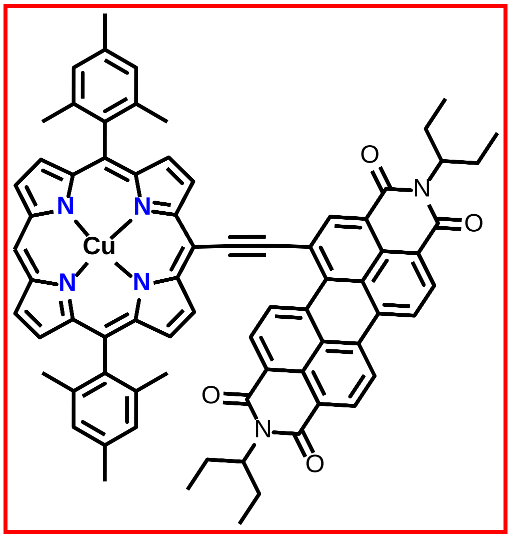
Quantum Chemical Calculations were performed using Gaussian 09 software suite.

Complete Synthetic and Analytical Details of all the Synthesized Molecules



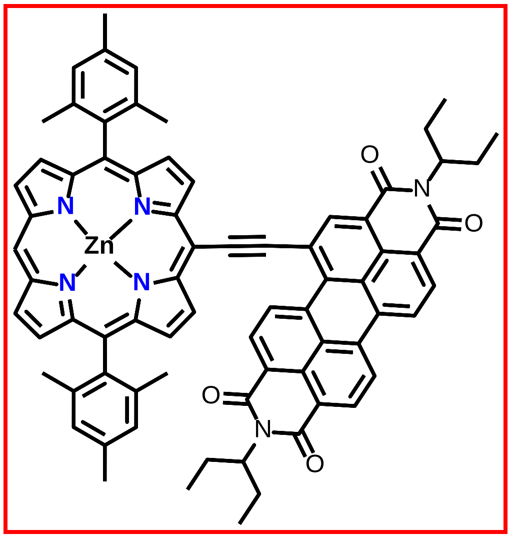
1-Ni (Ni-Porp-PBI dyad)

***Synthesis of Dyad 1-Ni (Ni-Porp-PBI dyad)*:** In a dry Schlenk tube, $PdCl_2(PPh_3)_2$ (6 mg, 0.007 mmol) and CuI (catalytic) were added. To this 5 mL each of solvents, THF and diisopropylamine (DIA) was added. After degassing, compound **1-BromoPBI** (0.040g, 0.066 mmol) was added, and the reaction mixture was further stirred for 5 min. Then **7-CH** (0.040g, 0.063 mmol) was added under argon atmosphere, and the reaction mixture was refluxed overnight. After removal of solvent under vacuum, the reaction mixture was purified by gel permeation chromatography with toluene to afford two major bands characterized as porphyrin homo-coupled product and the desired cross-coupled dyad. Later product was further purified by basic alumina chromatography to get the desired product in 45% yield. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ (ppm) = 0.89 (m, 12H), 1.78 (s, 12H), 1.88-1.96 (m, 4H), 2.20-2.30 (m, 4H), 2.55 (s, 6H), 5.04 (m, 2H), 7.20 (s, 4H), 8.63 (d, *J* = 4.7 Hz, 2H), 8.66-8.71(m, 4H), 8.71 (d, *J* = 4.8 Hz, 2H), 8.82 (d, *J* = 8.2 Hz, 1H), 9.01 (d, *J* = 4.7 Hz, 2H), 9.31 (s, 1H), 9.64 (d, *J* = 4.8 Hz, 2H), 9.73 (s, 1H), 10.83 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR (176 MHz, $CDCl_3$)** δ (ppm) 162.85, 143.72, 142.53, 141.86, 141.38, 137.85, 136.97, 135.59, 133.95, 133.55, 133.15, 132.58, 132.04, 131.78, 130.61, 130.06, 128.43, 127.64, 126.88, 126.58, 126.06, 125.90, 122.70, 121.99, 119.90, 117.76, 105.65, 101.52, 97.36, 96.14, 56.83, 56.66, 30.53, 28.64, 24.02, 24.00, 21.60, 20.39, 20.33, 13.08, 10.36, 10.33. **HRMS Mass**: Calc. for $C_{74}H_{60}N_6O_4Ni$: 1154.4024; found: 1154.4044.



2-Cu (Cu-Porp-PBI dyad)

Synthesis of Dyad 2-Cu (Cu-Porp-PBI dyad)**:** The synthesis was done using above written procedure employing **8-CH** and desired product was isolated in 40% yields. <u>Since the synthesized molecule is paramagnetic in nature, so could not characterized by NMR spectroscopy</u>. **HRMS Mass**: Calc. for $C_{74}H_{60}N_6O_4Cu$: 1159.3967; found: 1159.3956.



3-Zn (Zn-Porp-PBI dyad)

***Synthesis of Dyad 3-Zn (Zn-Porp-PBI dyad)*:** The synthesis was done using above written procedure employing **9-CH** and the desired product was isolated in 40% yield. **^{1}H NMR** (500 MHz, CDCl$_3$): δ (ppm) = 0.92 (m, 12H), 1.80 (s, 12H), 1.93 (m, 4H), 2.27 (m, 4H), 2.60 (s, 6H), 5.04 (m, 2H), 7.19 (s, 4H), 8.66 - 8.73 (m, 4H), 8.79 (d, *J* = 4.4 Hz, 2H), 8.90 (d, *J* = 7.94 Hz, 1H), 8.93 (d, *J* = 4.5 Hz, 2H), 9.23 (d, *J* = 4.4 Hz, 2H), 9.45 (s, 1H), 9.83 (d, *J* = 4.5 Hz, 2H), 10.08 (s, 1H), 11.01 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR (176 MHz, CDCl$_3$)** δ (ppm) 173.74, 151.06, 149.74, 148.51, 148.47, 138.03, 137.26, 136.69, 134.16, 133.71, 133.48, 133.26, 132.08, 131.65, 131.54, 130.32, 129.63, 128.47, 127.53, 126.78, 126.66, 125.94, 122.66, 121.84, 120.47, 119.70, 107.11, 104.94, 104.78, 97.00, 96.43, 56.80, 56.64, 48.20, 29.17, 28.62, 28.26, 25.82, 24.19, 24.01, 20.59, 20.41, 16.40, 10.34, 10.32.**HRMS Mass**: Calc. for $C_{74}H_{60}N_6O_4Zn$: 1160.3962; found: 1160.3992.

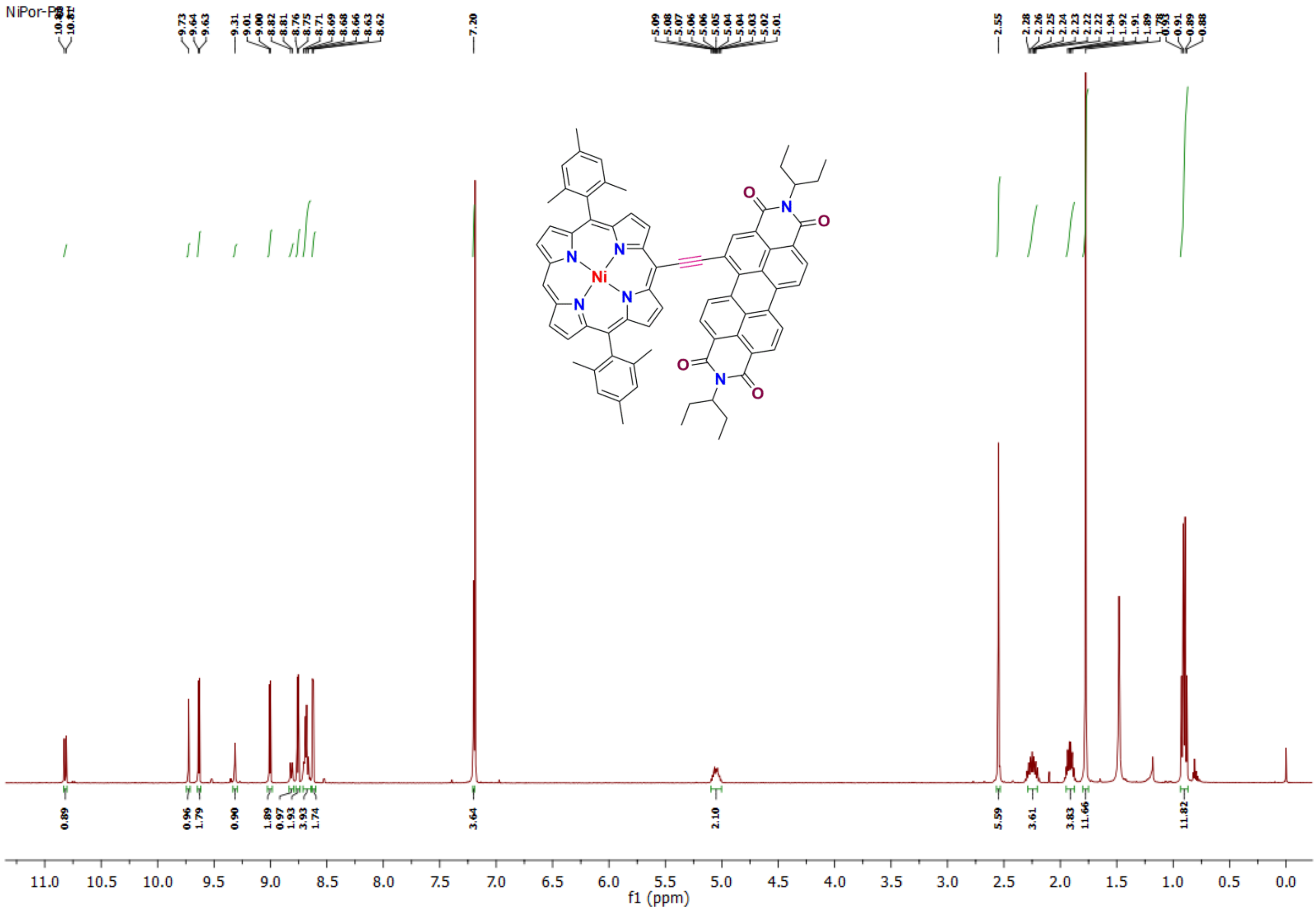


Figure S1. ^{1}H NMR spectrum of **1-Ni** in $CDCl_3$.

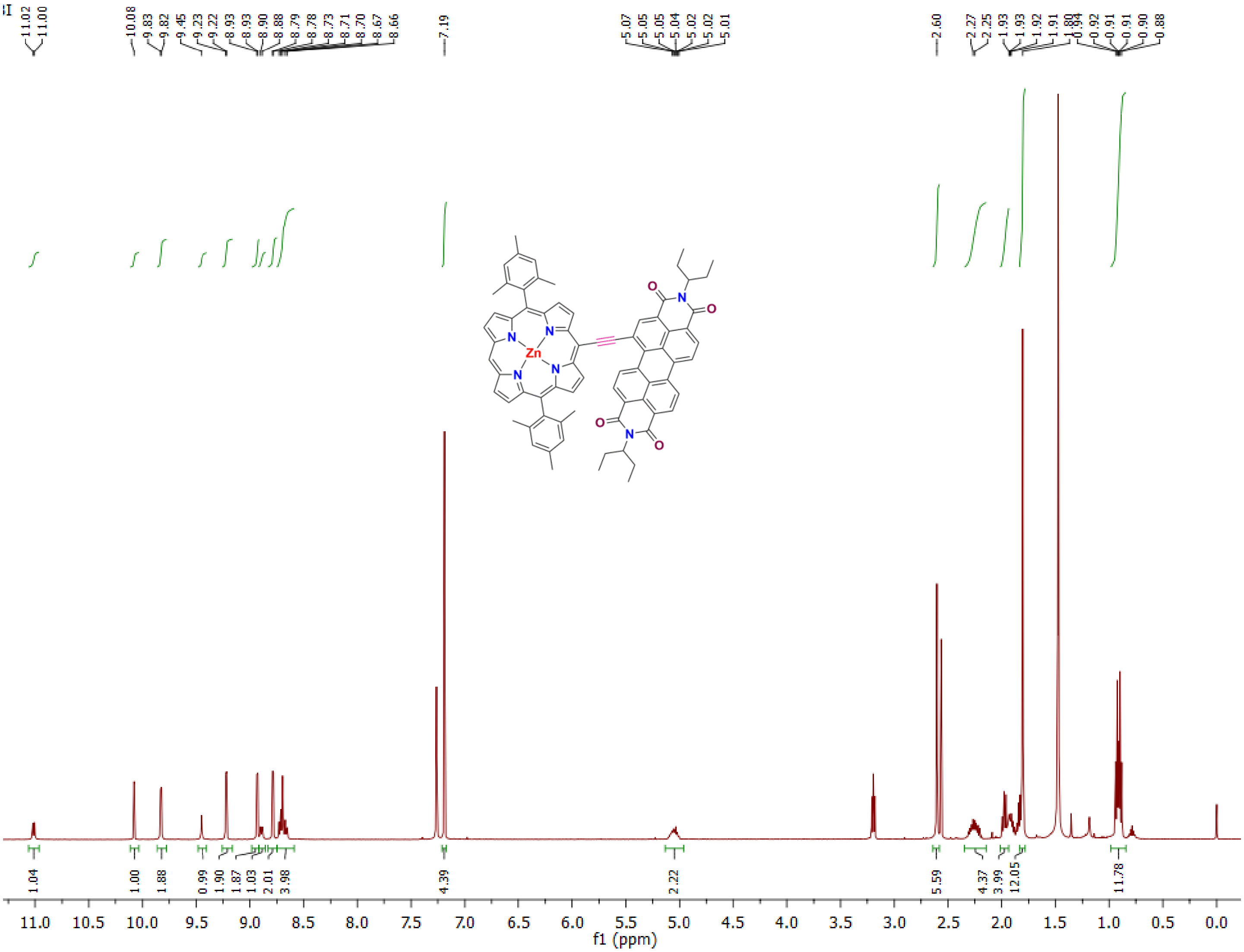


Figure S2. ^{1}H NMR spectrum of **3-Zn** in $CDCl_3$.

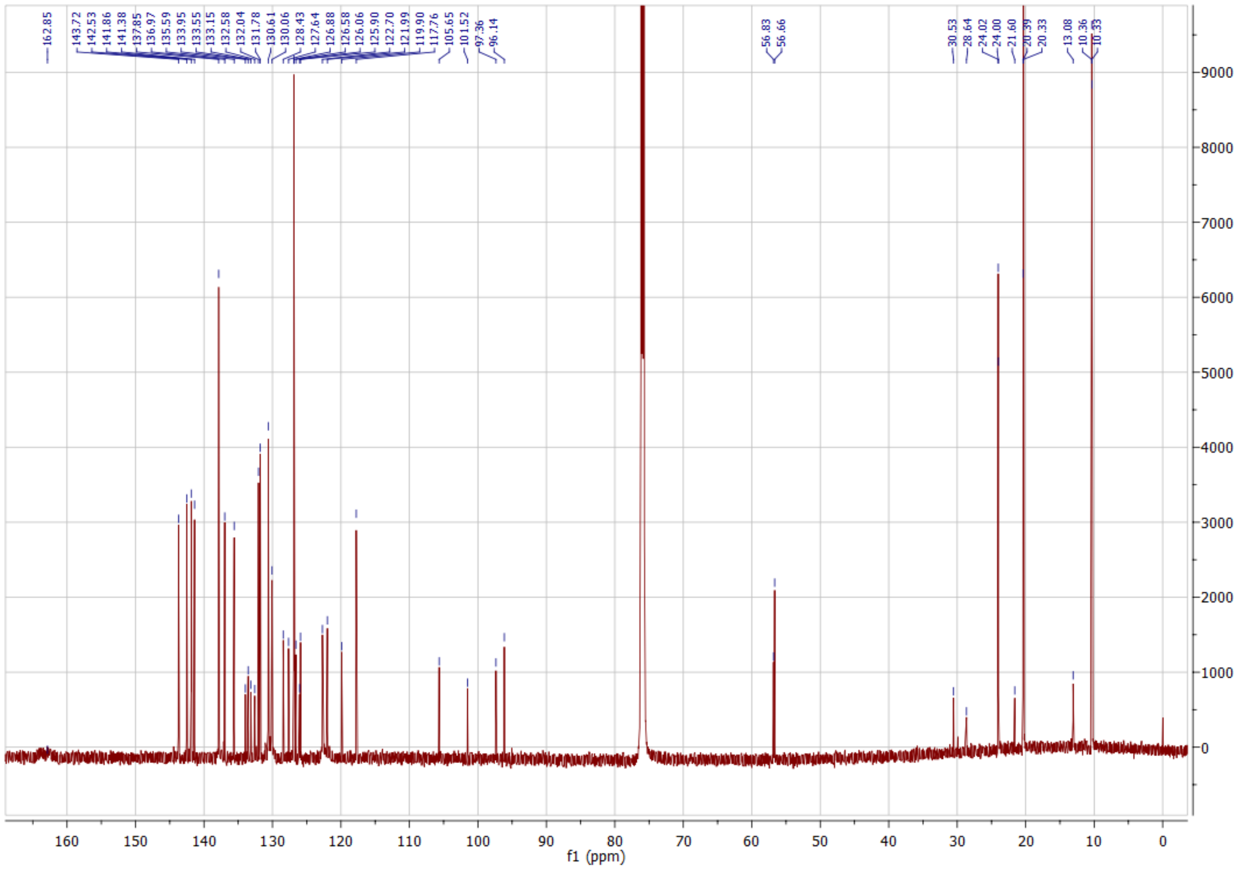


Figure S3. ^{13}C NMR spectrum of **1-Ni** in $CDCl_3$.

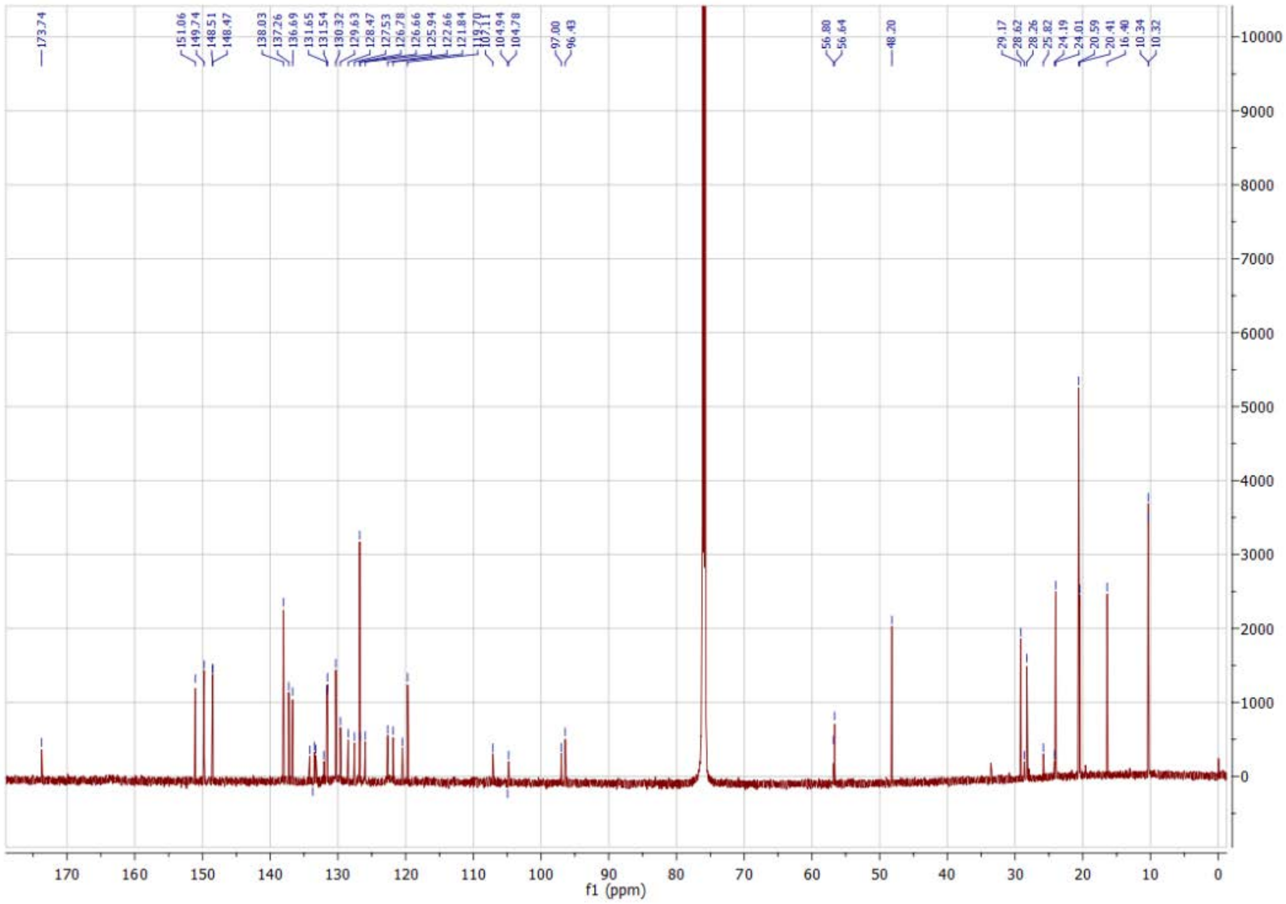


Figure S4. ^{13}C NMR spectrum of **3-Zn** in $CDCl_3$.

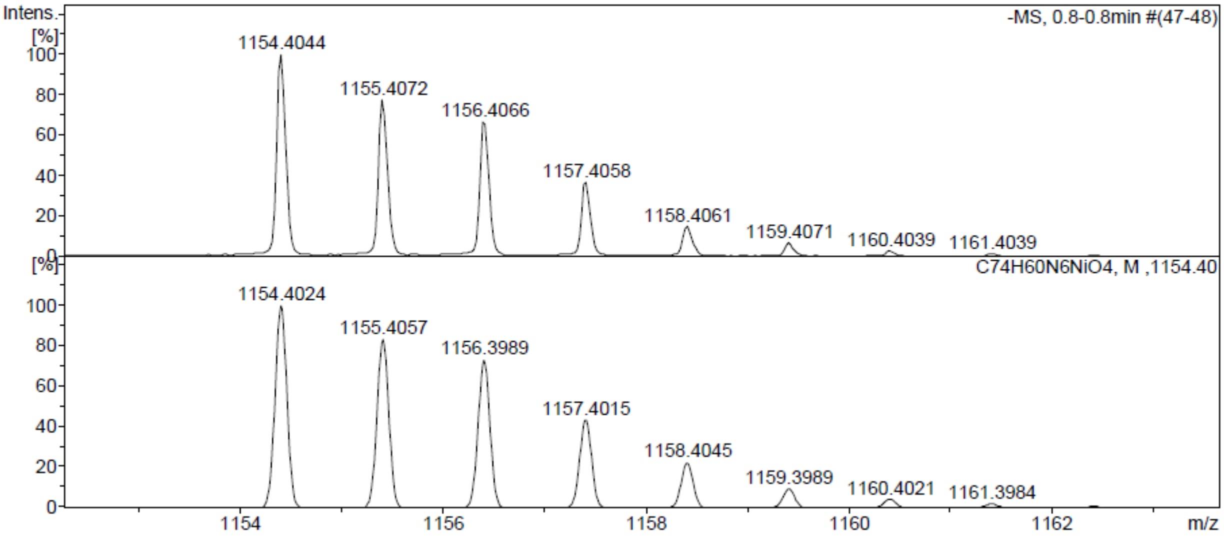


Figure S5. HRMS mass spectrum of **1-Ni.**

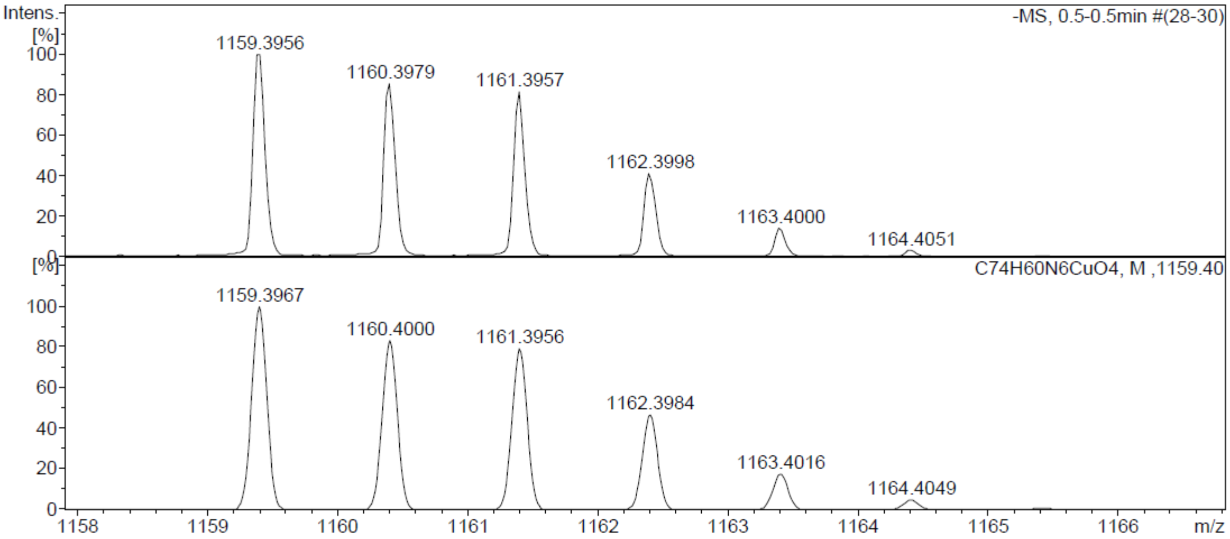


Figure S6. HRMS mass spectrum of **2-Cu.**

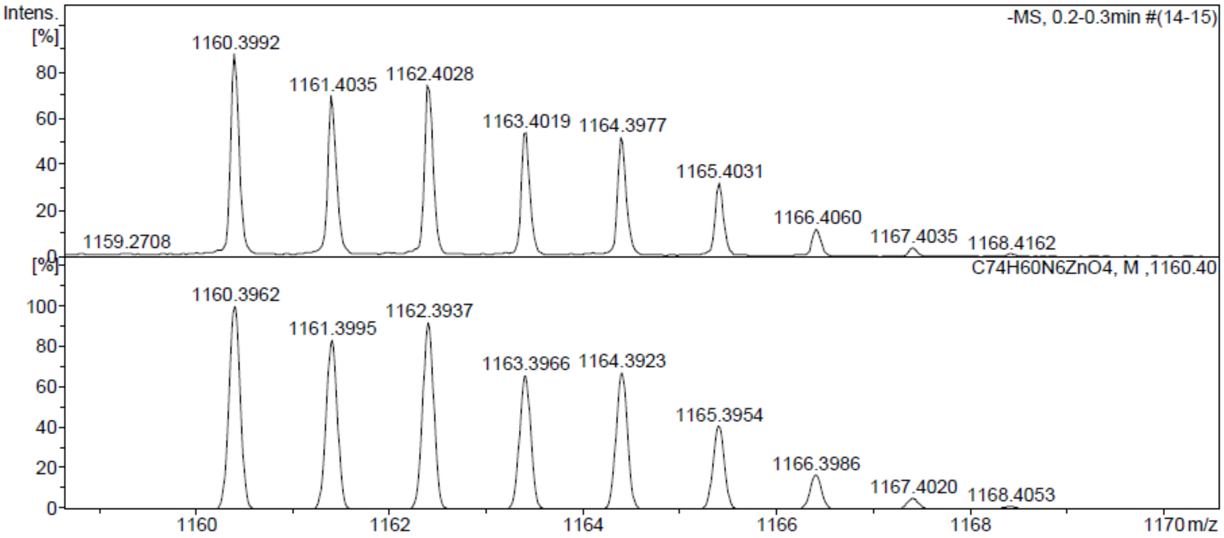
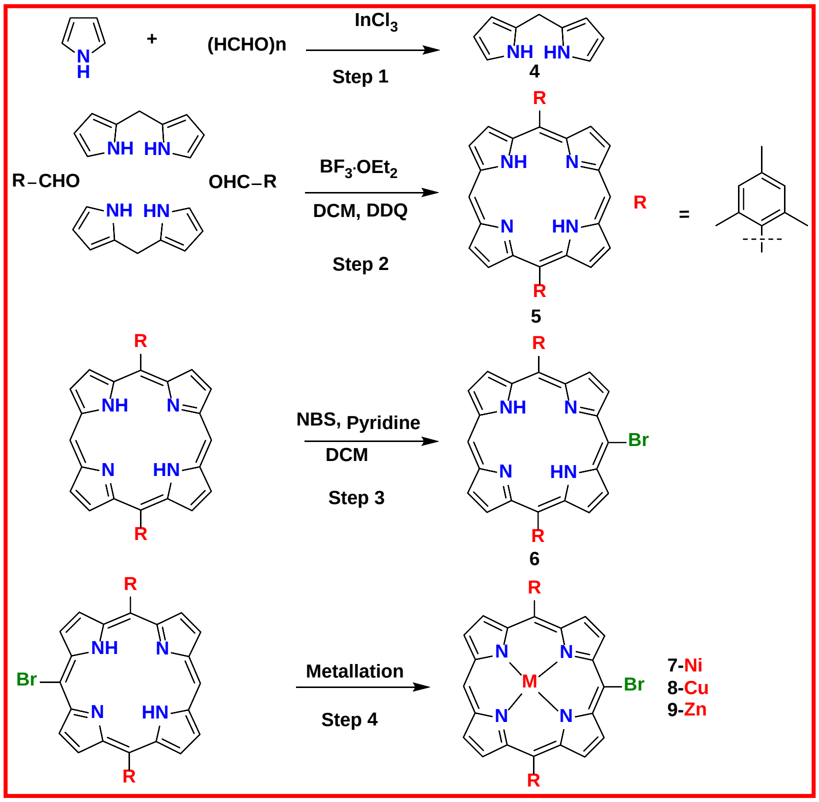
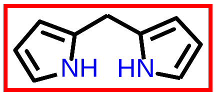


Figure S7. HRMS mass spectrum of **3-Zn.**



SchemeSI. Synthesis of 5,15-Dimesityl-10-bromoporphyrinato M(II)[11]

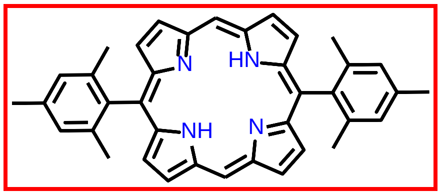
Synthesis of Precursors



Di(1-H-pyrrole-2-yl)methane

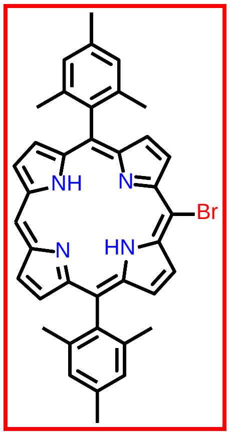
***a) Di(1-H-pyrrole-2-yl)methane (4)*:** A mixture of paraformaldehyde (0.45g, 15 mmol) and pyrrole (50 ml, 0.730 mol) in a round bottom flask was degassed with a stream of argon at room temperature. The mixture was heated at 55 ˚C and then $InCl_3$ (0.33 g, 1.5mmol) was added, and further stirred at 55 ˚C for 2.5 h. After cooling to room temperature NaOH (1.8g, 0.045mol) was added and stirred for 1 h and then filtered. The crude solid obtained after removing pyrrole was extracted with ethyl acetate/hexanes. The solvent was evaporated, and column chromatographed with silica gel afforded pale white crystals (45%).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 2H), 6.58 (dd, *J* = 3.9 Hz, 2H), 6.07 (dd, *J* = 5.7 Hz, 2H), 5.96 (s, 2H), 3.90 (s, 2H).



Synthesis of [5, 15-Dimesityl]PorH$_2$]

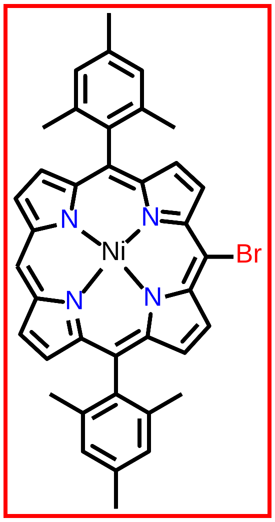
***b) Synthesis of [5, 15-Dimesityl]PorH$_2$]* (5) :** A round bottom flask was charged with **4** (1g, 6.8 mmol), mesitaldehyde (1 ml, 6.7 mmol), and 400 mL freshly distilled $CHCl_3$ and the solution was degassed with argon. $BF_3.Et_2O$ (0.4mL) was added drop by drop under vigorous stirring. The solution was stirred for 1 h upon which DDQ (2g) in toluene was added, and the solution was stirred for another 1 h. The reaction mixture was then passed through an alumina column. The crude product was further purified by silica gel column chromatography by means of gradient elution with $CHCl_3$/Hexane in yield of 13%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 10.13 (s, 2H), 9.23 (d, *J* = 4.6 Hz, 4H), 8.80 (d, *J* = 4.5 Hz, 4H), 7.24 (s, 4H), 2.58 (s, 6H), 1.77 (s, 12H), -3.14 (s, 2H). **MALDI-TOF Mass**: Calc. $C_{38}H_{34}N_4$: 546.703; found: 545.4.



5, 15-Dimesityl-10-bromoporphyrin

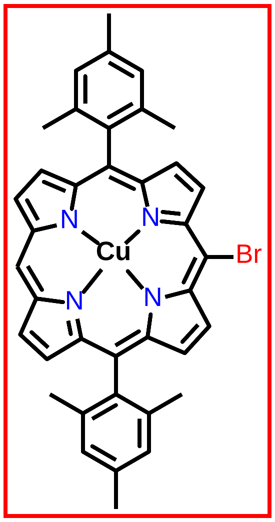
***c) Synthesis of 5, 15-Dimesityl-10-bromoporphyrin*(6) :** A solution of **5** (0.45g, 0.824 mmol) in $CHCl_3$ (200 mL) and pyridine (0.35 mL) was treated with NBS (0.12g, 0.688 mmol) at 0 $^{\circ}$C. After 25 min, the reaction was quenched with acetone (10mL). Then, the reaction mixture was washed with H_2O and dried over anhydrous $MgSO_4$. Chromatography (silica, $CHCl_3$/hexane) afforded three bands: dibrominted product, monobrominated and unreacted. The second band was characterized to monobromo porphyrin in yield of 65%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 9.59 (d, *J* = 4.8 Hz, 2H), 9.15 (d, *J* =

4.6 Hz, 2H), 8.71 (d, *J* = 4.7 Hz, 4H), 7.23 (s, 4H), 2.58 (s, 6H), 1.76 (s, 12H), -2.94 (s, 2H). **MALDI-TOF Mass:** Calc. $C_{38}H_{33}N_4Br$: 625.599; found: 625.3.



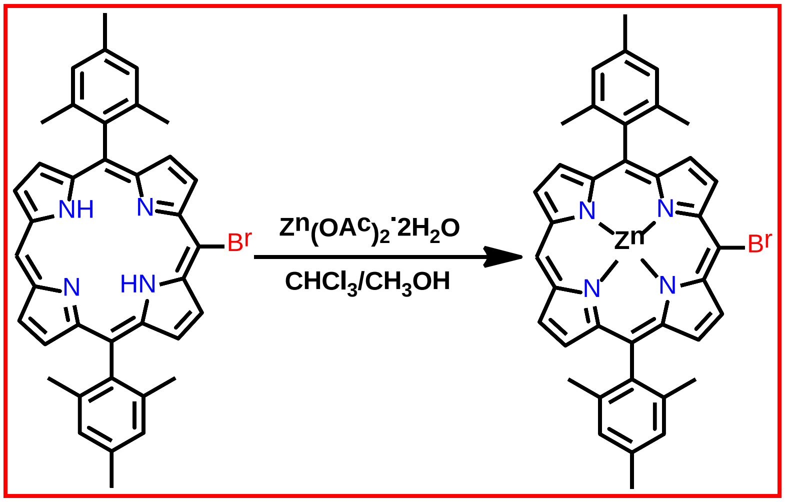
5, 15-Dimesityl-10-bromoporphyrinato Nickel (II)

d) Synthesis of 5, 15-Dimesityl-10-bromoporphyrinato Nickel (II) (7): Compound **6** (0.1g, 0.16 mmol) was dissolved in 25mL of DMF and nickel acetate tetrahydrate (1g, 4 mmol) was added. The solution was stirred at 150 °C for 12 h. The reaction mixture was extracted with H_2O and $CHCl_3$ and dried over anhydrous $MgSO_4$. The product was purified by silica gel column chromatography with $CHCl_3$/Hexane solvent mixture affording the desired compound in yield of 57.7 %. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.67 (s, 1H), 9.46 (d, *J* = 4.9 Hz, 2H), 8.98 (d, *J* = 4.7 Hz, 2H), 8.60 (d, *J* = 4.9 Hz, 4H), 7.16 (s, 4H), 2.52 (s, 6H), 1.71 (s, 12H). **MALDI-TOF Mass**: Calc. $C_{38}H_{31}BrN_4Ni$: 682.276; found: 682.7.



5, 15-Dimesityl-10-bromoporphyrinato Copper(II)

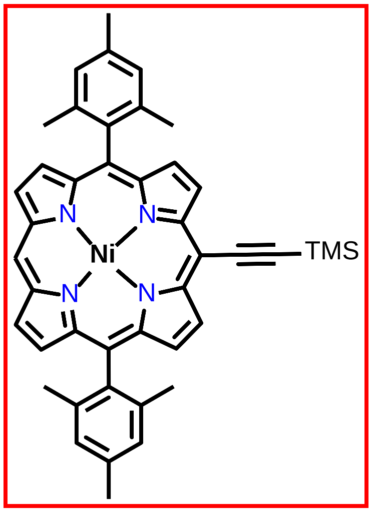
e) Synthesis of 5, 15-Dimesityl-10-bromoporphyrinato Copper(II) (8)**:** Compound **6** (0.094g, 0.15 mmol) was dissolved in 25mL of $CHCl_3$, and 5 mL of CH_3OH and copper acetate dihydrate (1g, 5mmol) was added. The solution was stirred at room temperature for 4 h. The reaction mixture was extracted with H_2O and $CHCl_3$ and dried over anhydrous $MgSO_4$. The product was purified by silica gel column chromatography with $CHCl_3$/Hexane solvent mixture affording the desired compound with a yield of 92 %. **MALDI-TOF Mass**: Calc. $C_{38}H_{31}BrN_4Cu$: 687.130; found: 686.7.



5, 15-Dimesityl-10-bromoporphyrinato Zinc(II)

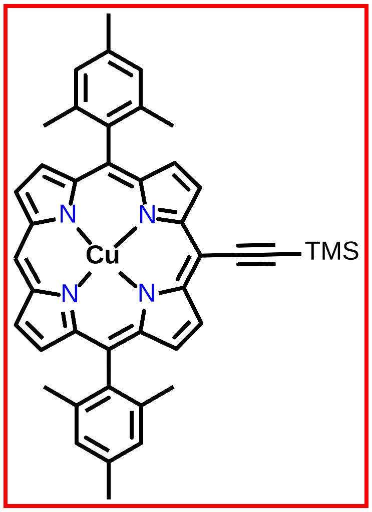
***f) Synthesis of 5, 15-Dimesityl-10-bromoporphyrinato Zinc(II)* (9) :** Compound **6**(0.088g, 0.14mmol) was dissolved in 25mL of $CHCl_3$ and 5 mL of CH_3OH and zinc acetate dihydrate (1g, 4.5mmol) was added.

The solution was stirred at room temperature for 4 h. After initial work up, the product was purified by silica gel column chromatography with $CHCl_3$/Hexane solvent mixture affording the desired compound **9** with a yield of 96 %. ^{1}**H NMR** (500 MHz, $CDCl_3$): δ (ppm) 1.80 (s, 12H), 2.64 (s, 6H), 7.24 (s, 4H), 8.87 (d, *J* = 4.44 Hz, 4H), 9.30 (d, *J* = 4.48 Hz, 2H), 9.73 (d, *J* = 4.71 Hz, 2H), 10.13 (s, 1H). **MALDI-TOF Mass**: Calc. $C_{38}H_{31}BrN_4Zn$: 688.963; found: 687.2.



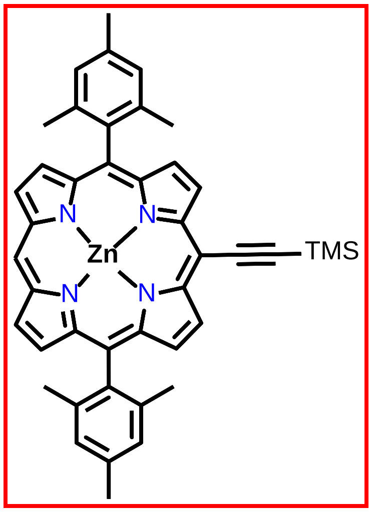
5, 15-Dimesityl-10-trimethylsilylacetylenylporphyrinato Nickel (II)

g) Synthesis of 5, 15-Dimesityl-10-trimethylsilylacetylenylporphyrinato Nickel (II) **(7-TMS)**: In a Schlenk tube, $PdCl_2(PPh_3)_2$ (0.007g, 0.01 mmol) and CuI (catalytic) were added. To this 4ml each of solvents, THF and Diisopropylamine (DIA) was added. This was followed by the addition of **7** (0.061g, 0.09 mmol) under degassed condition .The reaction mixture was then stirred for some more time followed by addition of ethynyltrimethylsilane (0.04g, 0.36 mmol). The reaction mixture was refluxed for 6 h. After the removal of solvent in vacuum, the reaction mixture was purified by basic alumina column chromatography with $CHCl_3$/Hexane solvent mixture to get the desired product with a yield of 77 %. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.69 (s, 1H), 9.46 (d, *J* = 4.8 Hz, 2H), 8.97 (d, *J* = 4.7 Hz, 2H), 8.61 (d, *J* = 4.8 Hz, 2H), 8.58 (d, *J* = 4.7 Hz, 2H), 7.16 (s, 4H), 2.53 (s, 6H), 1.72 (s, 12H), 0.46 (s, 9H). **MALDI-TOF Mass**: Calc. for $C_{38}H_{31}BrN_4NiSi$: 699.583; found: 699.9.



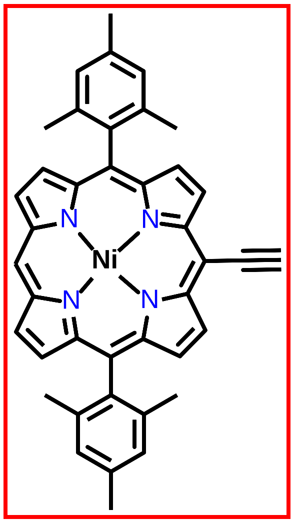
5, 15-Dimesityl-10-trimethylsilylacetylenylporphyrinato Copper (II)

h) Synthesis of 5, 15-Dimesityl-10-trimethylsilylacetylenylporphyrinato Copper (II) **(8-TMS):** This compound was synthesized from compound **8** by above procedure with 82 % yield. MALDI-TOF Mass: Calc. for $C_{43}H_{40}N_4CuSi$: 704.440; found: 704.7.



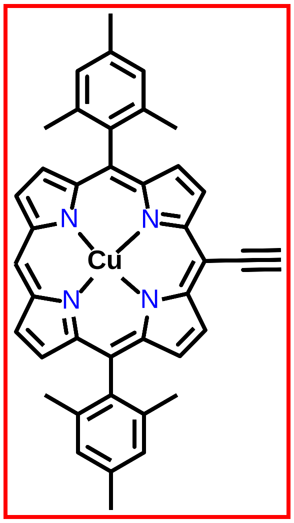
5, 15-Dimesityl-10-trimethylsilylacetylenylporphyrinato Zinc (II)

i) Synthesis of 5, 15-Dimesityl-10-trimethylsilylacetylenylporphyrinato Zinc (II) **(9-TMS).** This compound was synthesized from compound **9** by above procedure with 70 % yield. **MALDI-TOF Mass**: Calc. for $C_{43}H_{40}N_4ZnSi$: 704.440; found: 704.7.



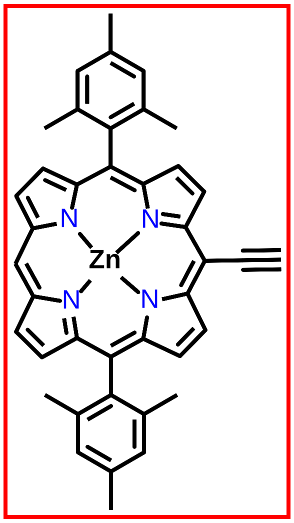
5, 15-Dimesityl-10-ethynyl-porphyrinato Nickel (II)

j) Synthesis of 5, 15-Dimesityl-10-ethynyl-porphyrinato Nickel (II) (7-CH): To a solution of **7-TMS** (0.060g) in THF, TBAF (0.3 mL) in THF was added under argon and stirred at room temperature for 1 h. Upon completion of reaction, the solvent was evaporated and mixture was purified by silica gel column chromatography ($CHCl_3$/ Hexane eluents) to get the desired compound in 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 9.72 (s, 1H), 9.48 (d, *J* = 4.8 Hz, 2H), 8.99 (d, *J* = 4.7 Hz, 2H), 8.63 (d, *J* = 4.9 Hz, 2H), 8.60 (d, *J* = 4.7 Hz, 2H), 7.17 (s, 4H), 3.97 (s, 1H), 2.53 (s, 6H), 1.72 (s, 12H).**MALDI-TOF Mass**: Calc. for $C_{40}H_{32}N_4Ni$: 627.404; found: 627.3.



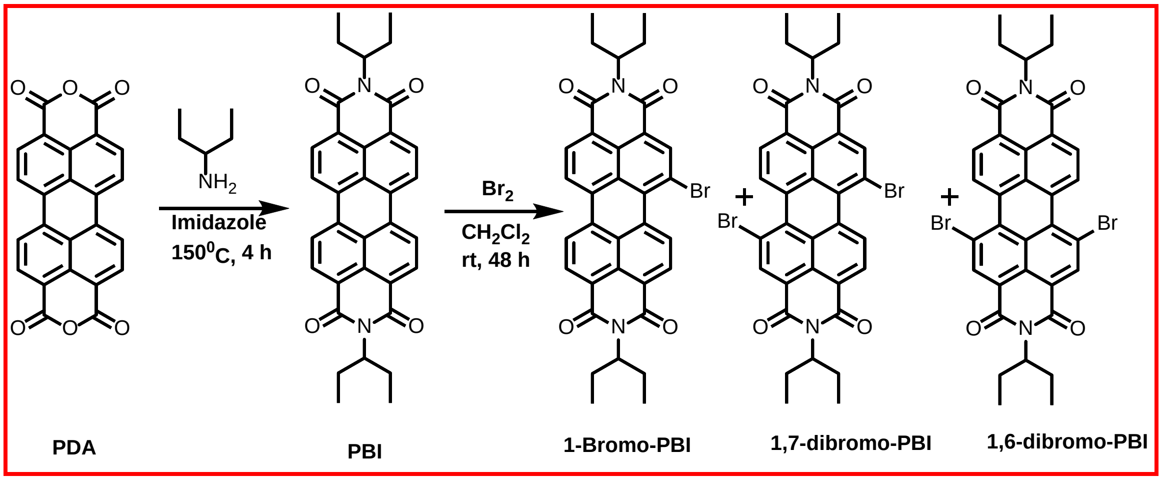
5, 15-Dimesityl-10-ethynyl-porphyrinato Copper (II)

k) Synthesis of 5, 15-Dimesityl-10-ethynyl-porphyrinato Copper (II) (8-CH)**:** To a solution of **8-TMS** (.060 g) in THF, TBAF (0.3 mL) in THF was added under argon and stirred at room temperature for 1 h. Upon completion of reaction, the solvent was evaporated under and mixture was purified by silica gel column chromatography ($CHCl_3$/ Hexane eluents) to get the desired compound in 74% yield. **HRMS**: Calc. for $C_{40}H_{32}N_4Cu$: 632.1996; found: 632.2.



5, 15-Dimesityl-10-ethynyl-porphyrinato Zinc (II)

l) Synthesis of 5, 15-Dimesityl-10-ethynyl-porphyrinato Zinc (II) (9-CH): To a solution of **9-TMS** (.060 g**)** in THF, TBAF (0.3 mL) in THF was added under argon and stirred at room temperature for 1 h. Upon completion of reaction, the solvent was evaporated and mixture was purified by silica gel column chromatography ($CHCl_3$/ Hexane eluents) to get the desired compound in 67% yield. **MALDI-TOF Mass**: Calc. $C_{40}H_{32}N_4Zn$: 632.19; found: 633.2.



Scheme S2. Synthesis of **Perylenebisimide** (PBI) and **1-Bromoperylenebisimide** (1-Bromo-PBI)[12]

***m) Synthesis of Perylenebisimide(PBI)* :** A solution of pent-3-ylamine (1.5 ml, 17 mmol), Perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) (2.8g, 7 mmol) in imidazole (40 g) was stirred at 150 °C for 4 h, and then the mixture was diluted with ethanol. This was followed by the addition of 2M HCl. The reaction mixture was allowed to settle down. The precipitates formed were collected by vacuum filtration, oven dried and purified by repetitive silica gel column chromatography (chloroform) to desired product of yield 80 %. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 8.59 (d, *J* = 7.9 Hz, 4H), 8.53 (d, *J* = 8.0 Hz, 4H), 5.00 (m, 2H), 2.25 – 2.14 (m, 4H), 1.94 – 1.83 (m, 4H), 0.86 (t, *J* = 7.5 Hz, 12H). **^{13}C NMR** (126 MHz), $CDCl_3$) δ (ppm) 158.81, 158.47, 134.76, 129.56, 126.39, 123.36, 115.64, 113.37, 58.24, 24.99, 11.29.

***n) Synthesis of 1-Bromo Perylenebisimide(1-Bromo-PBI)*:** Excess bromine (4ml, 86 mmol) was added to a solution of PBI (0.7, 1.3 mmol) in CH_2Cl_2 and the reaction mixture was stirred at room temperature for 48 h. The progress of the reaction was monitored by TLC. After the removal of excess bromine, compound was purified by repetitive silica gel column chromatography with hexane/chloroform as eluents. After purification mono-bromo PBI was obtained of yield 57%.

NMR Spectra of Synthesized Precursors

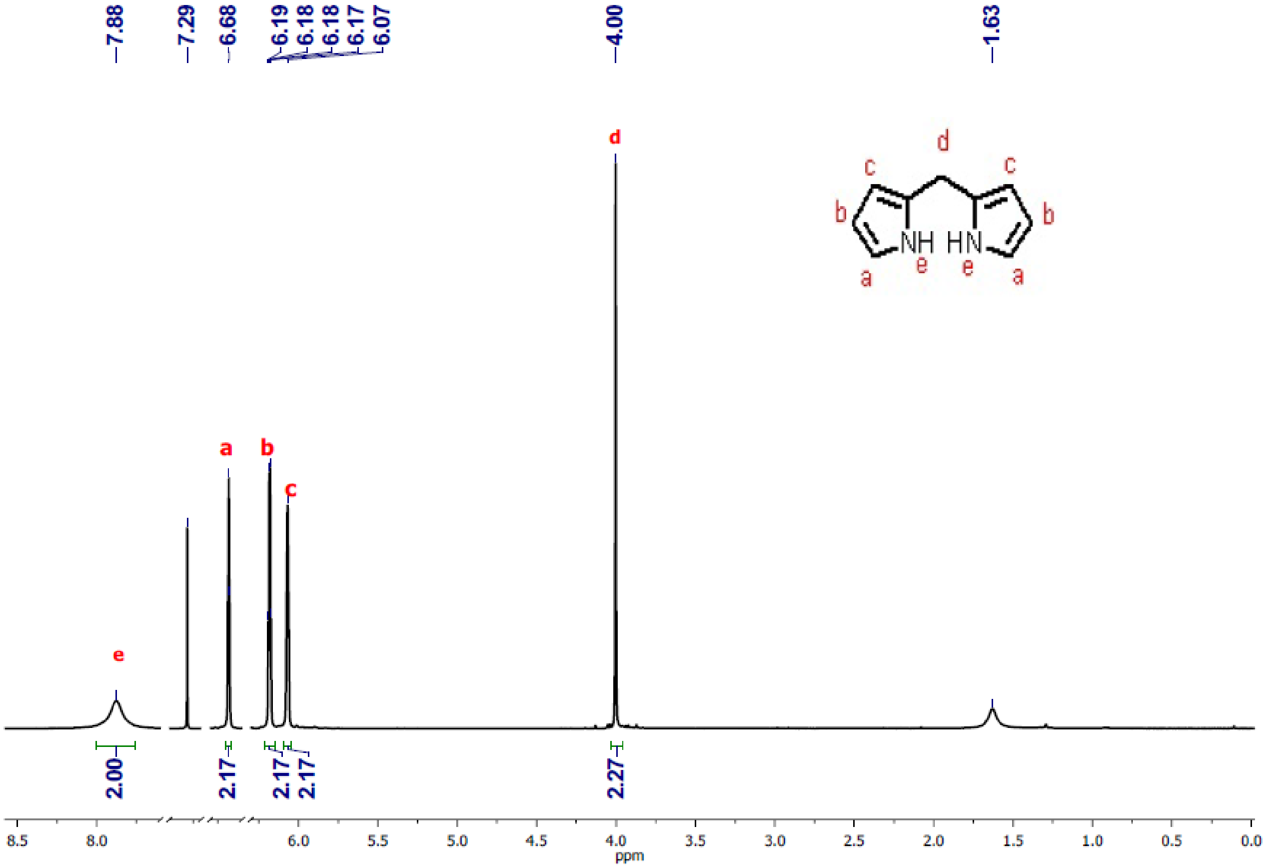


Figure S8. ^{1}HNMR spectrum of compound **4** in $CDCl_3$.

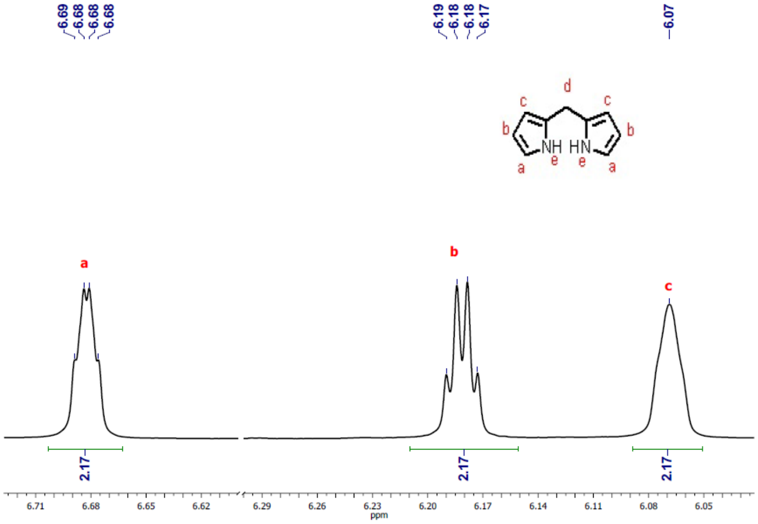


Figure S9. Partial ^{1}HNMR spectrum of compound **4** in $CDCl_3$.

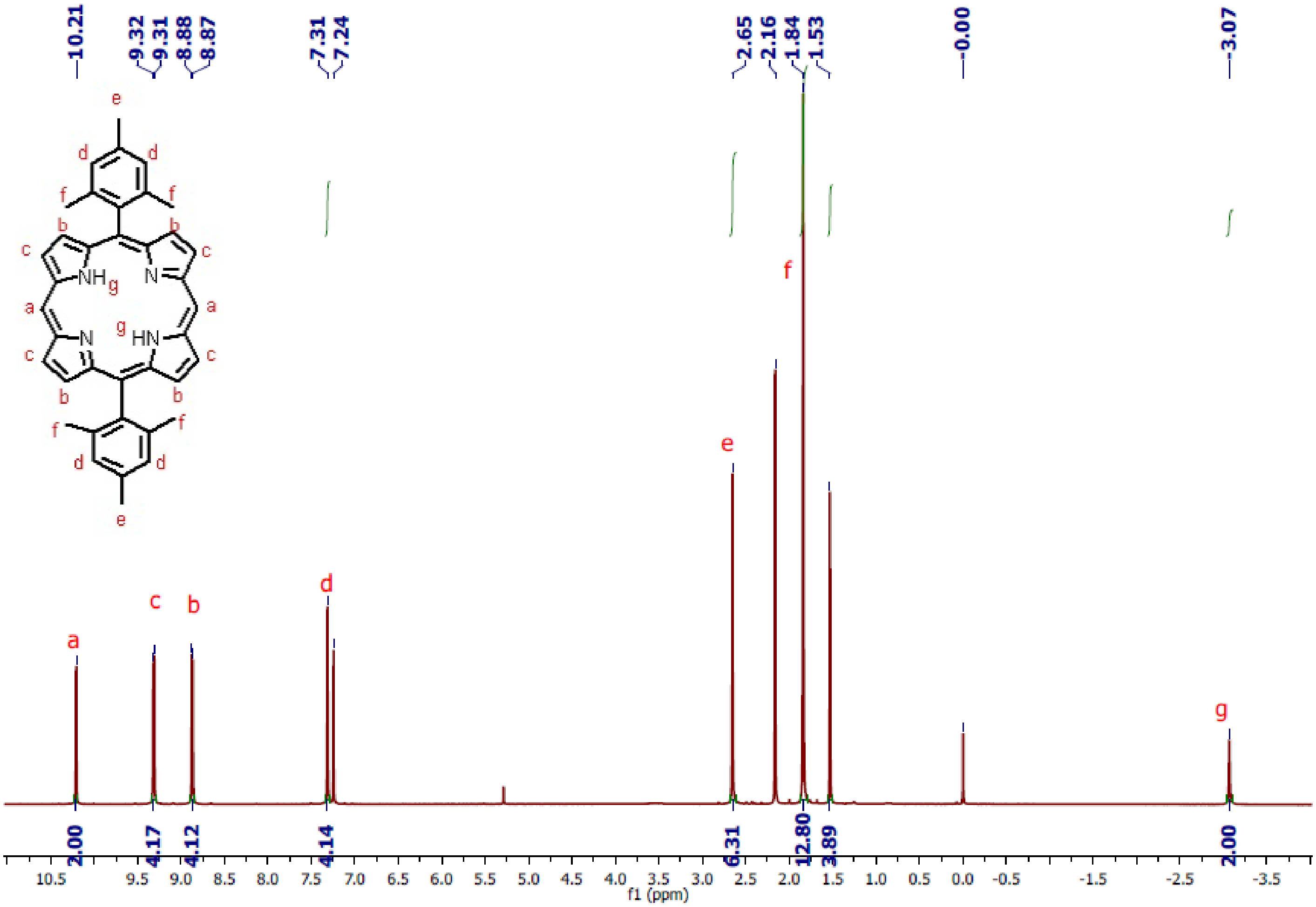


Figure S10: ^{1}HNMR of compound **5** in $CDCl_3$.

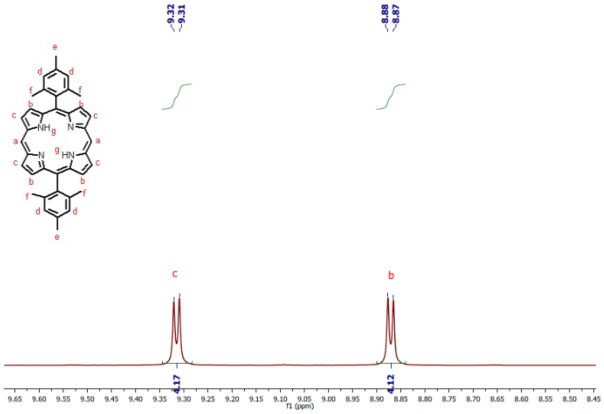


Figure S11. Partial ^{1}HNMR spectrum of compound **5** in $CDCl_3$.

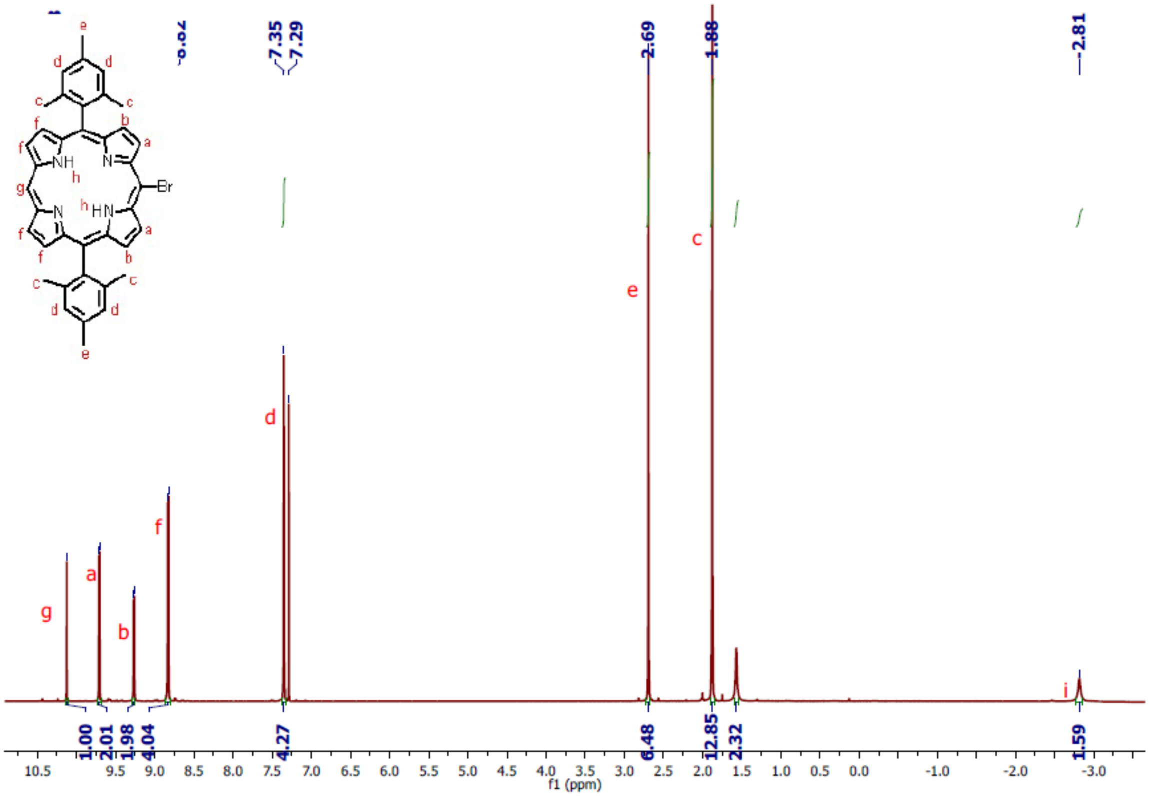


Figure S12. ^{1}HNMR of compound **6** in $CDCl_3$

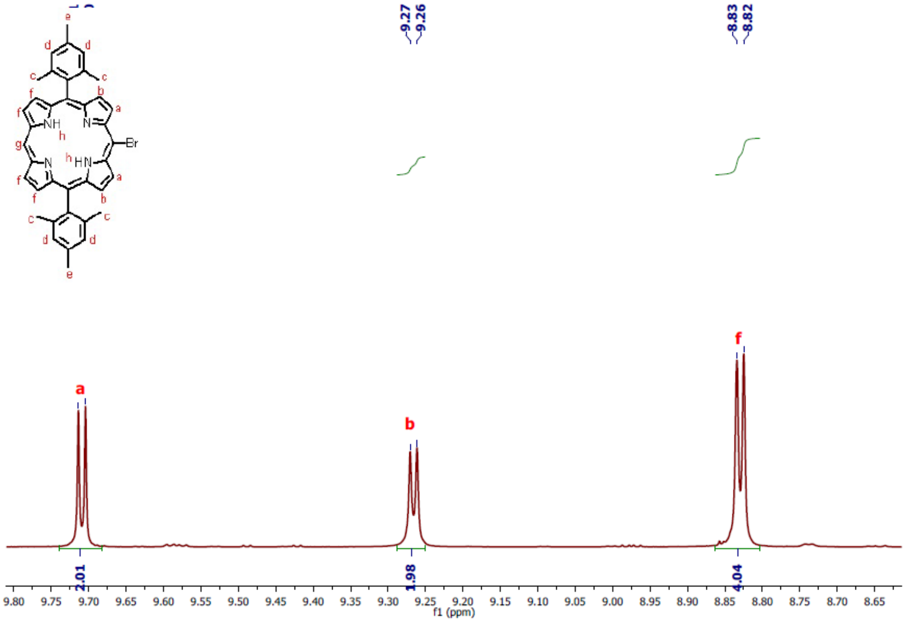


Figure S13. Partial ^{1}HNMR spectrum of compound **6** in $CDCl_3$

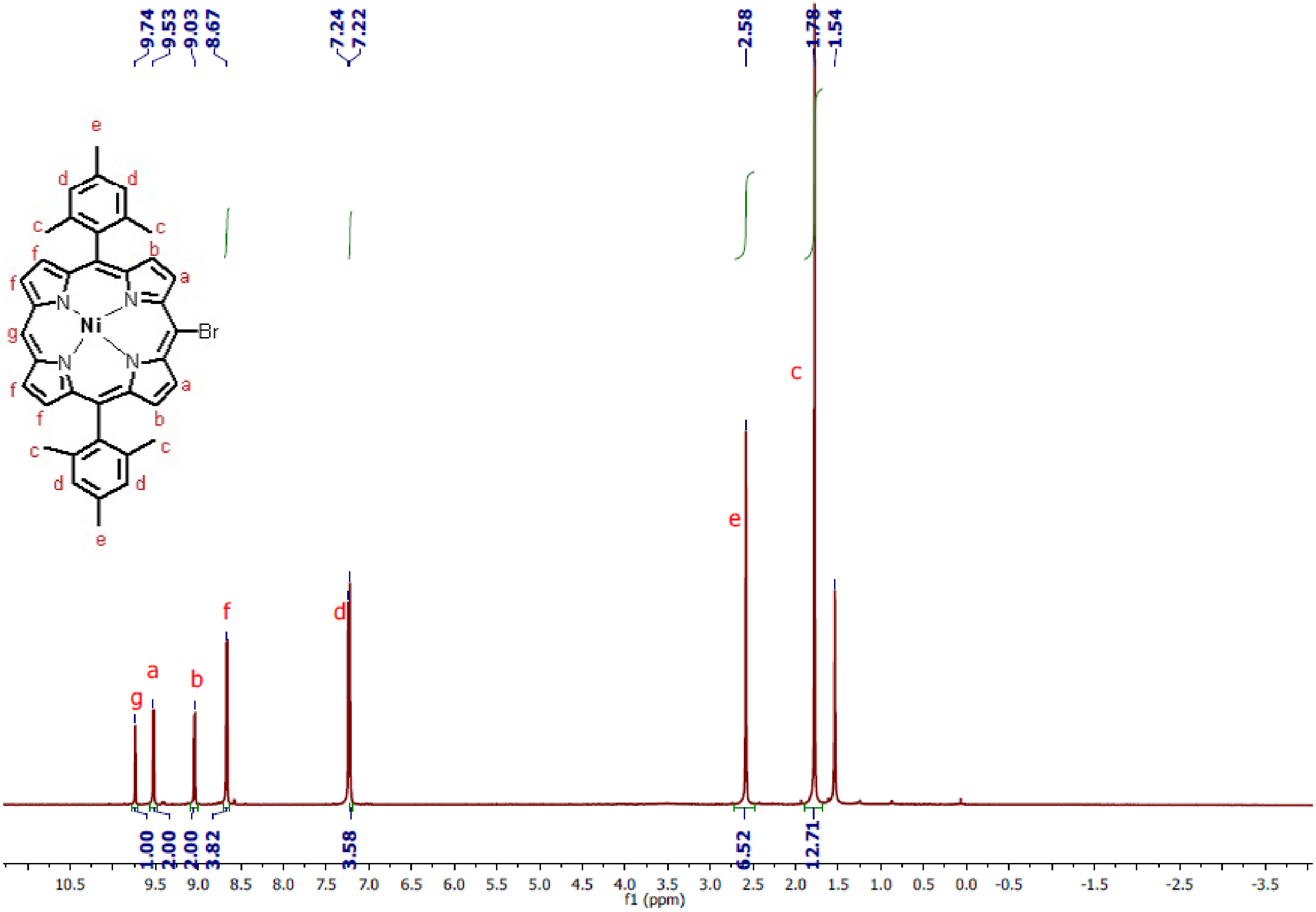


Figure S14. ^{1}HNMR spectrum of compound **7** in $CDCl_3$.

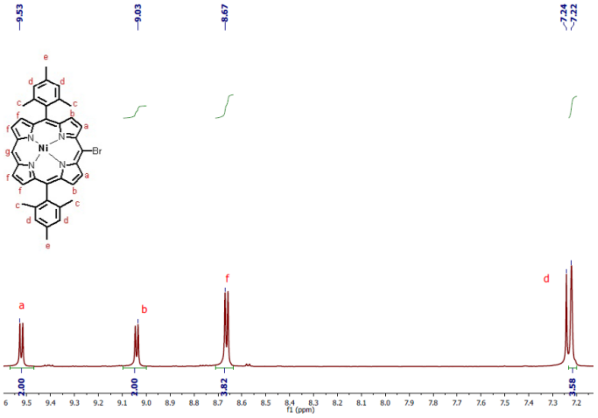


Figure S15. Partial ^{1}HNMR spectrum of compound **7** in $CDCl_3$.

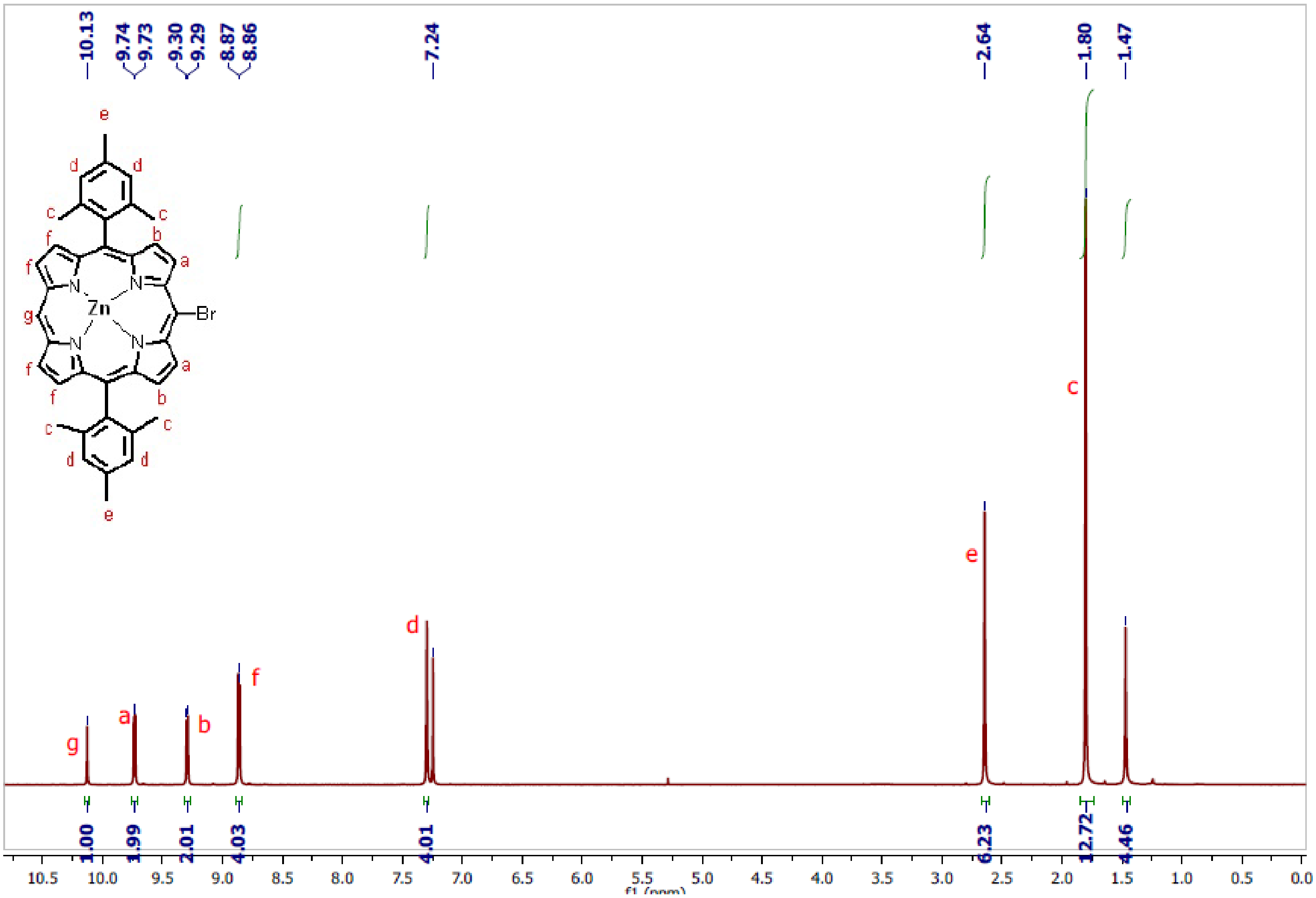


Figure S16. ^{1}HNMR spectrum of compound **9** in $CDCl_3$.

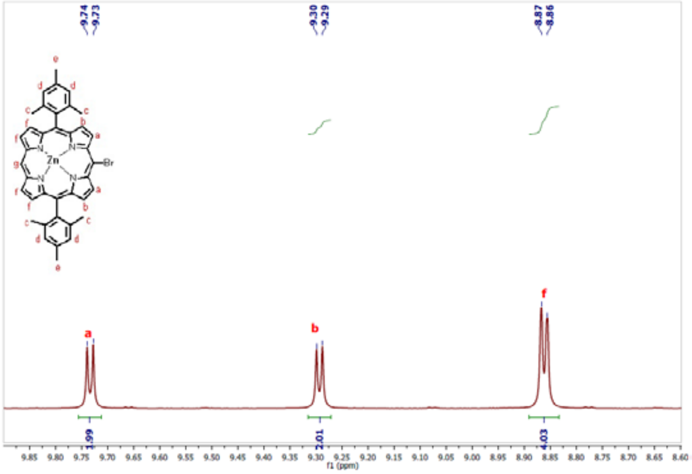


Figure S17. Partial ^{1}HNMR spectrum of compound **9** in $CDCl_3$.

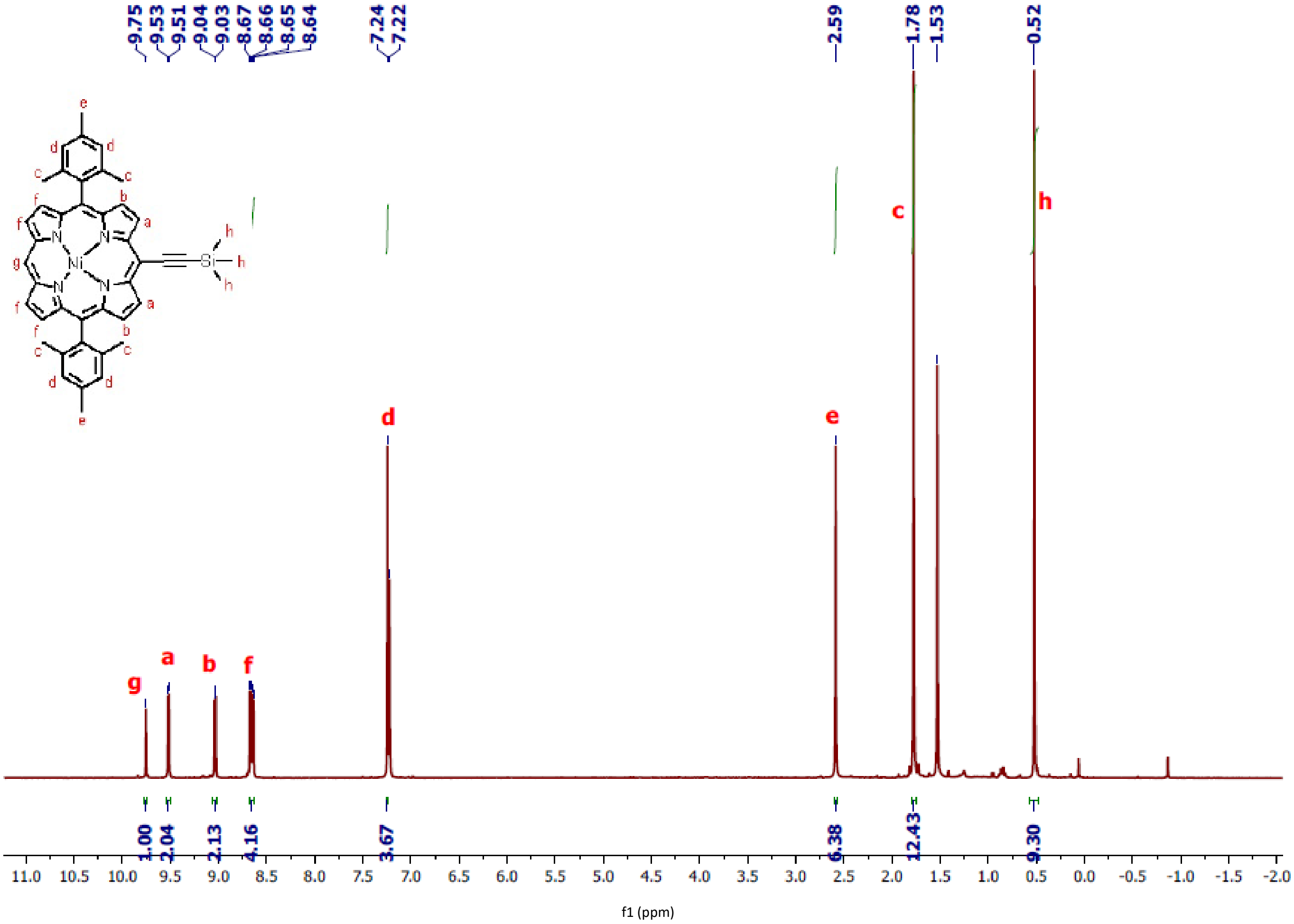


Figure S18. ^{1}HNMR spectrum of compound **7-TMS** in CDCl$_3$.

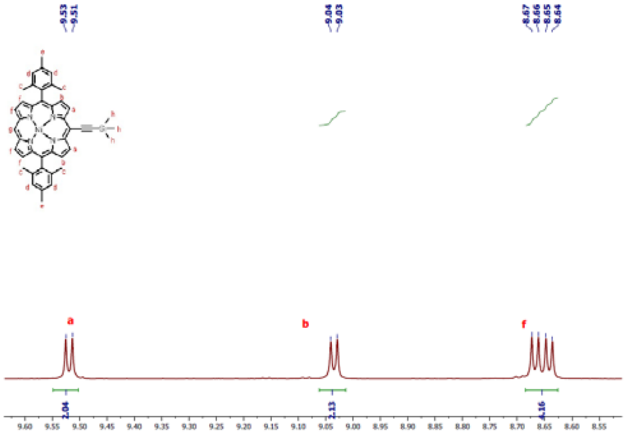


Figure S19. Partial ^{1}HNMR spectrum of compound **7-TMS** in CDCl$_3$.

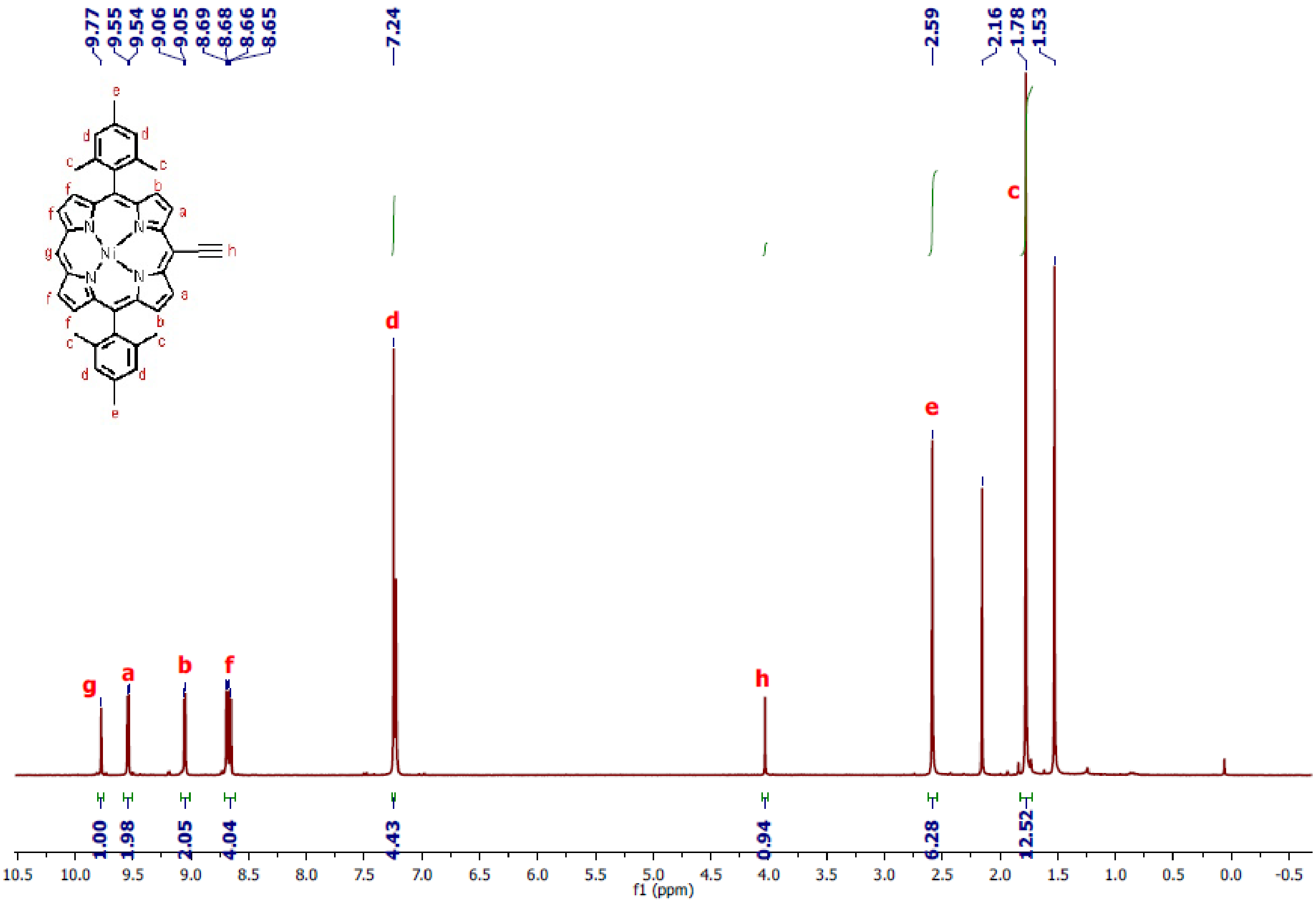


Figure S20. ^{1}HNMR spectrum of compound **7-CH** in $CDCl_3$.

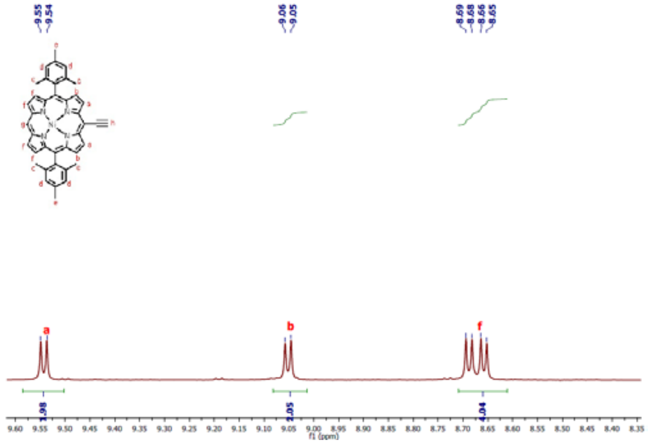


Figure S21. ^{1}HNMR spectrum of compound **7-CH** in $CDCl_3$

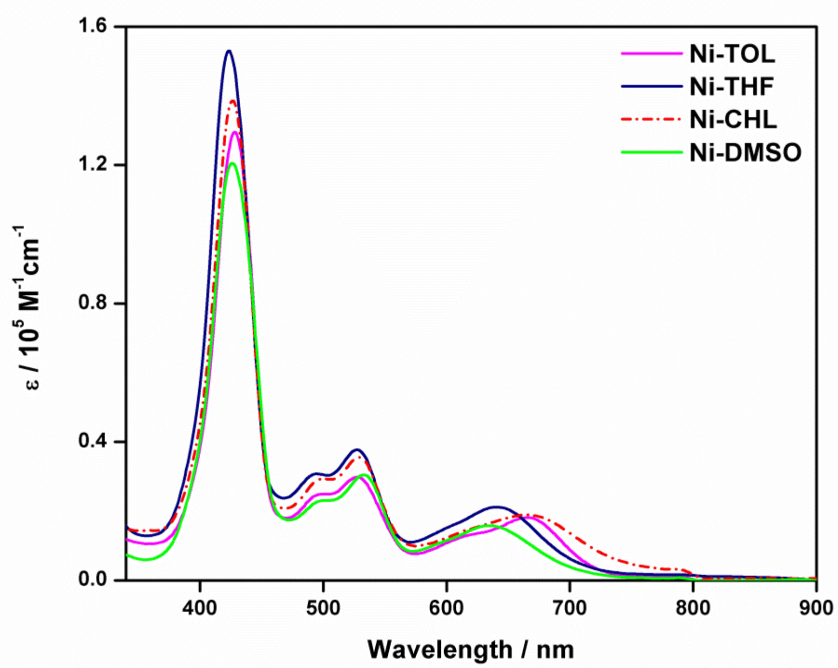


Figure S22. Absorption spectra of **1-Ni** in solvents of different polarity.

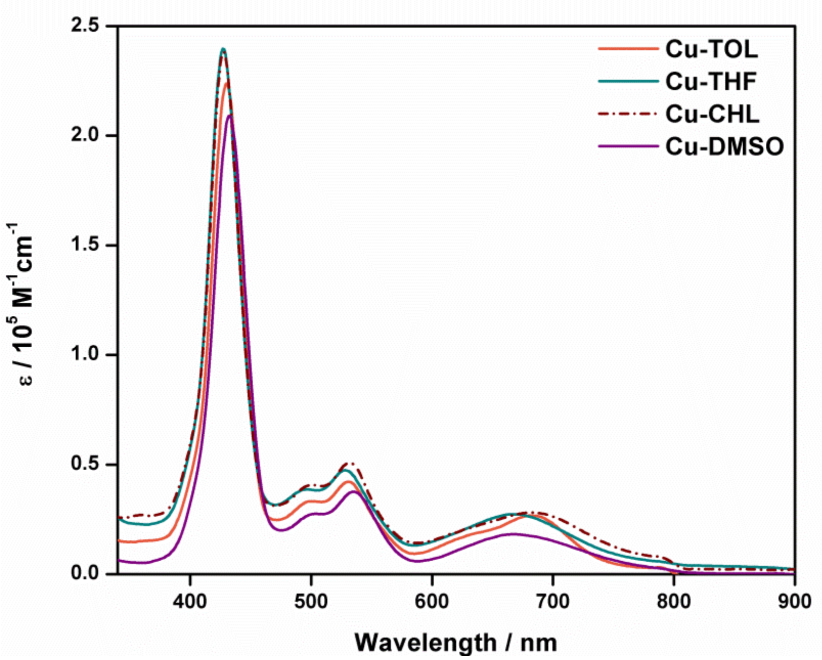


Figure S23. Absorption spectra of **2-Cu** in solvents of different polarity.

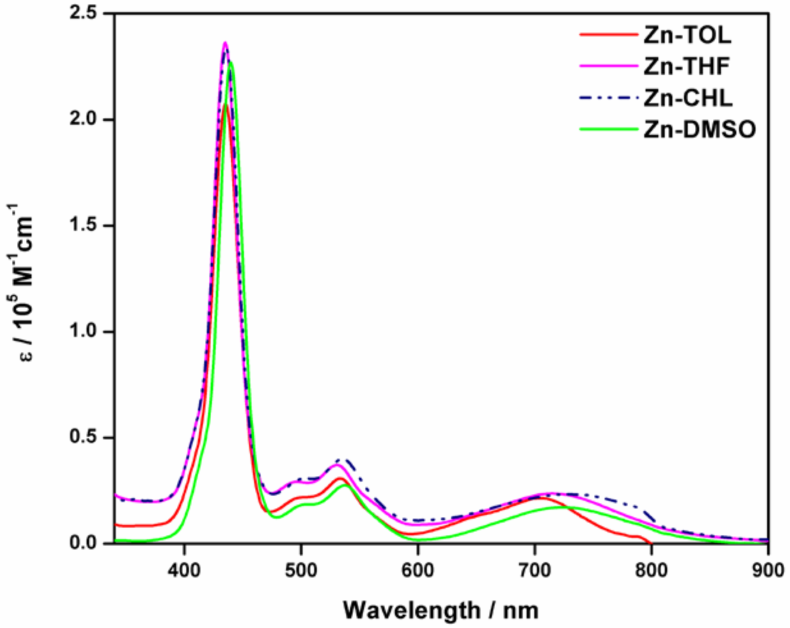


Figure S24. Absorption spectra of **3-Zn** in solvents of different polarity.

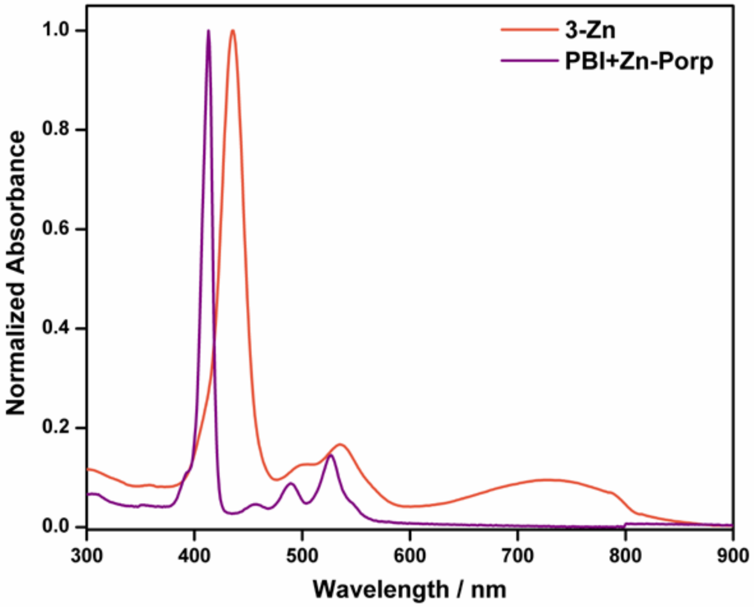


Figure S25. Absorption spectra of Electronic Absorption spectra of dyad **3-Zn** in comparison to PBI and porphyrin mixture recorded in $CHCl_3$.

Table S1 Absorption Spectroscopic Data.

Compound	λ_{max} (nm)	$\varepsilon / 10^5$ ($M^{-1} cm^{-1}$)
1-Ni	426	1.3
	499	0.3
	529	0.4
	(664CT)	0.19
2-Cu	428	2.3
	500	0.4
	532	0.5
	(682CT)	0.3
3-Zn	436	2.3
	505	0.3
	535	0.4
	(738CT)	0.23

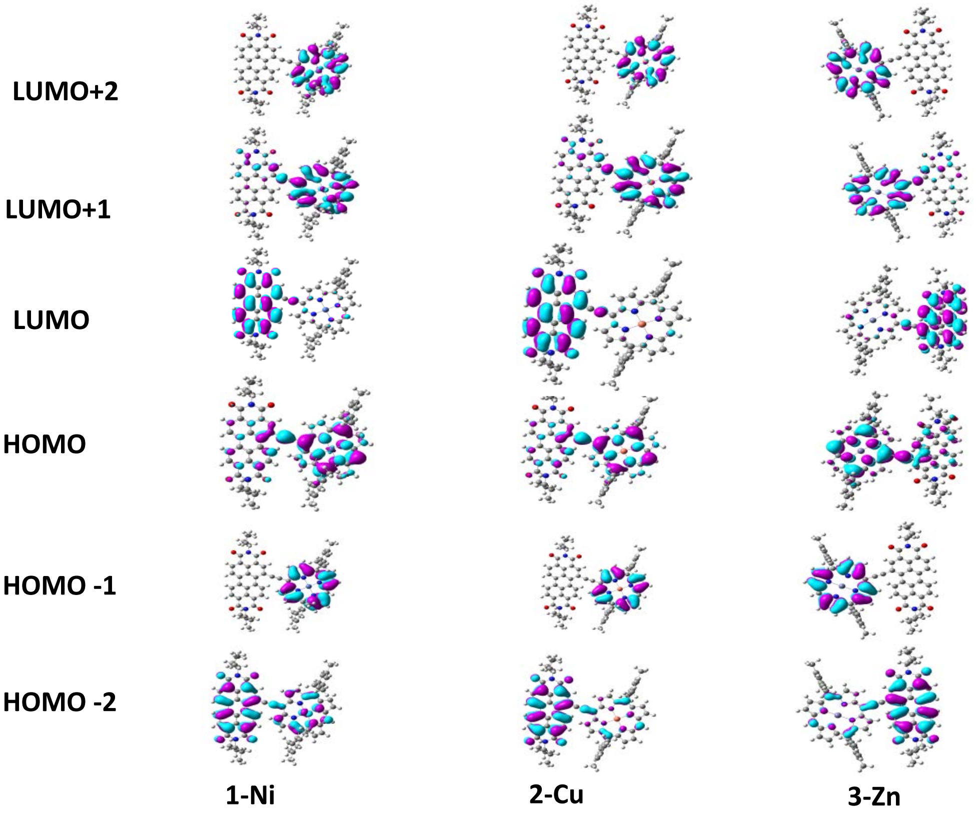


Figure S26. TD-DFT calculated frontier orbitals HOMO, HOMO-1, HOMO-2 and LUMO, LUMO+1, LUMO+2.

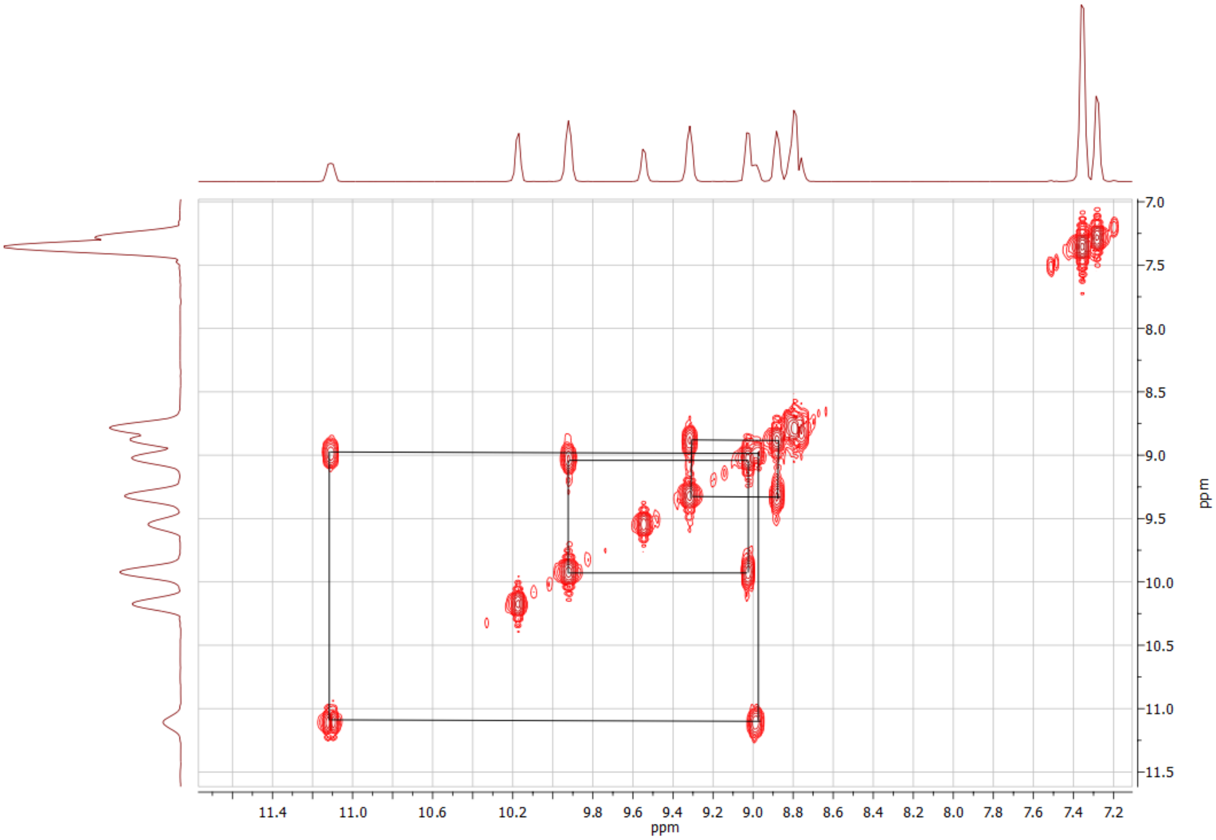


Figure S27. COSY spectrum of **3-Zn**.

Device Fabrication and Characterization

The BHJ organic solar cells were fabricated using the device architecture of glass/ITO/PEDOT:PSS/1or 2or 3: PC71BM with different weight ratios/PFN/Al. The indium tin oxide (ITO)-patterned substrates were cleaned by ultrasonic treatment in aqueous detergent, deionized water, isopropyl alcohol, and acetone sequentially and finally dried under ambient conditions. The anode consisted of glass substrates percolated with Indium Tin Oxide (ITO), modified by spin-coating with a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)PEDOT:PSS layer (40 nm) as a hole transport layer and heated for 10 min at 100°C. Mixtures of **1-Ni** or **2-Cu** or **3-Zn** with$PC_{71}BM$/ poly[(9,9-bis (3′-(N,N-dimethylamino) propyl) -2,7-fluorene-alt-2,7-(9,9-dioctylfluorene)]PC71BM (total concentration of 14 mg/ mL) with weight ratios of 1 : 0.5, 1 : 1, 1 : 2 and 1 : 2.5 in THF were prepared and then spin-cast onto the PEDOT:PSS layer and dried overnight in an ambient atmosphere. For the blend of **1** or **2** or **3** : PC71BM processed with 3% v/v pyridine in a THF solvent mixture, only the mixture with a 1 : 2 weight ratio was used. The approximate thickness of the active layers was 90 nm. A thin layer of PFN (25 nm) was deposited by spin coating from the PFN dissolved in methanol, on the top of active layer for all the devices.Finally, the aluminium (Al) top electrode was thermally deposited on the active layer in a vacuum of 10^{-5} Torr through a shadow mask area of 0.20 cm^2. All devices were fabricated and tested in an ambient atmosphere without encapsulation. The hole-only and electron-only devices with architectures of ITO/PEDOT:PSS/active layer/Au and ITO/Al/active layer/Al were also fabricated in a similar way in order to measure the hole and electron mobility, respectively. The current–voltage (J–V) characteristics of the BHJ organic solar cells were measured using a computer controlled Keithley 2400 source meter in the dark and under simulated AM1.5G illumination of 100 mW/ cm^2. A xenon light source coupled with an optical filter was used to provide stimulated irradiance at the surface of the devices. The incident photon-to-current efficiency (IPCE) of the devices was measured by illuminating the devices through the light source and a monochromator and the resulting current was measured using a Keithley electrometer under short-circuit conditions.

We estimated the maximum generation rate of charge carrier (G_{max}) according to $G_{max} = J_{ph}^{sat}/qL$, where J_{ph}^{sat} is photocurrent density at full saturation, q is electronic charge and L is the thickness of the active layer.

11 (a) J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise, and Lindsey, J. S. *Org. Process. R& D,* 2003, **7**, 799-812; (b) F. Sguerra, V. Bulach, and M. W. Hosseini, *Dalton Trans.,* 2012, **41**, 14683-14689; (c) L. Yu, K. Muthukumaran, I. V. Sazanovich, C. Kirmaier, E. Hindin, J. R. Diers, P. D. Boyle, D. F. Bocian, D. Holten, and J. S. Lindsey, *Inorg. Chem.*, 2003, **42**, 6629-6647; (d) A.K. Mandal, M. Taniguchi, J. R. Diers, D. M. Niedzwiedzki, C. Kirmaier, J. S. Lindsey, D. F. Bocian, and D. Holten, *J. Phys. Chem. A*, 2016, **120,** 9719-9731.

12 (a) H. Langhals, O. Krotz, K. Polborn, and P. Mayer, *Angew. Chem. Int. Ed.,* 2005, **44**, 2427-2428; (b) P. Rajasingh, R. Cohen, E. Shirman, L. J. W. Shimon and B. Rybtchinski, *J. Org. Chem.* 2007, **72**, 5973-5979. (c) R. Mishra, J. M. Lim, M. Son, P. Panini, D. Kim, and J. Sankar, *Chem. -Eur. J.,* 2014, **20**, 5776-5786.

13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A. 02; Gaussian, Inc., Wallingford CT, **2009**.