Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic supplementary information

Electrochemical fabrication of one-dimensional porphyrinic wires on electrodes

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S1 Experimental methods.

Synthesis of 5-(4-Nitrophenyl)dipyrromethane (S1) [23]

Pyrrole (44 mL, 634.20 mmol) and 4-nitrobenzaldehyde (3.83 g, 25.36 mmol) were added to a 200 mL of triple-neck round-bottomed flask and degassed with a stream of N_2 for 15 min. Then, trifluoroacetic acid (0.20 mL, 2.60 mmol) was added to the mixture. The solution was stirred under N_2 at room temperature for 10 min and then quenched with 0.1 M NaOH. The organic phase was extracted with dichloromethane and washed with water. The organic layer then dried over Mg_2SO_4, and the solvent was removed after filtration under reduced pressure. Purification was done by column chromatography on silica gel using CH_2Cl_2:hexane (3:1) as eluent. Yellow solid was obtained as the final product (5.035 g, 74.4% yield). Mp: 157.5−159.2 ^{o}C; 1H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.82 Hz, 2H), 8.02 (br s, 2H), 7.39 (d, J = 8.35 Hz, 2H), 6.77-6.78 (m, 2H), 6.21 (q, J = 3.03 Hz, 2H), 5.89 (s, 2H), 5.61 (s, 1H).

Synthesis of 5,15-di(4-nitrophenyl)-10,20-diphenylporphyrin (S2)[24]

Compound S1 (1.0 g, 3.74 mmol) and benzaldehyde (0.4 g, 3.74 mmol) were dissolved in 500 mL of anhydrous dichloromethane under N_2. The reaction mixture and trifluoroacetic acid (15.2 mL, 193.60 mmol) were cooled at 0 ^{0}C with an ice bath and a PTFE cannula was used to add the acid slowly into the reaction mixture. The reaction vessel was protected from light by wrapping with aluminum foil and the reaction mixture was stirred at 0 ^{0}C for 40 minutes. p-chloranil (1.84g, 7.48 mmol) was then added and the mixture continuously stirred at room temperature for 1 hour. Then, the reaction was quenched by adding triethylamine (27 mL, 193.60 mmol). Organic phase was washed with water and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and column chromatography was conducted on silica gel with dichloromethane as eluent. Purple solid was obtained as final product (1.513 g, 57.45% yield). Mp >320 ^{o}C; 1H NMR (500 MHz, $CDCl_3$) δ 8.91 (d, J = 4.61 Hz, 4H), 8.76 (d, J = 4.71 Hz, 4H), 8.65 (d, J = 8.46 Hz, 4H), 8.41 (d, J = 8.39 Hz, 4H), 8.21 (d, J = 7.42 Hz, 4H), 7.75-7.82 (m, 6H), -2.78 (s, 2H).

Synthesis of 5,15-di(4-aminophenyl)-10,20-diphenylporphyrin (S3)[25]

Compound S2 (0.5 g, 0.71 mmol) was dissolved in 300 mL of concentrated hydrochloric acid under N_2. $SnCl_2.2H_2O$ (0.96 g, 4.26 mmol) was added to the solution, and refluxed for 4 hours. The reaction mixture left to cool, and cold water was added to quench the reaction. Then, pH of the reaction mixture was adjusted to pH 8-9 with concentrated ammonium hydroxide. Dichloromethane was added to extract the organic phase and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and purification was done by column chromatography on silica gel with dichloromethane as eluent (0.151 g, 33%). Mp >320 °C; 1H NMR (500 MHz, CDCl3) δ 8.93 (d, J = 3.57 Hz, 4H), 8.83 (d, J = 3.84 Hz, 4H), 8.21-8.23 (m, 4H), 7.99 (d, J = 8.25 Hz, 4H), 7.75-7.78 (m, 6H), 7.08 (d, J = 8.28 Hz, 4H), 4.04 (s, 4H), -2.75 (s, 2H).

5,15-di(4-aminophenyl)-10,20-diphenylporphyrinatozinc(II), 1[26]

$Zn(OAc)_2$ (0.768 g, 3.50 mmol) was dissolved in 10 mL methanol and added to 100 ml reaction flask containing S3 (0.023 g, 0.035 mmol) in 40 mL dichloromethane. The reaction mixture was refluxed for 4 h with continuously stirring. TLC was used to check completion of the reaction. Once the reaction was completed, water then added and the organic phase was extracted by adding excessive dichloromethane. After extraction, the organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was passed through flash column chromatography on silica gel (eluent: CH_2Cl_2/CH_3OH = 100:5) to get purple powder (0.021 g, 79.3%). 1H NMR (500 MHz, $CDCl_3$, ppm) δ 8.94 (s, 8H), 8.24 (d, 8H, J =6.38 Hz), 7.78 (m, 12H). HR-FAB-MS: 706.1844 $[M]^+$, calcd. for: $C_{44}H_{30}N_6Zn^+$: 706.182

S2 Electropolymerization of 1 on ITO and SnO_2.

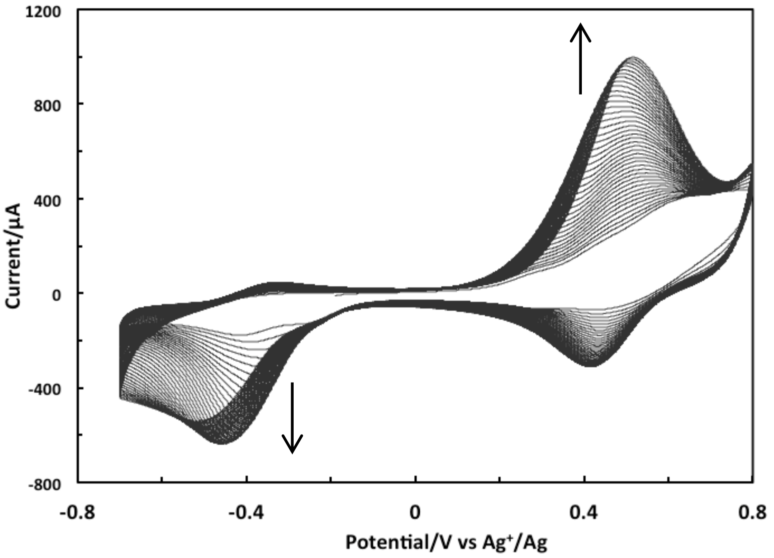

Fig. S1 Cyclic voltammogram for 1 (2 mM) upon repetitive scans (from 1st to 50th cycles) in 0.1 M Bu_4NClO_4- CH_2Cl_2 at ITO.

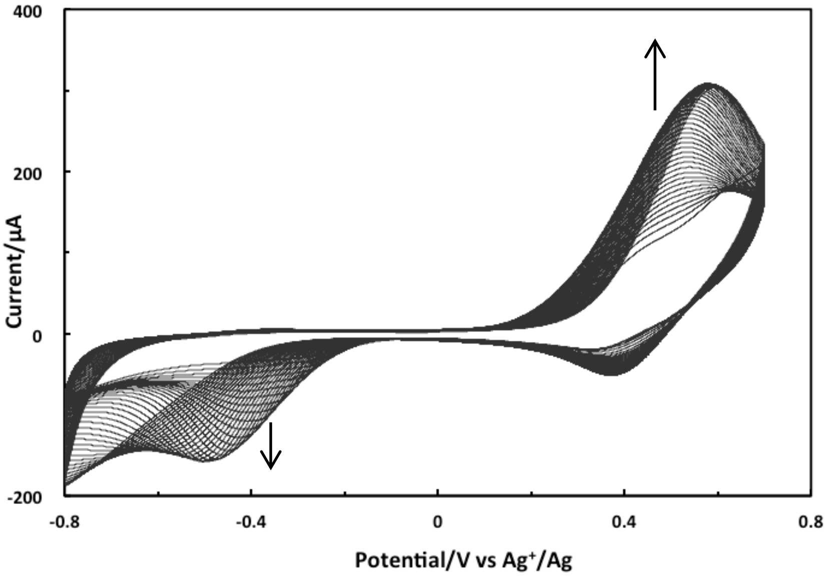

Fig. S2 Cyclic voltammogram for **1** upon repetitive scans (from 1st to 50th cycles) in 0.1 M Bu_4NClO_4-CH_2Cl_2 at SnO_2.