Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Sub-phthalocyanine incorporated Fe(II) metallo-supramolecular polymer exhibiting blue-to-transmissive electrochromic transition with high transmittance and coloration efficiency

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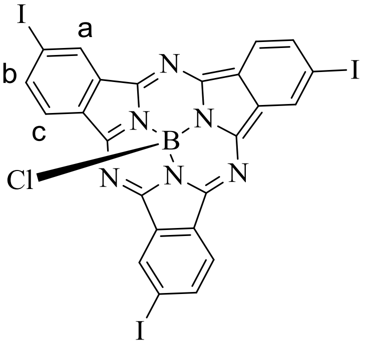
Synthesis of 1(tri-iodo-subphthalocyanine):

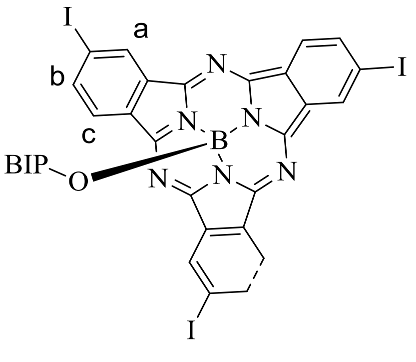
1



4-iodo phthalonitrile (1 g, 0.0039 mol) was dissolved in 10 ml of *o*-dichlorobenzene and purged with argon gas for 10 mins, after that, slowly added 0.46 g (4 ml)(0.0039 mol) of BCl_3.xylene, then stirred at 140 °C for 6 hour. The completion of reaction was confimed by TLC and then cooled to room temperature. The solvent was evaporated under the reduced pressure and the crude product was purified by column chromatography (silica gel; hexane: DCM). The product was obtained as a purple solid (yield 51 %, m.p. >250 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm): 9.18 (d,J_m = 1.4 Hz, 3H, Ha), 8.54 (d, J_o = 7.8 Hz, 3H, Hc), 8.20 (dd, J_o = 7.8. Hz ,J_m = 1.4 Hz, 3H, Hb).

Synthesis of 2 (PIB-tri-iodo-subphthalocyanine):

2

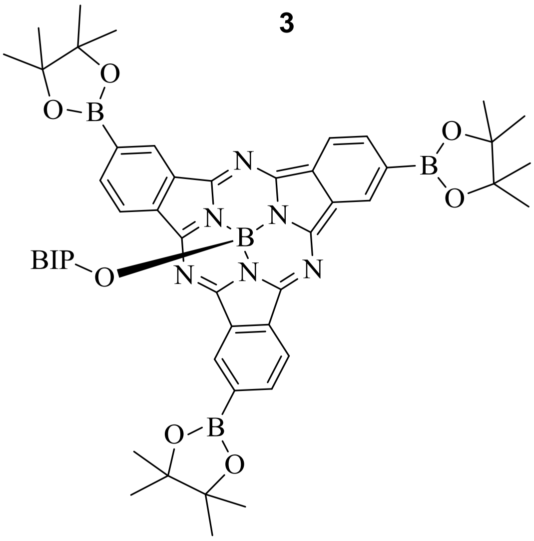


Tri-iodo-subphthalocyanine **1** (0.5 g, 0.00061 mol) was dissolved in 15 ml of o-dichlorobenezene and then hydroxyl terminated poly-isobutylene(PIB-1000) 0.75g (0.00074) was added and stirred at 140 °C for 10 hour, after that, the reaction mass was cooled to room temperature and the solvent was evaporated under the reduced pressure. The crude was purified by colum chromatography (silica gel 60-200; hexane) and the product was obtained as a purple viscous solid (yield 84%).^{1}H NMR (500 MHz,

$CDCl_3$) δ(ppm): 9.19 (d,J_m = 1.4 Hz, 3H, Ha), 8.54 (d, J_o = 8.3 Hz 3H, Hc), 8.20 (dd, J_o = 8.3 Hz ,J_m = 1.4 Hz, 3H, Hb), 1.6-0.9(multiple peaks-poly isobutylene).

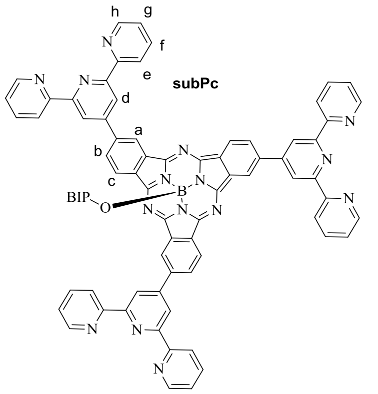
Synthesis of 3 (PIB-tri-pinacoloborate-subphthalocyanine):

3



PIB-tri-iodo subphthalocyanine **2** (0.5 g, 0.00027 mol) and bis(pinacolato)diboron (0.23g, 0.00090 mol) was dissolved in 10 ml of dry DMSO under argon atmosphere and continued the argon gas purging, after 15 mins anhydrous potassium acetate (KOAc) (0.23g, 0.0023 mol) and [1.1-bis(diphenylphosphino)ferrocene]dichloropalladium(II).complex with dichloromethane ($PdCl_2(dppf).CH_2Cl_2$) (0.020g) were added consequently and stirred at 80 °C for 16 hour. The completion of reaction was confirmed by TLC and the product was extracted with toluene and washed with water and dried over magnesium sulfate, after that filtered and the solvent was removed under the reduced pressure. The solid residue was dissolved in cold hexane and filtered, the product was obtained as a pink viscous liquid after the evaporation of hexane (Yield 60%).^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm): 9.26 (d,J_m = 1.8 Hz, 3H, Ha), 8.60 (d, J_o = 8.2 Hz 3H, Hc), 8.28 (dd, J_o = 8.2 Hz ,J_m = 1.8 Hz, 3H, Hb), 1.6-0.9(multiple peaks-polyisobutylene and boronic ester methyl protons).

Synthesis of subPc ligand (tri-terpyridine subphthalocyanine):



subPc

3 (0.18 g, 0.0001 mol) and 4’-bromo-2,2’:6’,2’’-terpyridine (0.1092 g, 0.00035 mol) was dissolved in anhydrous toluene (5ml) and H_2O (5ml) under argon atmosphere and purged argon for 20 min. Cesium carbonate (0.1137 g, 0.00035 mol) and [1.1-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.010 g) were added consequently and stirred at 90 °C for 15 hour. After that, the product was extracted with toluene and washed with excess of water and dried over magnesium sulfate. After filteration and evaporation the solid residue was purified by column chromatography (neutral alumina, DCM:Methanol) and obtained the product as a pink solid (yield 47%, m.p. >250 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm): 8.95-8.44(m, Ha, Hb, Hc, Hh), 7.61-7.30(m, Hd, He,Hf, Hh), 1.6-0.9(multiple peaks-polyisobutylene). MALDI-TOF MS calculated: 2104.41: found: cleaved product mass.

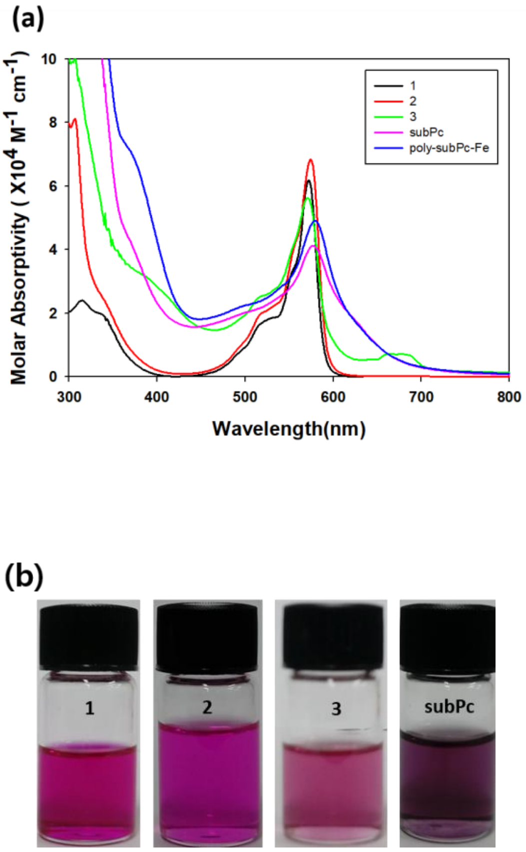


Fig. S1 (a) Molar absorptivity of **1**, **2**, **3**, and **subPc** in DCM and **poly-subPc-Fe** in DMF; (b) photo-images of **1**, **2**, **3** and **subPc** in DCM.

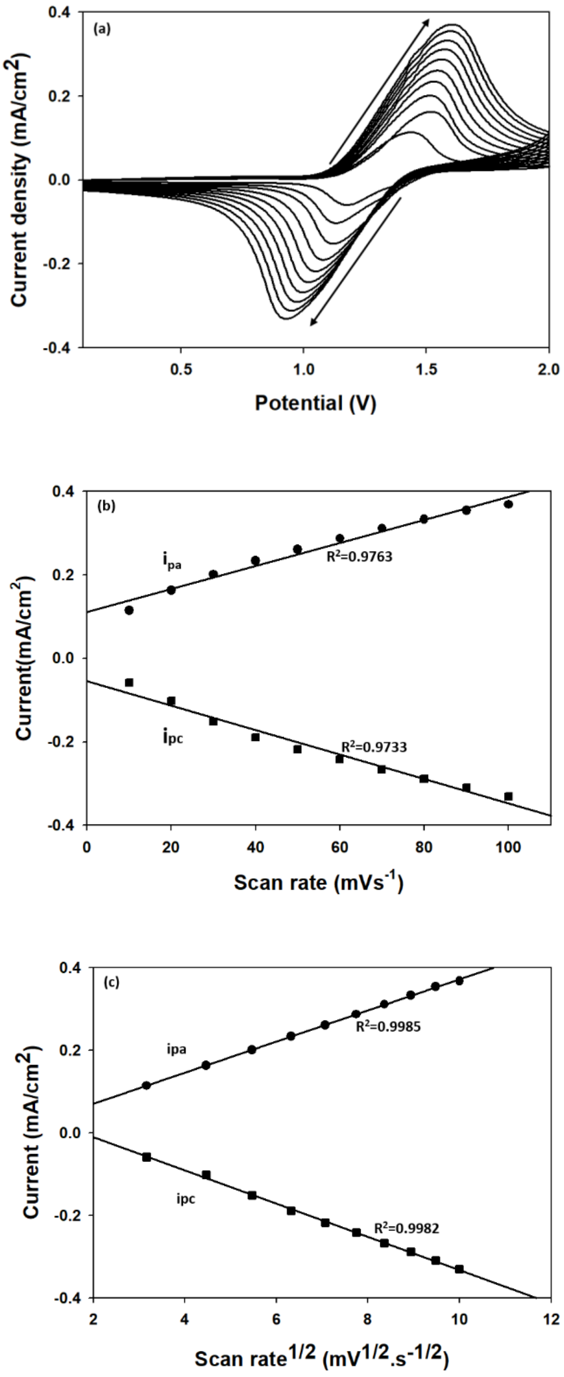


Fig. S2 (a) Cyclic volatammograms of **poly-subPC-Fe** film at different scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV/s). Linear relationship between the anodic and cathodic peak currents in the oxidation of Fe(II) with (b) the scan rate and (c) the square root of scan rate.

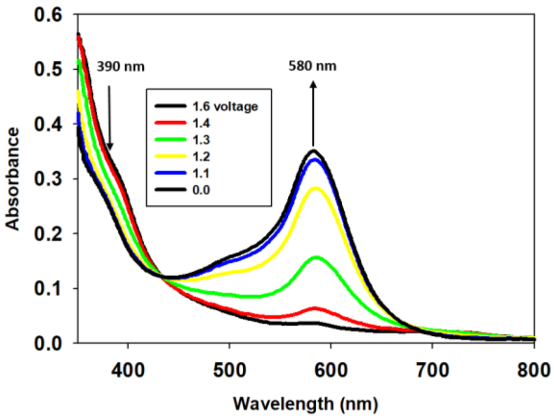


Fig. S3 Change in absorbance at 580 nm of **poly-subPc-Fe** coated on ITO glass by applying voltage from +1.6 to 0.0.

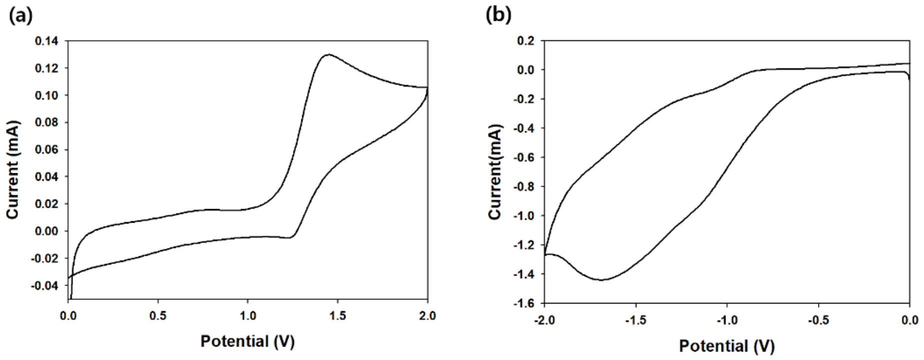


Fig. S4 Cyclic voltammograms of **subPc** film (a) oxidation, (b) in 0.1M TBAP/DCM solution at scan rate of 100 mV s^{-1}.

Table S1 Optical and electrochemical properties of **subPc**.

λ_{abs} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	E_{ox}	$E_{ox,onset}$	HOMO (eV)	E_{red}	$E_{red,onset}$	LUMO (eV)	E_g^{ec} (eV)
575, 623(sh)	676	1.83	1.45	1.12	-5.92	-1.69	-0.77	-4.19	1.89

Sh=sholulder peak; E_g^{opt}=1240/λ_{onset}; HOMO=-($E_{ox,onset}$ vs. $E_{ferrocene}$)-4.8; LUMO=-($E_{red,onset}$ vs. $E_{ferrocene}$)-4.8; E_g^{opt}=optical band-gap; E_g^{ec}=electrochemical band-gap

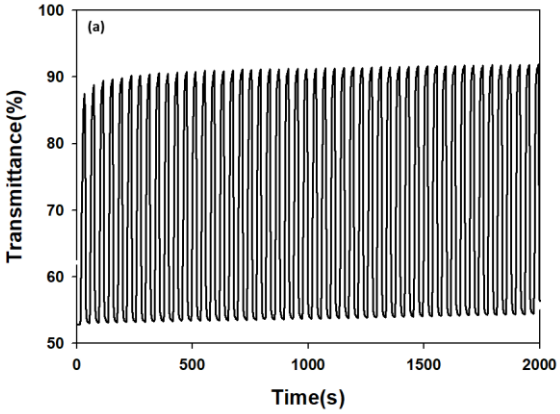
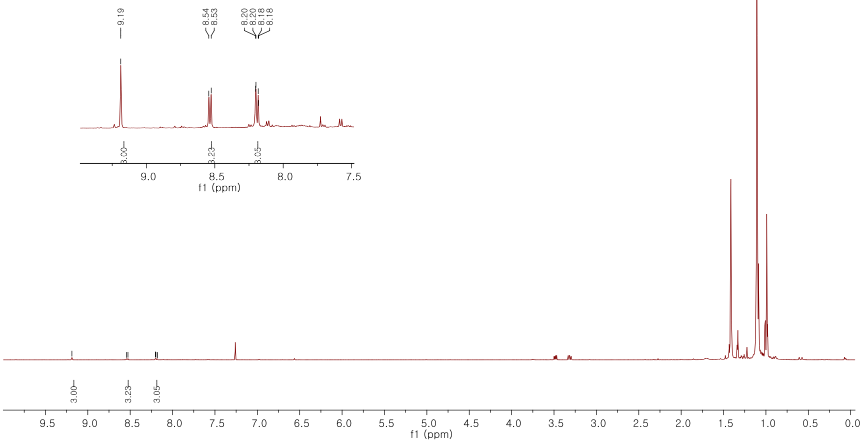
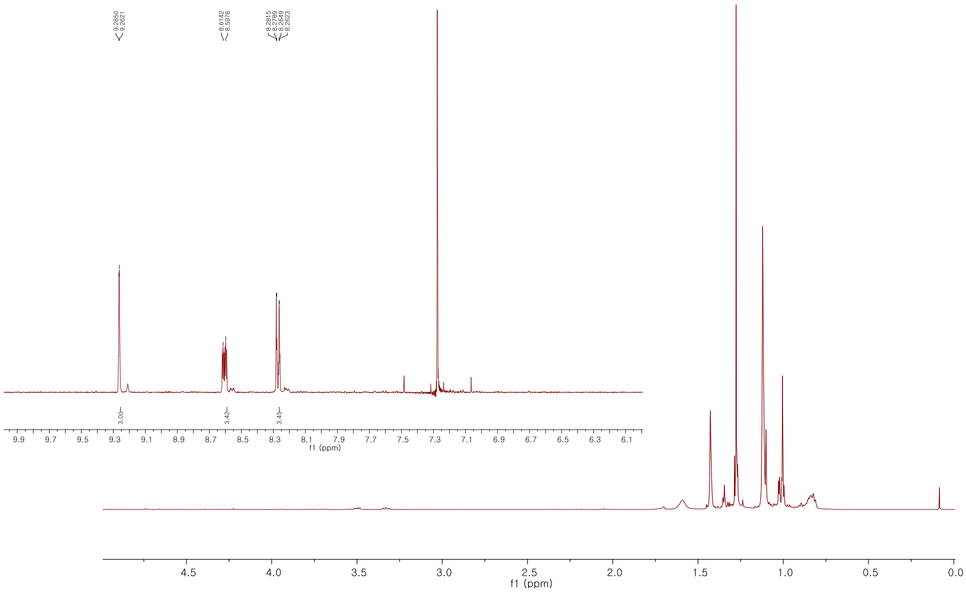


Fig. S5 Cyclic stability test of **poly-subPc-Fe** by monitoring the change in absorbance at 580 nm by switching the potential between 0.0 to +1.6 V (time interval of 20 s for both bleached and colored state) in 0.1 M TBAP/ DCM.

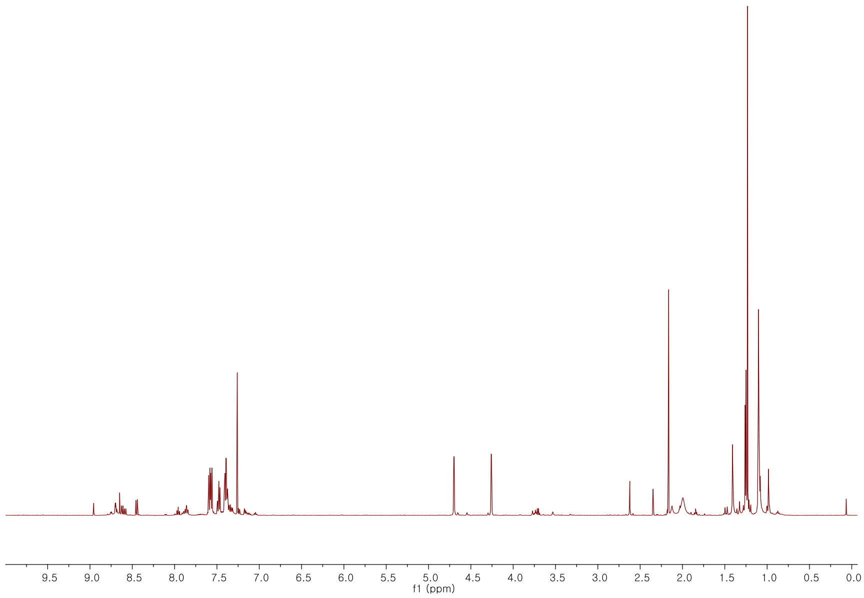
^{1}H-NMR spectrum of **2**



^{1}H-NMR spectrum of **3**



^{1}H-NMR spectrum of **subPc**



MALDI-TOF MS spectrum of **subPc**