Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Vice-Versa Donor Acceptor Fluorene-Ferrocene Alternate Copolymer: A Twisted Ribbon for Electrical Switching

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Table of Content

1. Materials

All the reagents ($CuBr_2$, Fluorene, 1-bromooctane, alumina, malononitrile, 1,1′-ferrocenediboronicacid, $Pd(PPh_3)_4$, Bromobenzene, and TBAB from Sigma-Aldrich and rest from Merck India) were used without further purification. All the experiments were performed at room temperature. All the solvents (DMSO, THF, CH_2Cl_2 and acetic acid) were used after distillation. Suzuki coupling reaction was conducted under N_2 environment and avoiding light exposure.

2. Instrumentation

The ^1H NMR spectra were acquired on a 300 MHz Bruker DPX spectrometer, using $CDCl_3$ as solvent and TMS as standard reference, with chemical shift given in parts per million. The two polymers PFFC-1 and PFFC-2 were synthesized according to Scheme 1. The FTIR spectra were recorded in an FTIR-8400S instrument (Shimadzu) using the KBr pellets of the samples. The high resolution mass spectra of the samples were recorded from their acetonitrile solution in a quadrupole time-of-flight (Qtof) Micro YA263 mass spectrometer. The UV-Vis spectra of all samples were studied with Hewlett-Packard UV-Vis spectrophotometer (model 8453). Fluorescence studies of all samples were carried out in a Horiba Jobin Yvon Fluoromax 3 spectrometer. The CD spectra of all the solutions were taken in a spectro polarimeter (JASCO, model J-815) in a 1 mm quartz quvette. Cyclic Voltammetry was performed by Metrohm Autolab Electrochemical Analyzer with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium hexafluorophosphate solution in CH_2Cl_2 at room temperature under nitrogen atmosphere with a scanning rate of 100 mVs^{-1}. A glassy carbon working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ (0.01 M in acetonitrile) reference electrode were used. Polymer concentration used 2 mg/5 mL in every set of the experiments. Gel-permeation chromatography (GPC) was performed on a Shimadzu size-exclusion chromatographer (SEC) equipped with a guard column and a styragel HT-6E (7.8x 300 mm, Waters) column with differential refractive index and UV/Vis detection by using THF as an eluent (1 mL/min at 35 ^{o}C) and polystyrene standard. To investigate the morphological features of the PFFC-1 during oxidation, scanning electron microscope (SEM) studies were performed through a FESEM instrument (JEOL, JSM 6700F) operating at 5 KV. PFFC-1 was dissolved in minimum amount of $CHCl_3$ and methanol and hexane (1:1) were added gently to the polymer solution and kept overnight for self-assembly. The SEM images was taken by taking the interface layer of methanol and hexane (1:1) mixture. The devices ITO/PEDOT:PSS/PFFC-1/Al and ITO/PEDOT:PSS/PFFC-2/Al were fabricated by the following way. At first, the ITO coated glass was cleaned ultrasonically in ethanol, methanol and acetone sequentially. PEDOT:PSS was spin-coated onto the ITO substrate and dried at 110 ^{o}C for one hour. The active layer of polymers were deposited from the THF solution (10 mg/mL) onto the PEDOT:PSS layer by spin coating. Aluminium electrode was deposited by thermal evaporation to complete the devices. *J-V* properties of the devices were measured a four-probe method using an electrometer (Keithley model - 617). The curve was recorded by scanning the initially applied voltage from -3 to +3 V and ended at -3 V.

The DFT calculation was done by taking one repeating unit of PFFC-1, PFFC-2 and oxidized product of PFFC-1. Geometry optimization was performed at spin unrestricted DFT with Becke's [S1] three parameters hybrid exchange functional with the Lee-Yang-Parr [S2] correlation (B3LYP) along with 6-31G(d) basis set for all atoms. All the electronics structure calculations were performed using the Gaussian 09 suite of quantum chemistry programs.[S3]

3. Synthesis of compounds

3.1 Synthesis of 2,7-dibromofluorene (1)

i) Preparation of $CuBr_2$ on Alumina: To a solution of copper (II) bromide (10 g, 44.8 mmol) in distilled water (100 mL) was added 20 g of neutral alumina (150 mesh). The water was removed under reduced pressure in fridge dryer, and the dry mixture gave a brown powder. The solid was dried overnight at 90 °C in vacuum.

ii) Synthesis of 2,7- dibromofluorene: To a solution of fluorene (1.5 g, 9.0 mmol) in CCl_4 (80 mL) was added 30 g of copper (II) bromide on alumina. The mixture was stirred at reflux for 5 h. Then, the solution was cooled to room temperature and the solid material was filtered and washed with CCl_4 (50 mL). The organic solution was dried over magnesium sulfate. Removal of solvent produced 2.87 g (98%) of the title product as yellow solids. Recrystallization was made in a mixture of ethyl acetate/ hexane (5:95 v/v) to give pale yellow crystals as pure product **1.** ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.65 (2H, s) 7.60 (2H, d, $J = 8$ Hz) 7.51 (2H, dd, $J = 8$ Hz), 3.85 (2H, s). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 144.92, 139.81, 130.27, 128.43, 121.31, 121.07, 36.68. HRMS. Calculated for $C_{13}H_8Br_2$: 321.898. Found: 321.769.

3.2 Synthesis of 2,7-Dibromofluoren-9-one (2)

To a suspension of 2,7-dibromofluorene (1 g, 3.1 mmol) in anhydrous acetic acid (10 mL), was added a solution of chromium oxide in anhydrous acetic acid (10 mL, 10%). The mixture was stirred at room temperature for 6 h and pH of the mixture was neutralized by addition a solution of sodium bicarbonate. The yellow solid was filtered through a Buchner funnel and was washed with H_2O to give a residue, which was purified by recrystallization in ethanol/toluene, giving 2,7-dibromofluoren-9-one (2) 1.02 g (98%) as a yellow solid, ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.76 (2H, s) 7.63 (2H, dd, $J = 8$ Hz) 7.61 (2H, dd, $J = 8$ Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 142.15, 137.36, 135.35, 130.27, 123.21, 121.74, 121.07. HRMS. Calculated for $C_{13}H_6Br_2O$: 337.994. Found: 337.881.

3.3 Synthesis of 9,9-dioctyl-2,7-dibromofluorene (3)

2,7-Dibromofluorene (1.61 g, 5 mmol) was added to a mixture of aqueous potassium hydroxide (100 mL, 50 wt%), tetrabutylammonium bromide (0.330 g, 1 mmol) and 1-

bromooctane (9.65 g, 50 mmol) at 75°C in N_2 atmosphere. After 15 min, the mixture was cooled to room temperature. After extraction with CH_2Cl_2, the combined organic layers were washed successively with water, aqueous HCl (1 M), again water, and brine and then dried over Na_2SO_4. After removal of the solvent and the excess 1-bromooctane, the residue was purified by silica-gel column chromatography using hexane and dichloromethane (1:2) as the eluent to give 1.22 g (72%) of pale yellow title product. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.61 (2H, s) 7.43-7.55 (4H, m), 1.88-1.93 (4H, m), 1.09-1.25 (20H, m), 0.82-0.88 (6H, m), 0.57 (4H, m). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 148.82, 140.31, 131.07, 129.13, 121.45, 121.23, 56.71, 40.23, 30.22, 29.94, 29.76, 29.22, 23.26, 22.83, 14.12. HRMS. Calculated for $C_{29}H_{40}Br_2$: 548.440. Found: 548.239.

3.4 Synthesis of (2,7-dibromo-9*H*-fluoren-9-ylidene)-malononitrile (4)

A mixture of 2,7-dibromofluoren-9-one (203 mg, 0.60 mmol) and malononitrile (43.6 mg, 0.66 mmol) in dry DMSO (3 mL) was heated at 110 °C for 5 h, during which the starting yellow suspension turned dark red. The red crystal was then filtered off and washed with acetonitrile and dried under vacuum at 60 °C to give 4 in almost quantitative yield (224 mg, 97%). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.50 (2H, s) 7.67 (2H, dd, $J = 8$ Hz) 7.44 (2H, d, $J = 8$ Hz). HRMS. Calculated for $C_{16}H_6Br_2N_2$: 386.040. Found: 385.921.

3.5 Synthesis of polymer PFFC-1

In a three-necked flask, 9,9-dioctyl-2,7-dibromofluorene (3) (823 mg, 1.5 mmol), 1,1′-ferrocenediboronicacid (410 mg, 1.5 mmol) and 3.6 mL of anhydrous toluene were added. The air-sensitive catalyst $Pd(PPh_3)_4$ (2 mol %, 0.034 g) was added into the mixture under a nitrogen atmosphere. Degassed 2 M aqueous potassium carbonate (2.4 mL, 4.8 mmol) was transferred to the mixture via syringe. The reaction mixture was stirred and heated under nitrogen at 85 °C for 72 h. At the end of polymerization, the terminal boronic ester group was end-capped by adding excess bromobenzene (37.0 mg, 0.15 mmol) and refluxing 12 h. The reaction mixture was cooled to about 50 °C and slowly added to a vigorously stirred mixture of methanol (100 mL) and 1 M aqueous HCl (10 mL). The precipitate was collected by filtration from methanol. The polymers were further purified by Soxhlet extraction in acetone for 2 days to remove oligomers and catalyst residues. The final polymer PFFC-1 was obtained as a yellow solid with a yield of 0.51 g (58.0%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.75-7.10 (6H, br, fluorene), 4.45 (2H, br-d, J = 4.8 Hz, ferrocene), 4.18 (2H, br-d, J = 4.8 Hz, ferrocene), 1.92 (4H, br, fluorene aliphaltic), 1.28-0.90 (20H, br, fluorene aliphaltic), 0.72 (14H, br, fluorene aliphaltic). GPC study (THF, Polystyrene standard): M_w = 11643 and PDI = 1.49.

3.6 Synthesis of polymer PFFC-2

In a three-necked flask (2,7-dibromo-9*H*-fluoren-9-ylidene)-malononitrile (4) (579 mg, 1.5 mmol), 1,1′-ferrocenediboronicacid (410 mg, 1.5 mmol) and 3.6 mL of anhydrous toluene were added. The air-sensitive catalyst $Pd(PPh_3)_4$ (2 mol %, 0.034 g) was added into the mixture under a nitrogen atmosphere. Degassed 2 M aqueous potassium carbonate (2.4 mL, 4.8 mmol) was transferred to the mixture via syringe. The reaction mixture was stirred and heated under nitrogen at 85 °C for 72 h. At the end of polymerization, the terminal boronic ester group was end-capped by adding excess bromobenzene (37.0 mg, 0.15 mmol) and refluxing 12 h. The reaction mixture was cooled to about 50 °C and slowly added to a vigorously stirred mixture of methanol (100 mL) and 1 M aqueous HCl (10 mL). The precipitate was collected by filtration from methanol. The polymers were further purified by Soxhlet extraction in acetone for 2 days to remove oligomers and catalyst residues. The final polymer PFFC-2 was obtained as a brawn solid with a yield of 0.40 g (52.0%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.77 (2H, br, fluorene), 7.61 (2H, br, fluorene), 7.37 (2H, br, fluorene), 5.80 (2H, br, ferrocene), 5.01 (2H, br, ferrocene). GPC study (THF, Polystyrene standard): M_w = 15,706 and PDI = 2.47.

4. ^{1}H NMR signals polymers

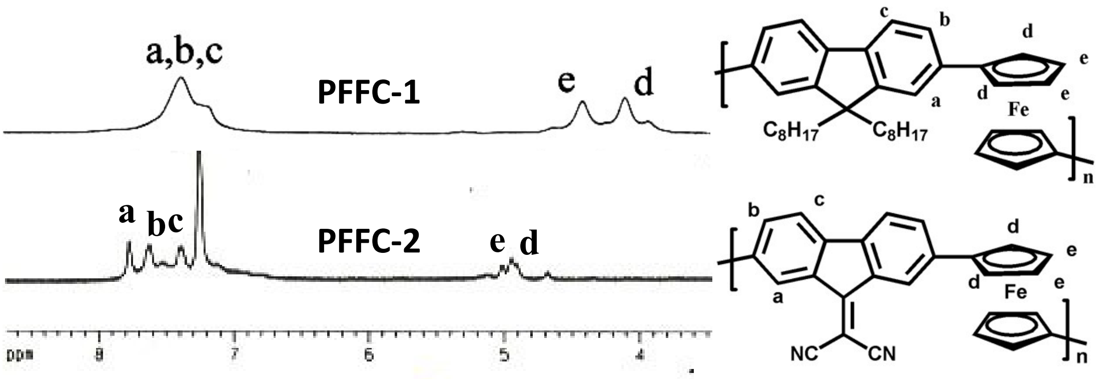

Fig. S1 ^{1}H resonance of protons on ferrocene and fluorene segments in the range of 3.5-8.5 ppm in PFFC-1 and PFFC-2. Corresponding structural formula of polymers are given in right panel. Assignments of corresponding protons are also shown.

5. ^{1}H-NMR Titration upon addition $FeCl_3$

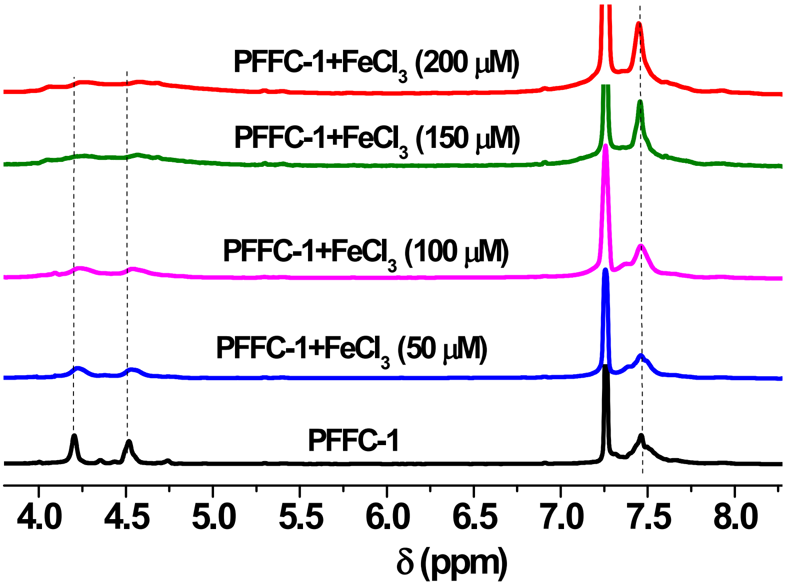

Fig. S2 ^{1}H-NMR titration plot of PFFC-1 upon successive addition of $FeCl_3$ in $CDCl_3$ (300 MHz) at room temperature.

This titration suggests that the upon oxidation when Fe(II) is converted to Fe(III) in Fc unit of PFFC-1, the protons of Fc unit are shifted to downfield i.e. higher δ value (4.18 to 4.25 ppm and 4.45 to 4.58ppm) than pristine PFFC-1.

6. Photoluminescence spectra

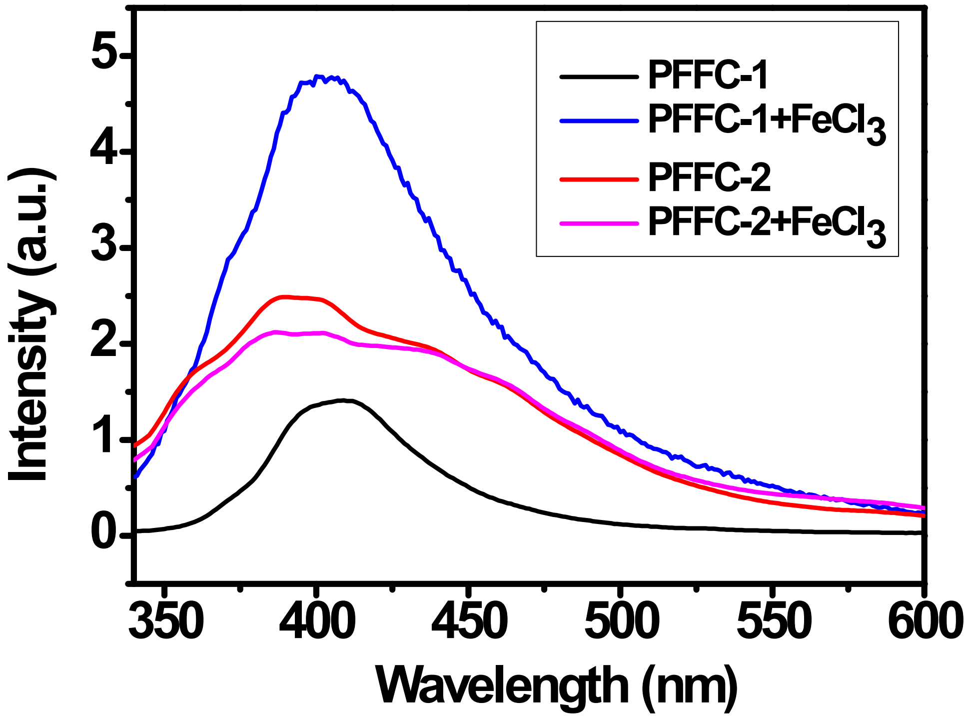

Fig. S3 Photoluminescence spectra of PFFC-1 and PFFC-2 before and after oxidation by $FeCl_3$ in $CHCl_3$ solution (excitation wavelength 330 nm)

7. Cyclic voltametry

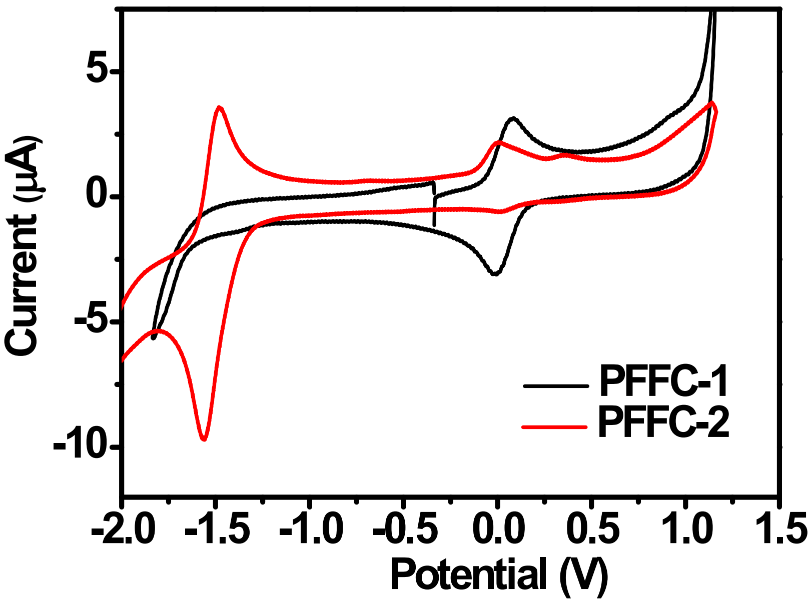

Fig. S4 Cyclic voltammograms of PFFC-1 and PFFC-2 measured in a CH_2Cl_2 solution of 0.1 M tetrabutylammonium hexafluorophosphate at 100 mV/s.

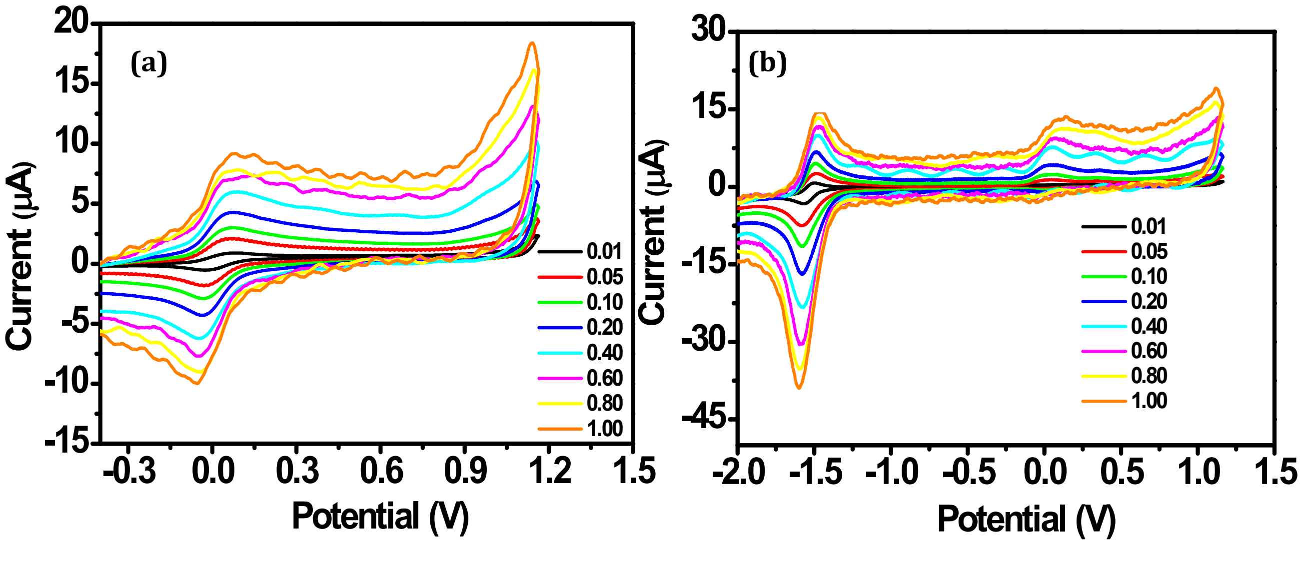

Fig. S5 Scan rate dependent cyclic voltammograms of (a) PFFC-1 and (b) PFFC-2, measured in a CH_2Cl_2 solution of 0.1 M nBu_4NPF_6 at 100 mV/s.

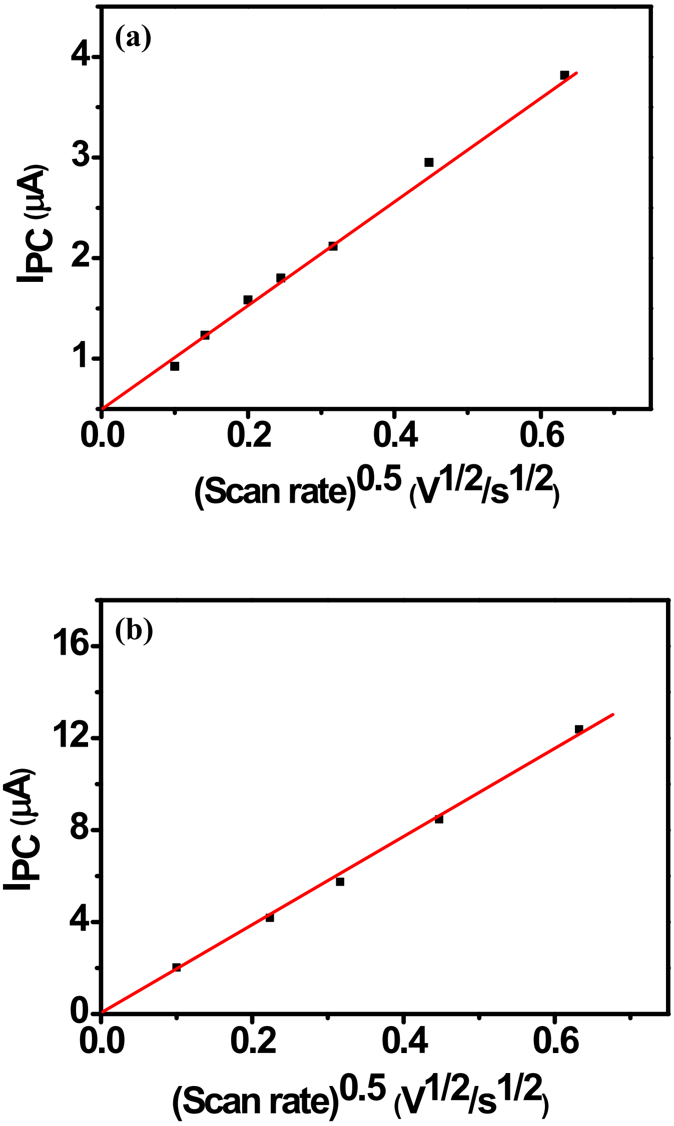

Fig. S6 (a) and (b) plot of I_{PC} against square root of the scan rate of PFFC-1 and PFFC-2 respectively.

The scan rate dependent cyclic voltammetry studies of **PFFC-1** and **PFFC-2** have been performed at various scan rates from 0.01 to 1.0 V/s (Fig. S5a-b). The anodic current increases with the increasing of scan rate, and the corresponding oxidation potentials are remain independent. When oxidative peak current IPC is plotted against square root of the scan rate, linearity of the plot indicates that the oxidation waves are diffusion controlled in nature.

8. Cottrell equation

As oxidation waves in both of the polymers are diffusion controlled by the linear dependence of the oxidative peak currents (I/μA) on the square root of the scan rate ($v^{1/2}$/V$^{1/2}$ s$^{-1/2}$), and they demonstrated the zero intercept, diffusion coefficient (D) at 25 °C can be estimated using the following Cottrell equation:

$$I = 268.6ACD^{1/2}v^{1/2}$$

Where A (cm^2) is the area of the electrode, C (mol/L) is the concentration of the electrochemically active species, and v (V/s) is the sweep ratio, respectively.

9. Optimization of structure by DFT study

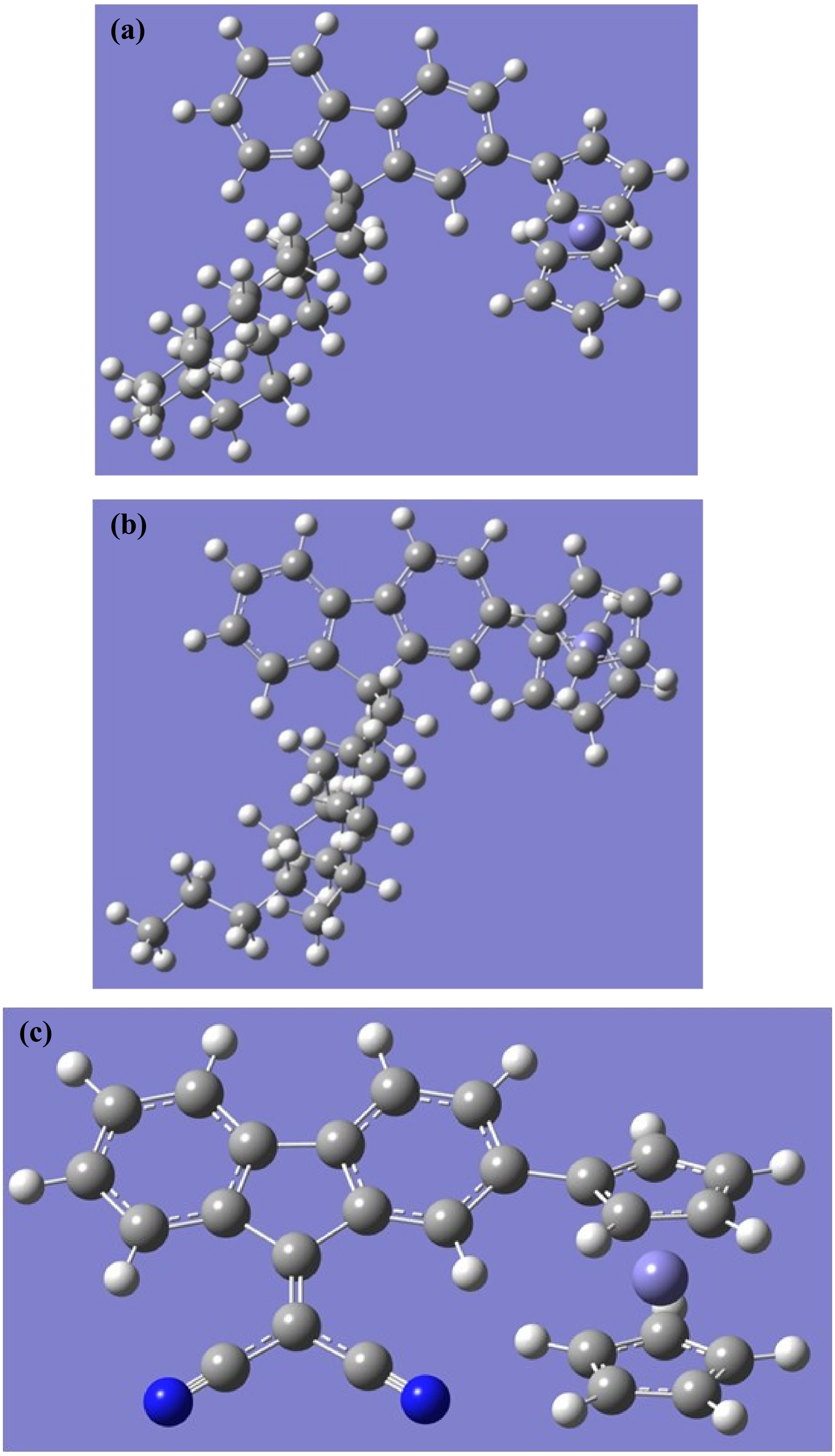

Fig. S7 Optimized structures of each repeating units of (a) PFFC-1, (b) oxidized form of PFFC-1, and (c) PFFC-2.

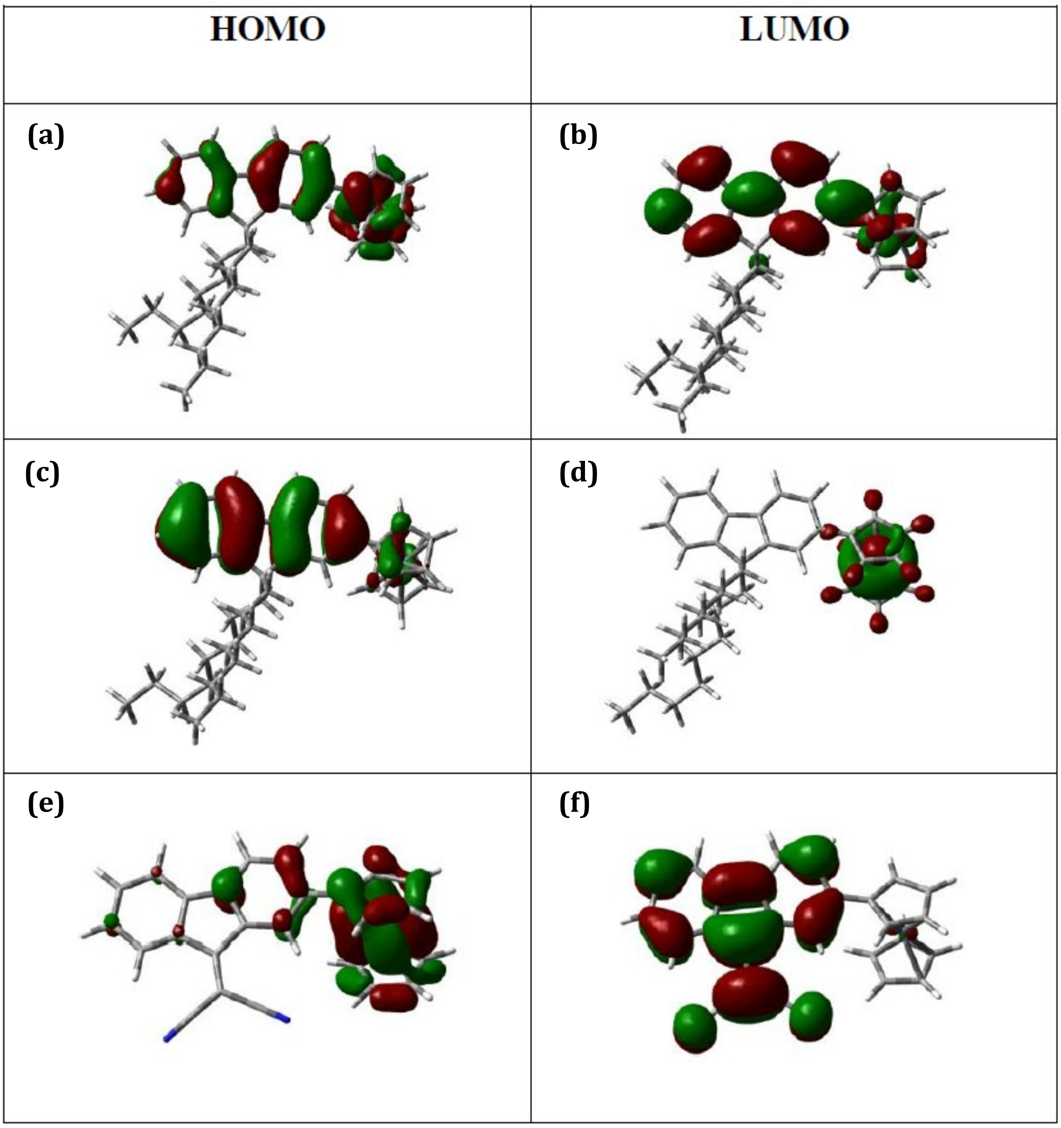

Fig. S8 HOMO and LUMO of one repeating unit of PFFC-1 (a-b), oxidized product of PFFC-1 (c-d), and PFFC-2 (e-f).

10. SEM image study

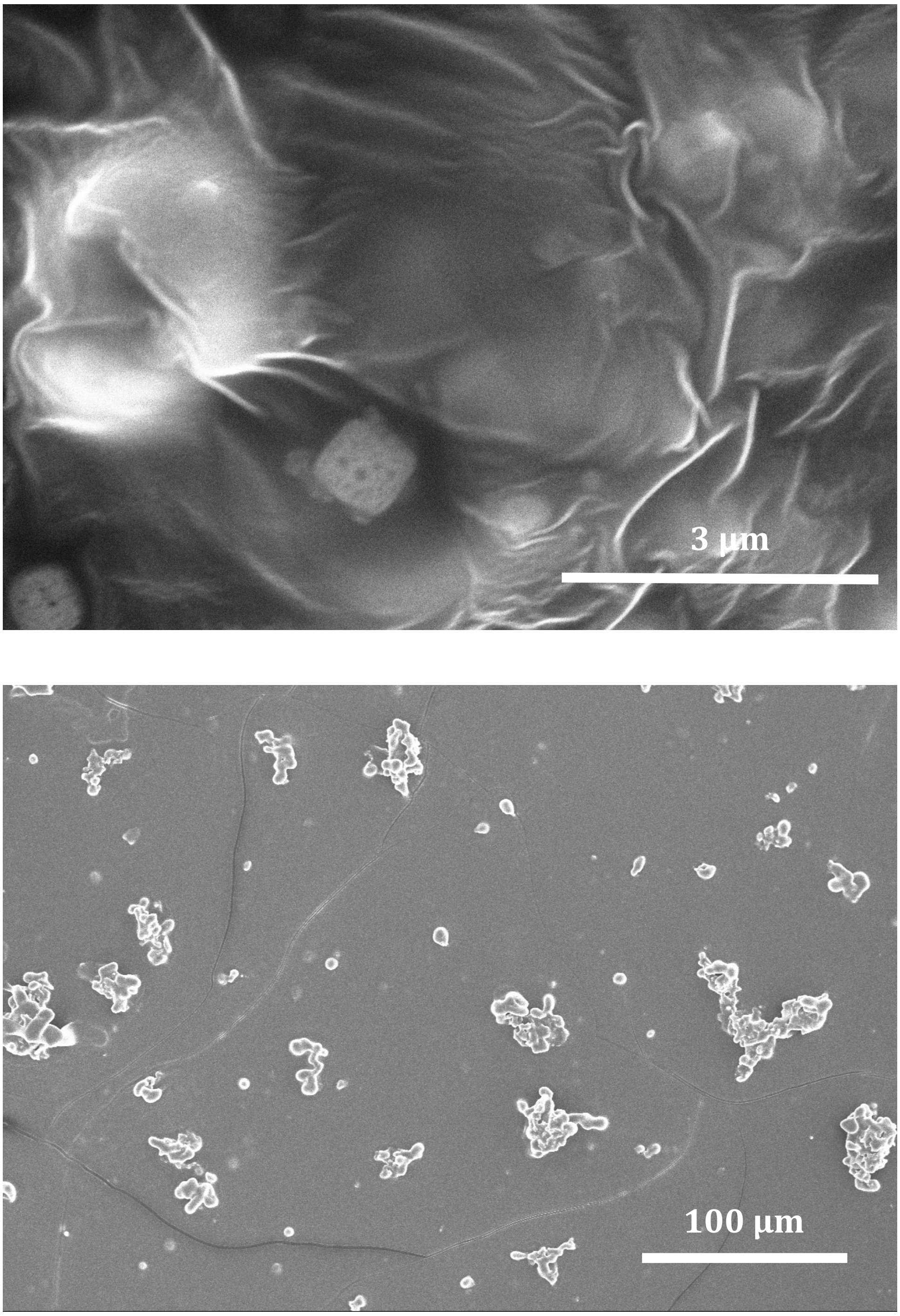

Fig. S9 SEM images of the PFFC-1 in (a) hexane and (b) methanol solution.

11. CD Study

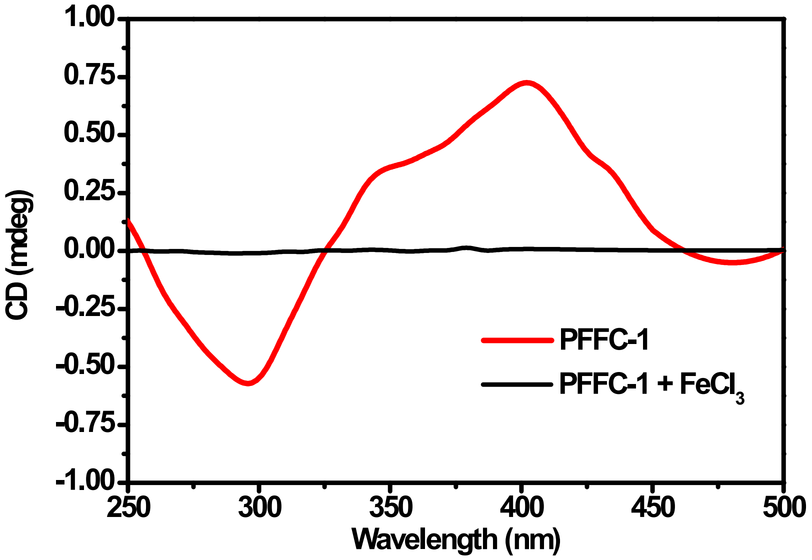

Fig. S10 CD study of PFFC-1 and PFFC-1 after oxidation in methanol/hexane (1:1) solvent mixture.

12. Temperature and concentration dependent CD Study

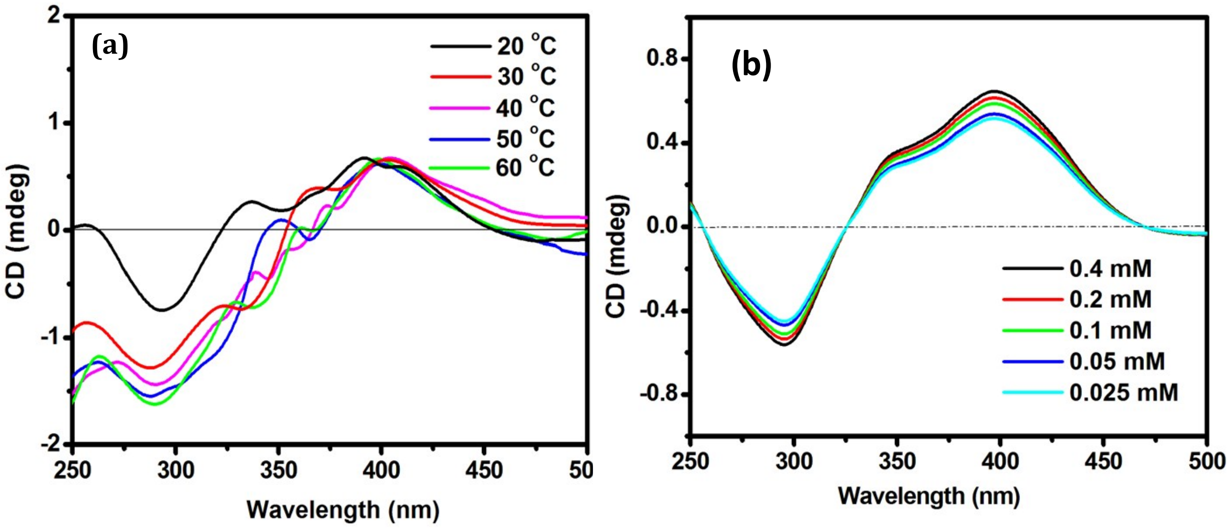

Fig. S11 (a) Temperature dependent CD of PFFC-1 (0.4 mM calculated with respect to repeat unit of PFFC-1) in 1:1 methanol and hexane mixed solvent and (b) Concentration dependent CD spectroscopy study at 25°C.

13. Concentration dependent SEM study

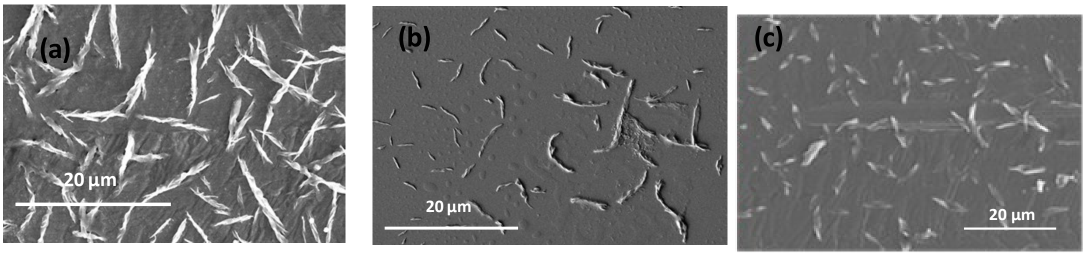

Fig. S12 SEM image study of PFFC-1 drop casted from 1:1 methanol-hexane solvent mixture at different concentration. (a) 0.4 mM, (b) 0.1 mM and (c) 0.025 mM with respect to repeat unit.

Reference:

S1) A. D. Becke, *Phys. Rev. A.,* 1988, **38**, 3098.

S2) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.

S3) 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, et al. Gaussian 09, rev. B.01, Gaussian, Inc., Wallingford CT, 2009.