

Electronic Supplemental Information

1. Assembling film electrodes using the functionalised polymers

1.1 PVC-Fe-A-MWCNTs film electrodes

A solution of **PVC-Fe-A** (10 mg) in THF (1 mL) and a suspension of MWCNTs (3 mg) in THF (1 mL) were prepared, respectively. The solution of the polymer (0.1 mL) was mixed with an appropriate amount of the MWCNTs suspension (0, 33, 50, 67, 83, 100 μL , respectively) and then the final volume of the mixture was made up to 0.2 mL. After supersonication for 10 min, 10 μL of the resultant mixture was dropped to the surface of a polished vitreous carbon electrode ($d = 5 \text{ mm}$) and spin-coating was followed at a spinning rate of 500 r min^{-1} . The film electrode as prepared was left for solvent-evaporation before its characterisation and electrochemical investigation.

1.2 Polymer-Nafion film electrodes

PVC-Fe-A/B/C (4 mg) was suspended in the solution of Nafion (0.4 mL) and the slurry was dispersed *via* supersonication for 0.5 h. The resultant mixture (5 μL) was dropped to the surface of a polished vitreous carbon electrode and spin-coating was followed at a spinning rate 500 r min^{-1} . The **PVC-Fe-A/B/C-Nafion** film electrode was ready for electrochemical evaluation after the evaporation of the solvents.

1.3 Polymer-MWCNTs-Nafion film electrodes

To assemble **PVC-Fe-B/C**-MWCNTs-Nafion film electrodes, the above mixture for assembling the **PVC-Fe-B/C**-Nafion film electrode was further blended with MWCNTs (1 mg) and the mixture was supersonicated for 0.5 h before spin-coating onto the surface of the vitreous carbon electrode using the same procedure as described above.

2. Supplemental Figures

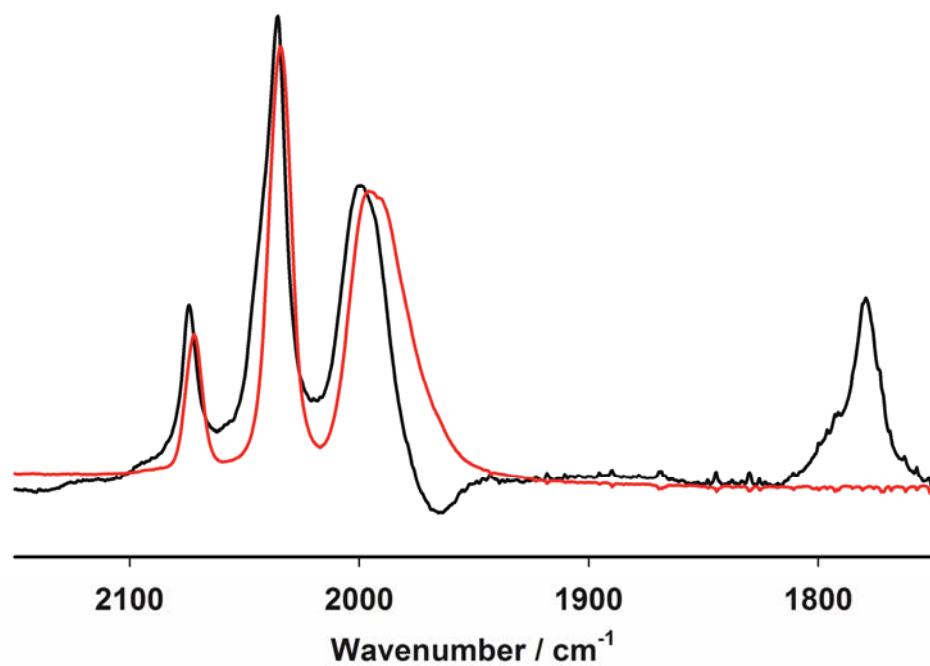


Figure S1 Infrared spectra **PVC-Fe-A** (red) and its thioester-containing analogue (black) in THF.

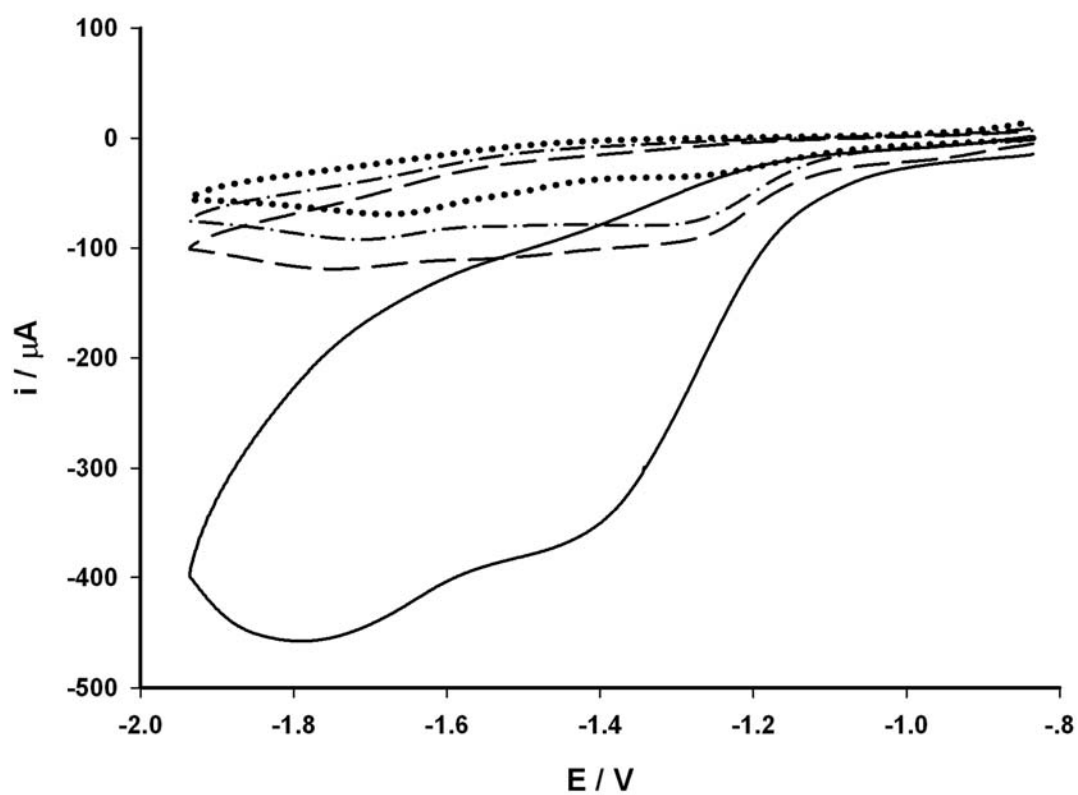


Figure S2 Cyclic voltammograms of the film electrode prepared from **PVC-Fe-C** -Nafion after repetitive scanning (1st, 2nd, 3rd, and 6th from the bottom to the top) in 0.1 mol L^{-1} $[\text{NBu}_4]\text{BF}_4\text{-CH}_3\text{CN}$ solution at a scanning rate of 0.1 V s^{-1} .

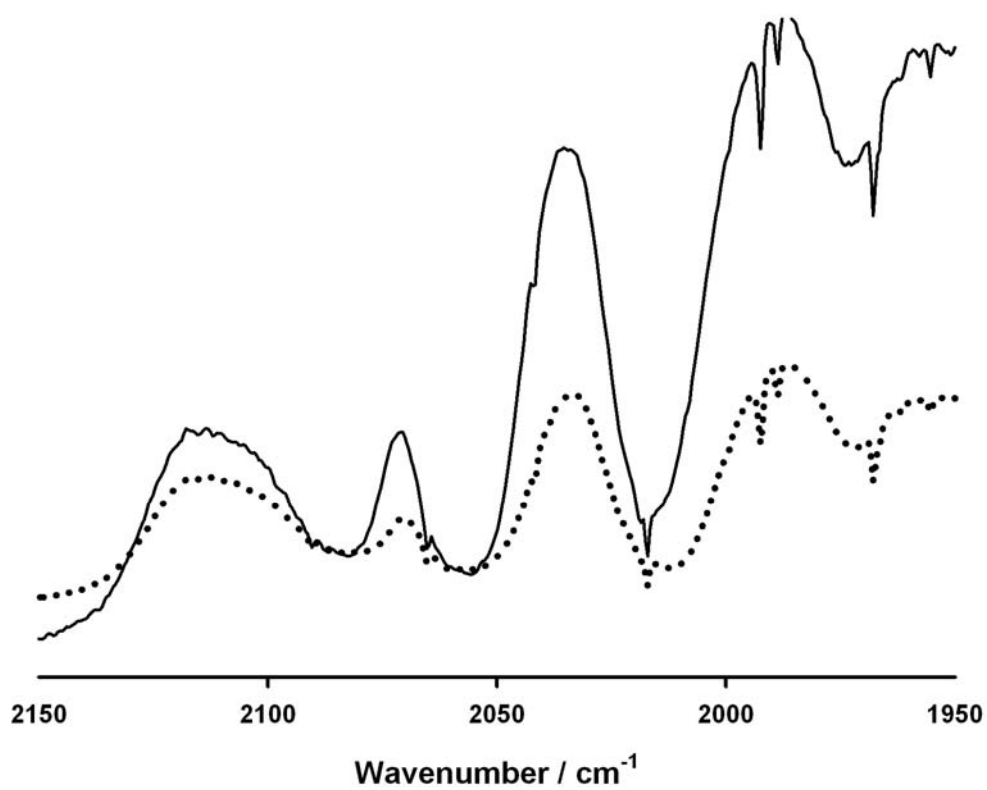


Figure S3 diffuse reflectance infrared spectroscopy of **PVC-Fe-C-Nafion** before (solid) and after (dot) electrochemistry.

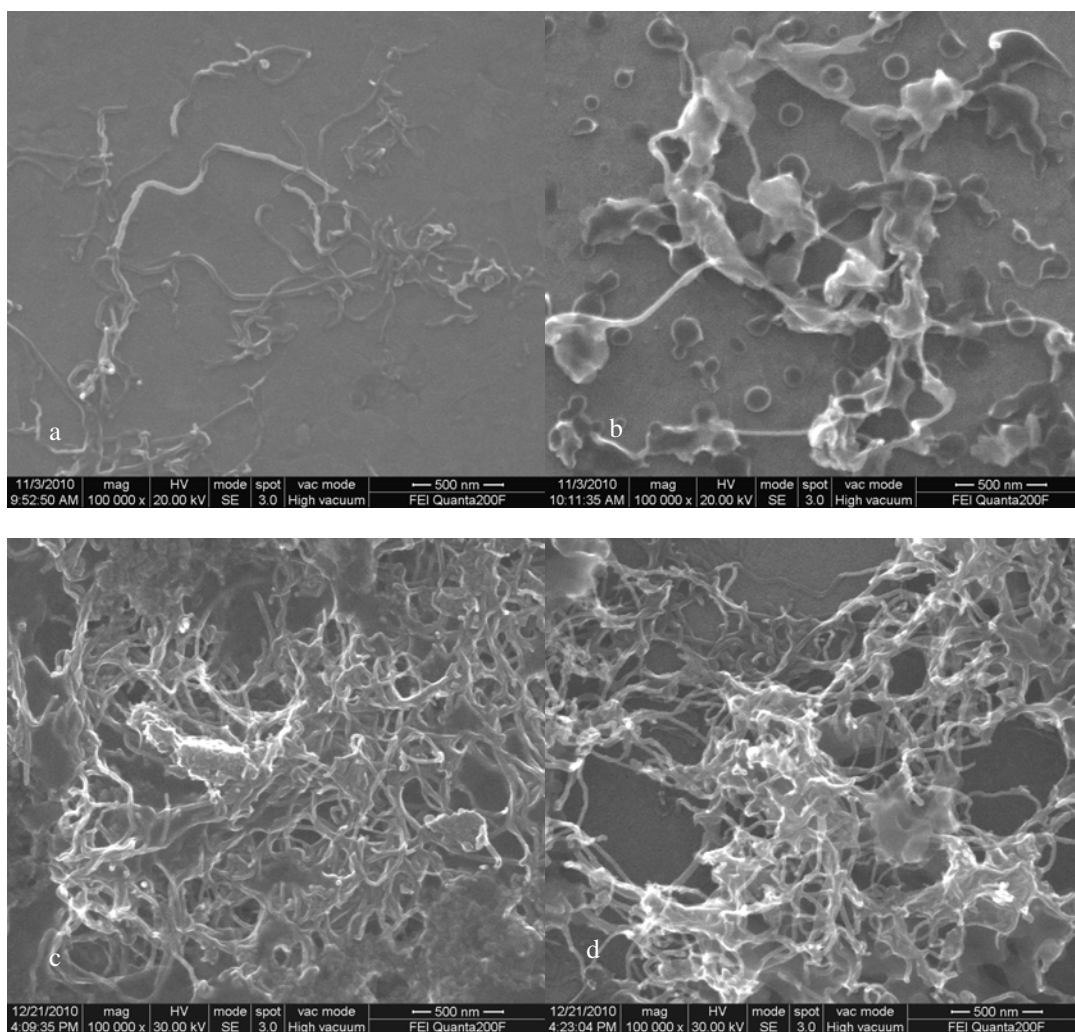


Figure S4 SEM images of the composites of polymers. MWCNTs (a), **PVC-Fe-A** (b), **-B** (c), and **-C** (d), respectively, with MWCNTs.