Supplementary Information

Electropolymerization of thienyl tethered comonomers and application towards electrocatalytic reduction of nitrobenzene

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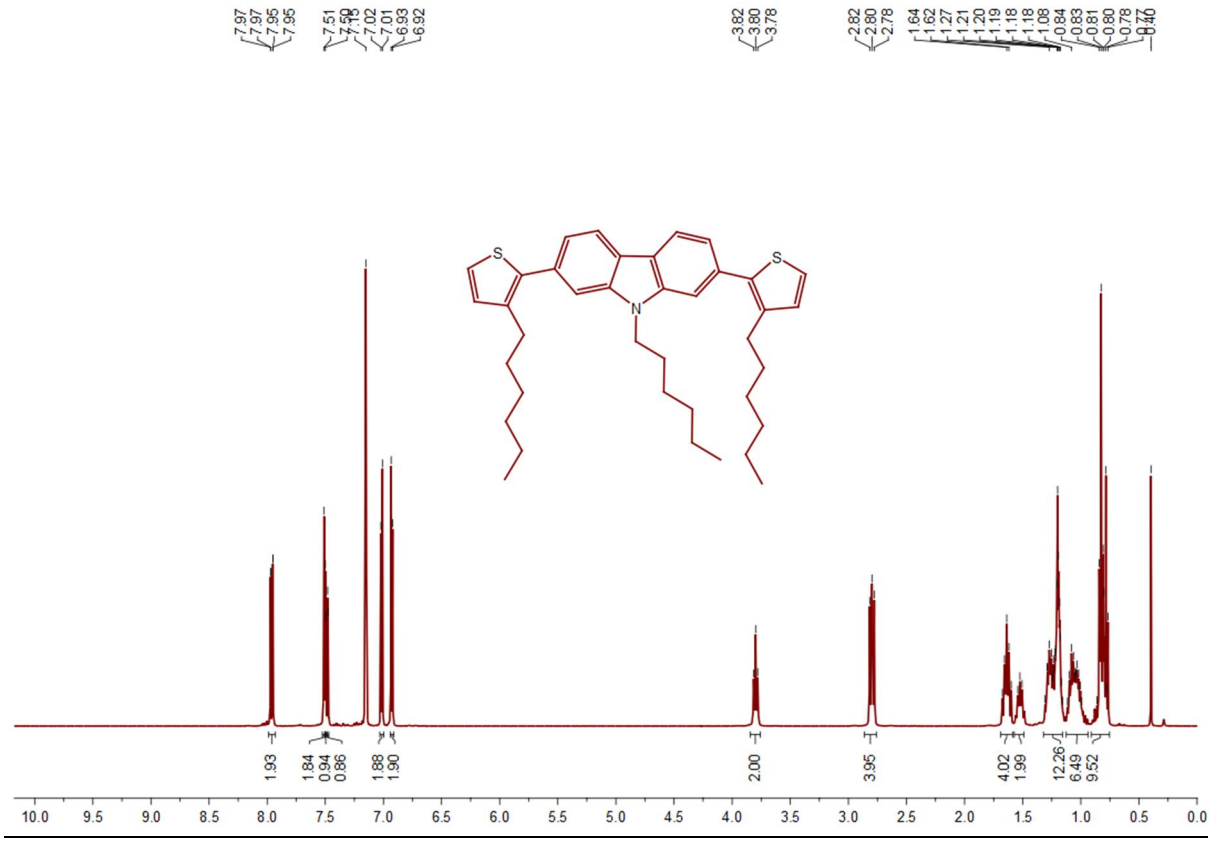
Contents

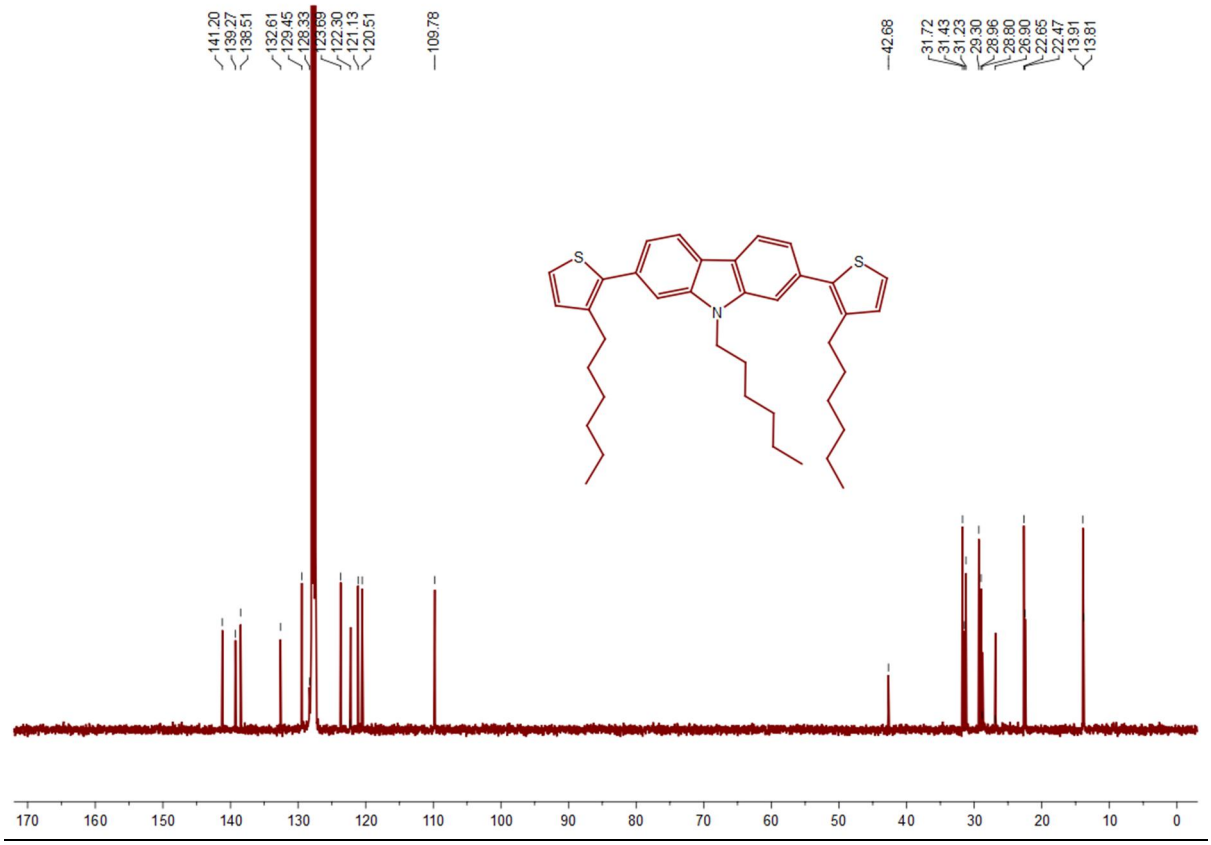
Instruments and measurements

The morphological structures of the prepared samples were captured using Scanning Electron Microscope (SEM) of TESCAN, VEGA 3 with Bruker Detector.FTIR analysis was carried out on a BRUKER - TENSOR 27 (Optik GmbH) using RT DLaTGS (Varian) Detector. UV-Vis spectra were recorded on a Hewlett-Pacard 8453 spectrometer. PL Fluorescence was recorded in Jasco spectrofluorometer (FP-8500). Cyclic voltammetry was carried on an autolab PGSTAT 302N workstation at room temperature in a standard three-electrode cell. ITO/GC electrode was used as a working electrode, Pt was used as a counter electrode and Ag/AgCl/KCl (3 M) was used as a reference electrode. The electrochemical polymerization was studied at room temperature using DCM and 0.1 M TBA.PF_6 as supporting electrolyte at a scan rate of 50 mVs^{-1}. ITO (300 mm × 300 mm × 1.1 mm), Resistivity: 8Ω. For all cyclic voltammetric experiments, 5 mg of the monomer was dissolved in 5 mL supporting electrolyte. Electrochemical polymerisation of hybrid thiophene based monomers was carried out in a three electrode set up using Autolab Potentiostat at room temperature using 10 times higher concentration as mentioned above in DCM and 0.1 M TBA.PF_6 as supporting electrolyte. Initially cyclic voltammograms were recorded for the monomers and based on the CV, oxidation potentials for constant potential electrolysis was fixed. All the bulk electrolysis was carried out on ITO electrode (onset potential + 200 mV) to obtain polymer films on the transparent electrode for preliminary electrochromism studies. Thick films of thiophene polymers were obtained on ITO electrodes, after polymerisation, the electrode was removed, rinsed and carefully dried. It was then subjected to electrochemical characterisation, AFM and SEM morphological analysis.

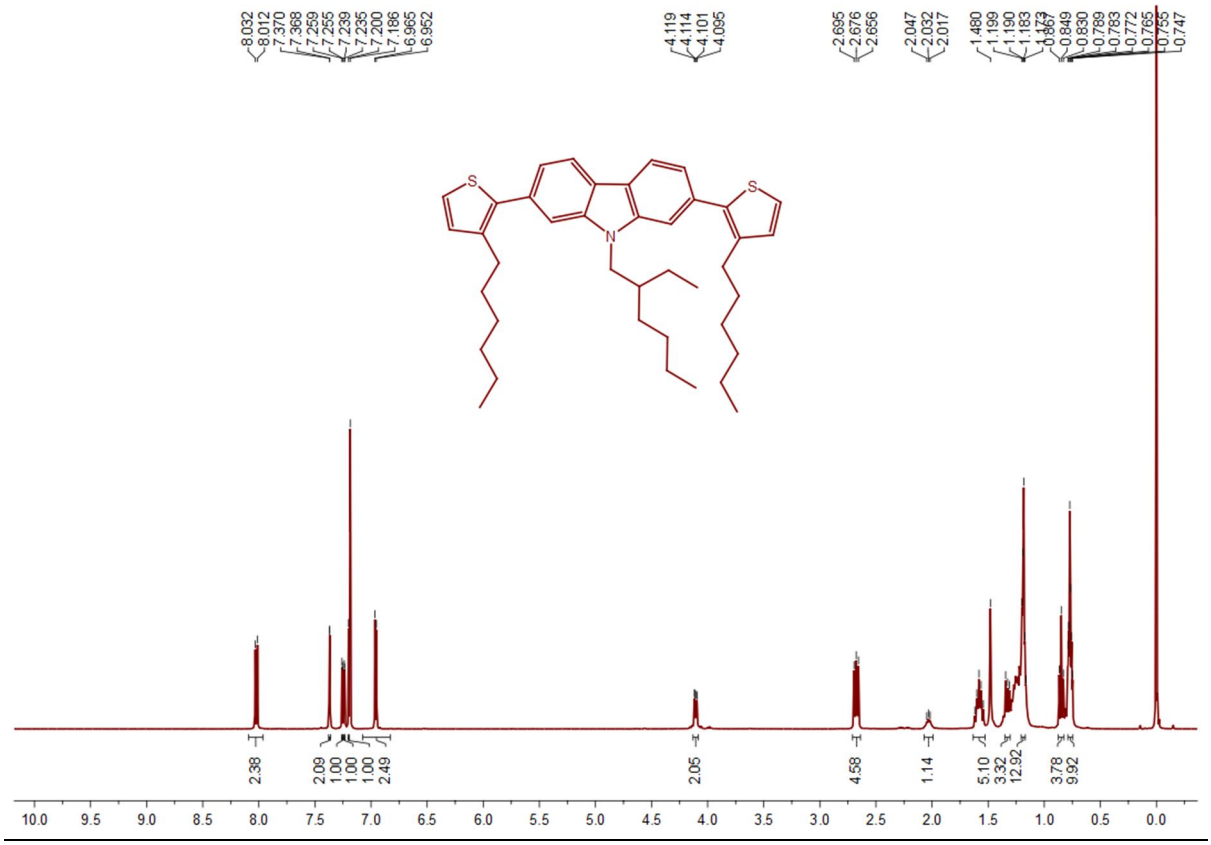
S.No	Polymer	No. of Cycles
1	**4a**	10
2	**4b**	12
3	**4c**	25
4	**4d**	10
5	**4e**	25
6	**4f**	10
7	**4g**	14
8	**4h**	12

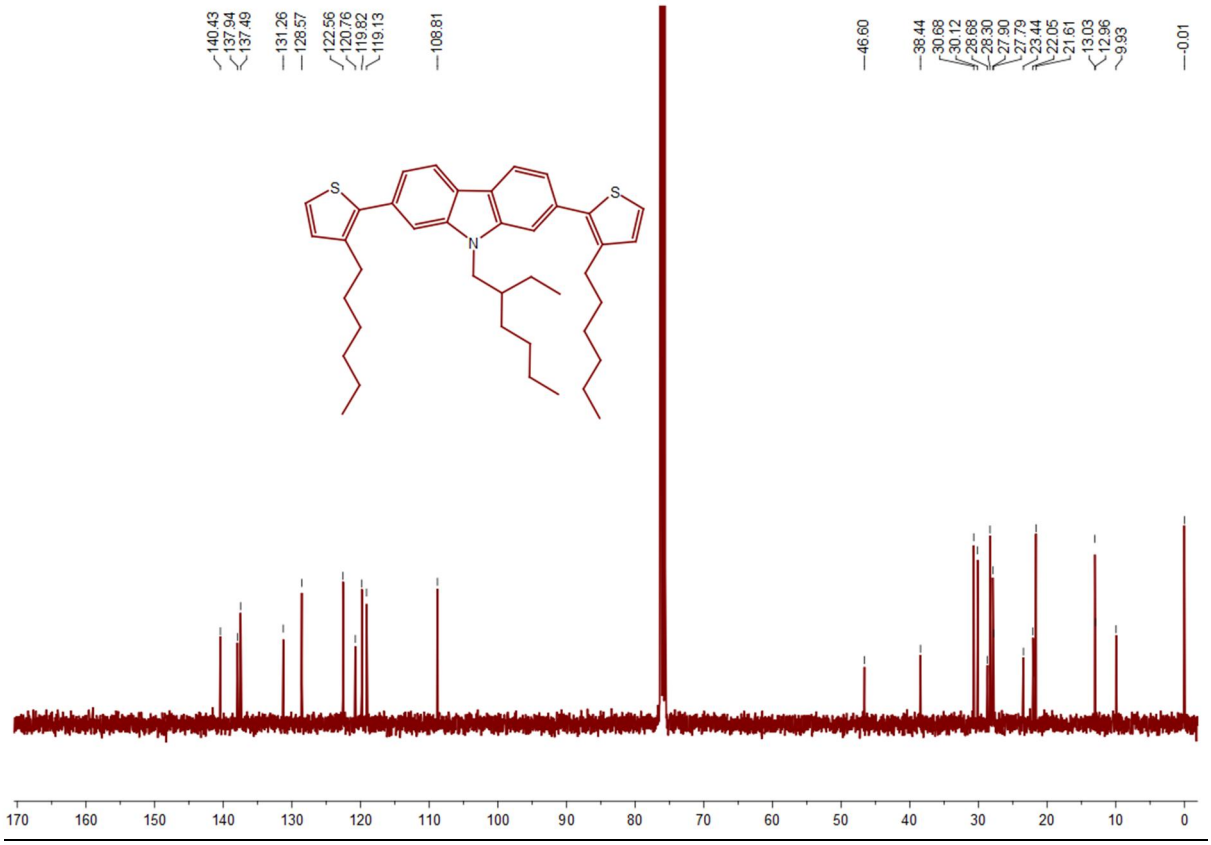
^{1}H & ^{13}C NMR Spectrum of Compound **3a**



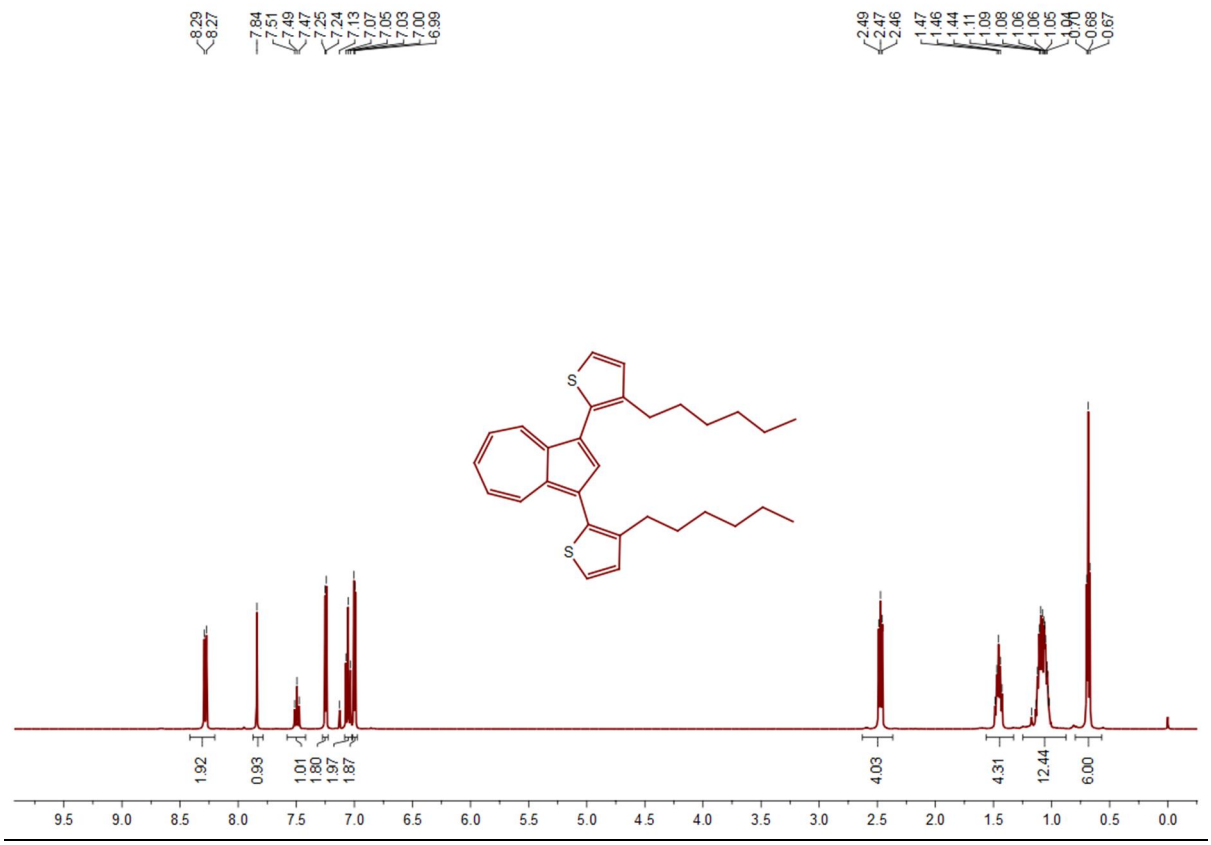


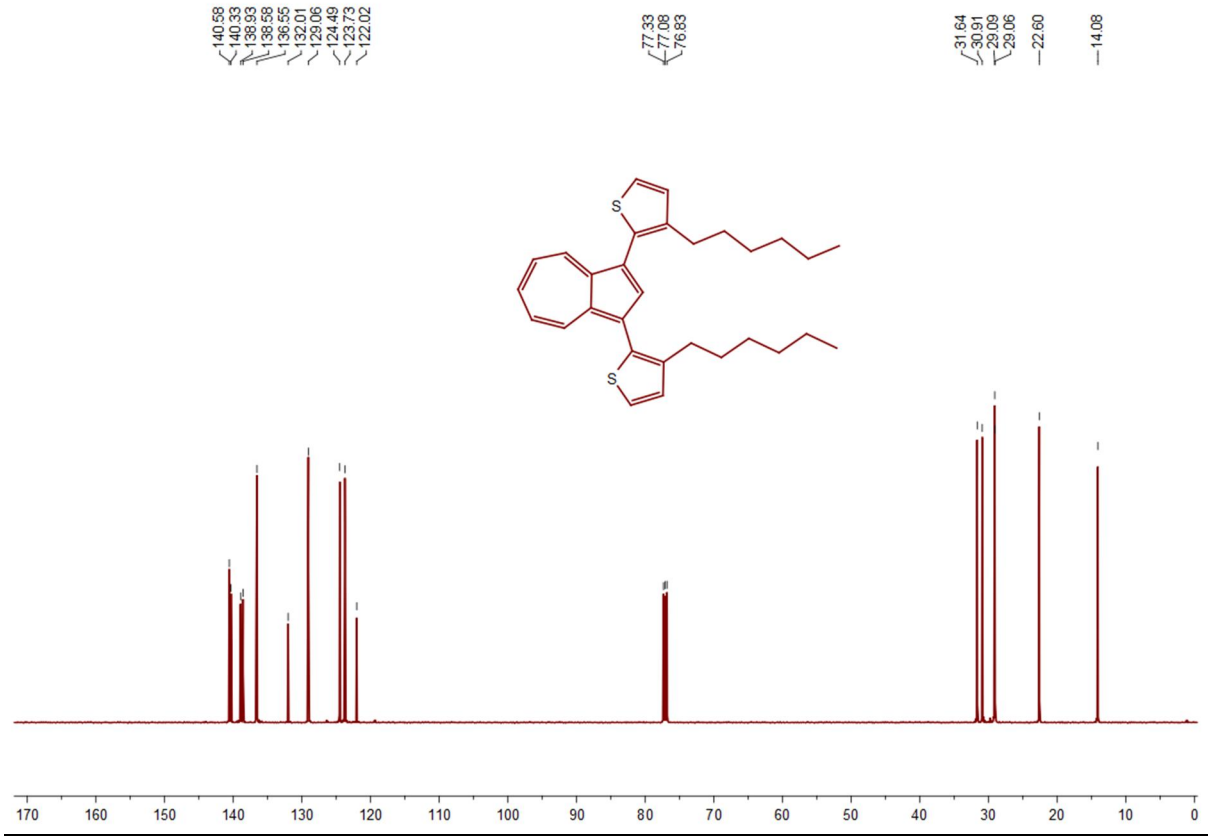
^{1}H & ^{13}C NMR Spectrum of Compound **3b**



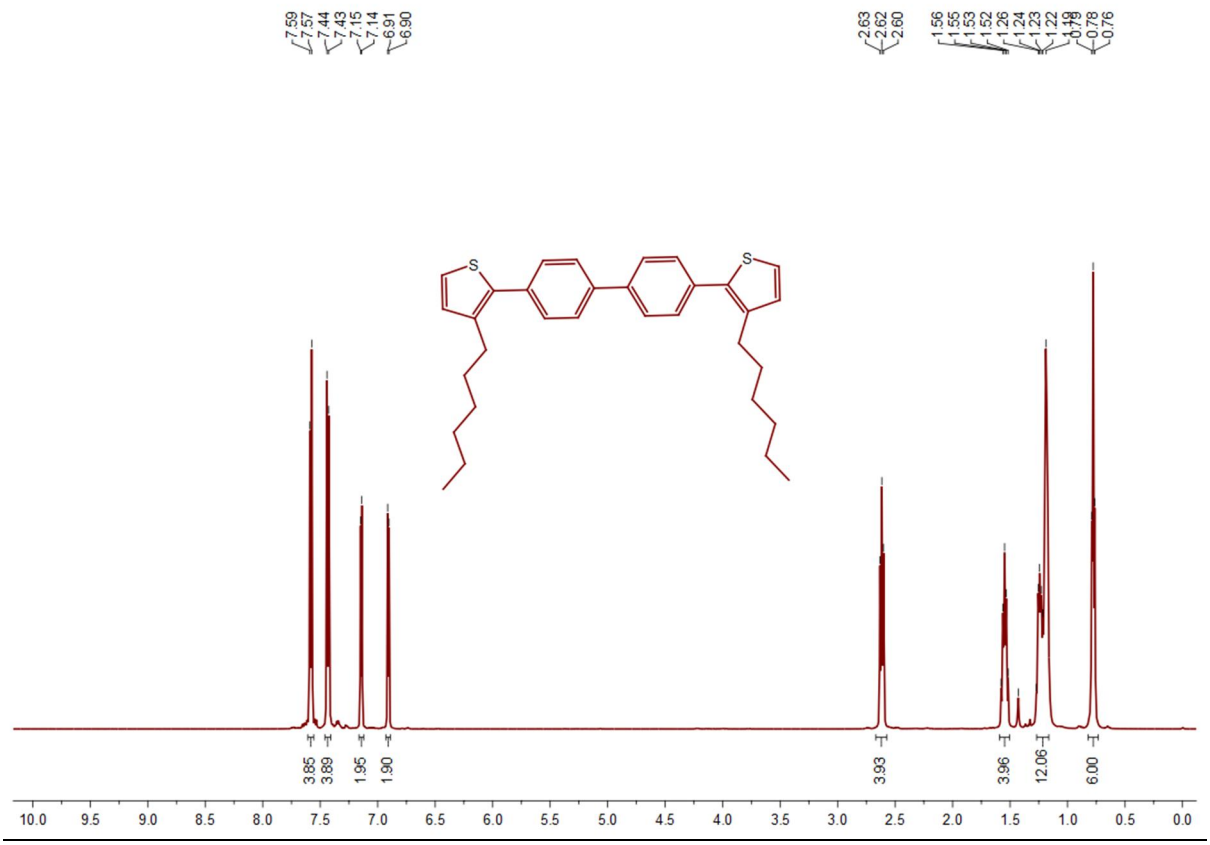


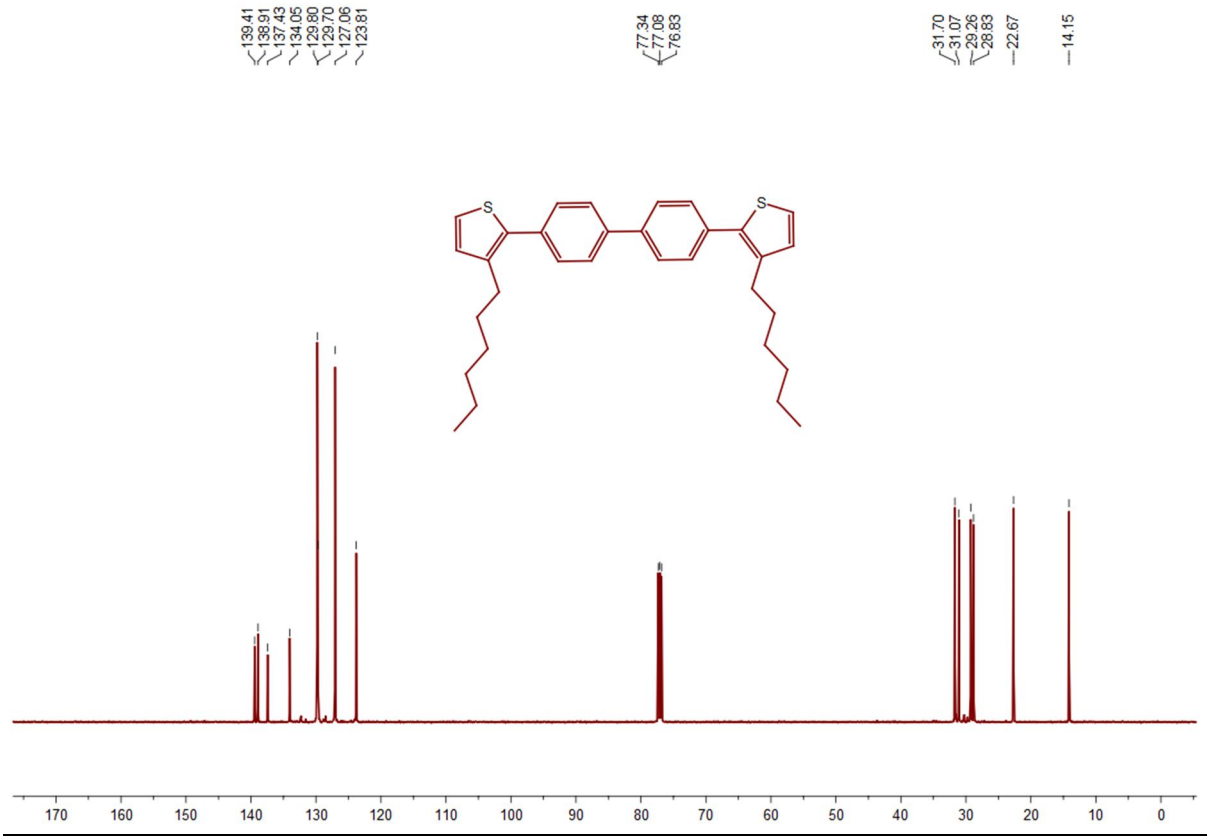
^{1}H & ^{13}C NMR Spectrum of Compound **3c**



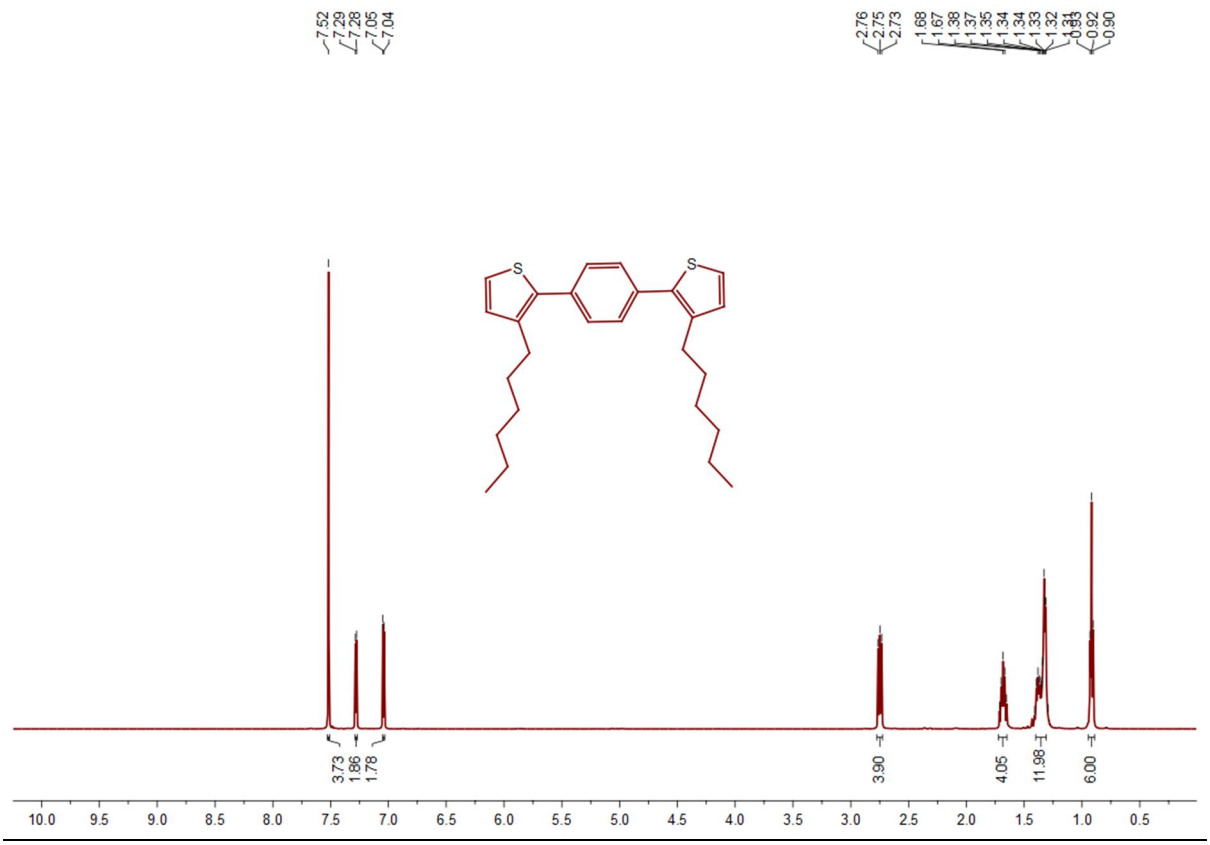


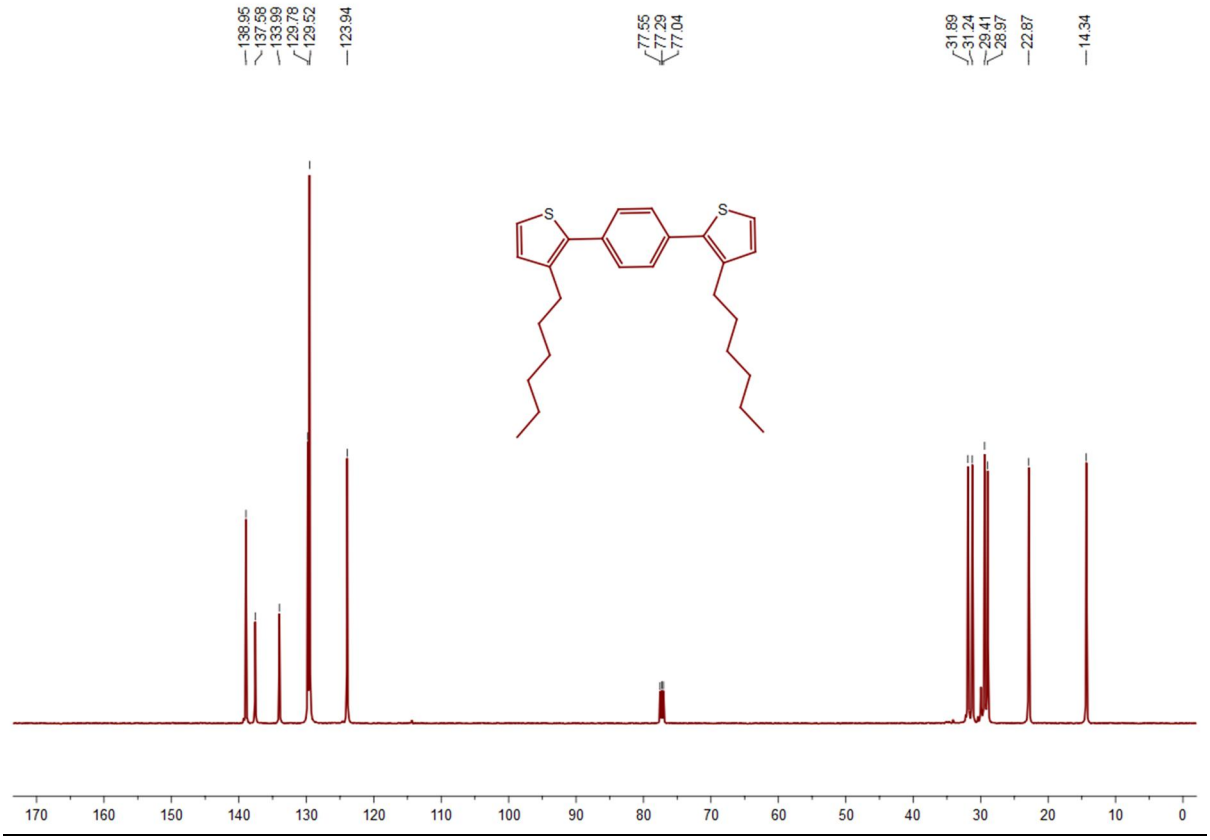
^{1}H & ^{13}C NMR Spectrum of Compound **3d**



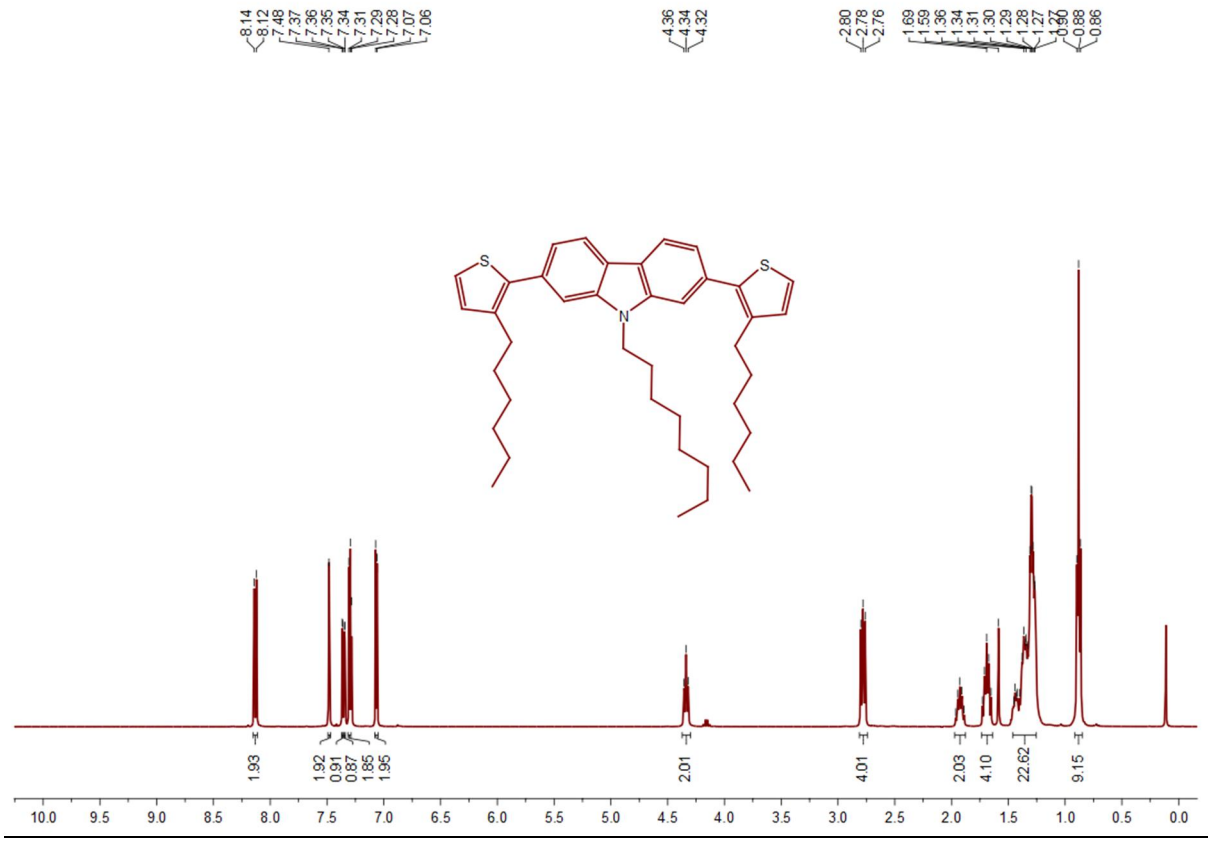


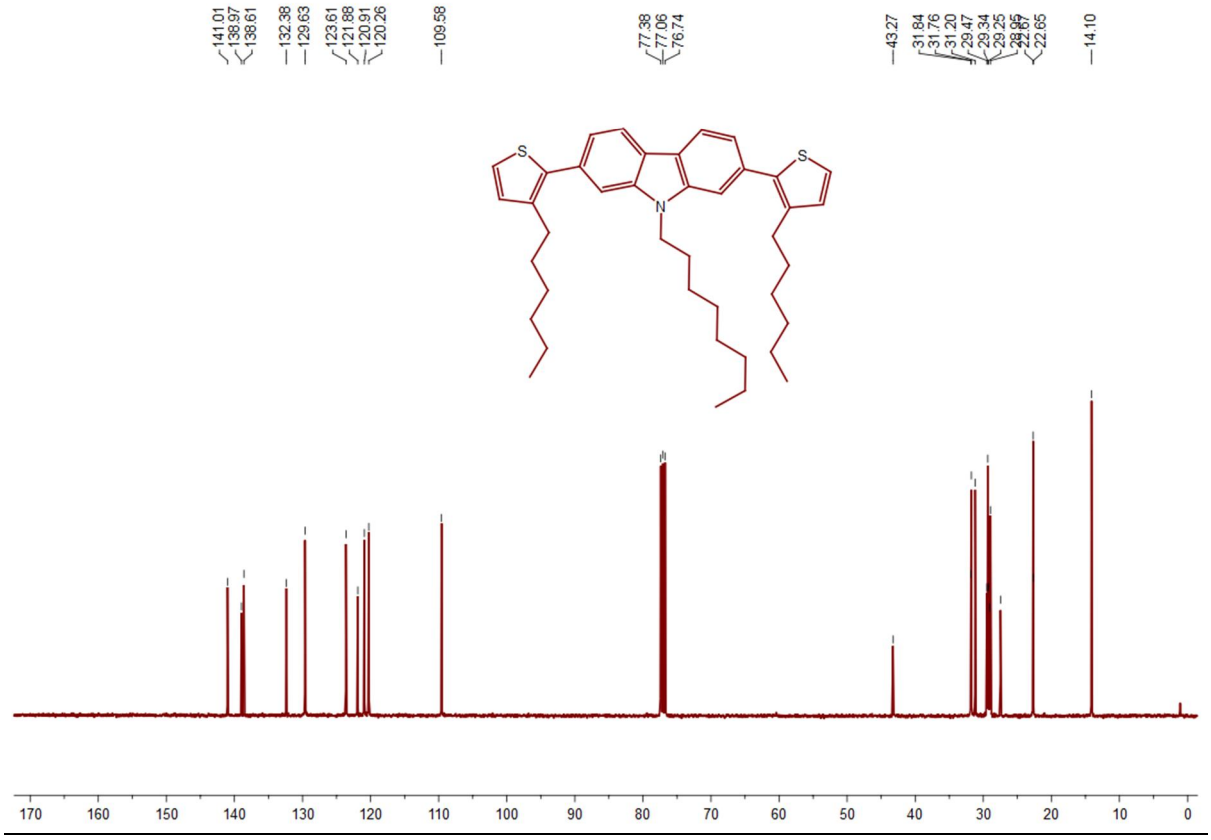
^{1}H & ^{13}C NMR Spectrum of Compound **3e**



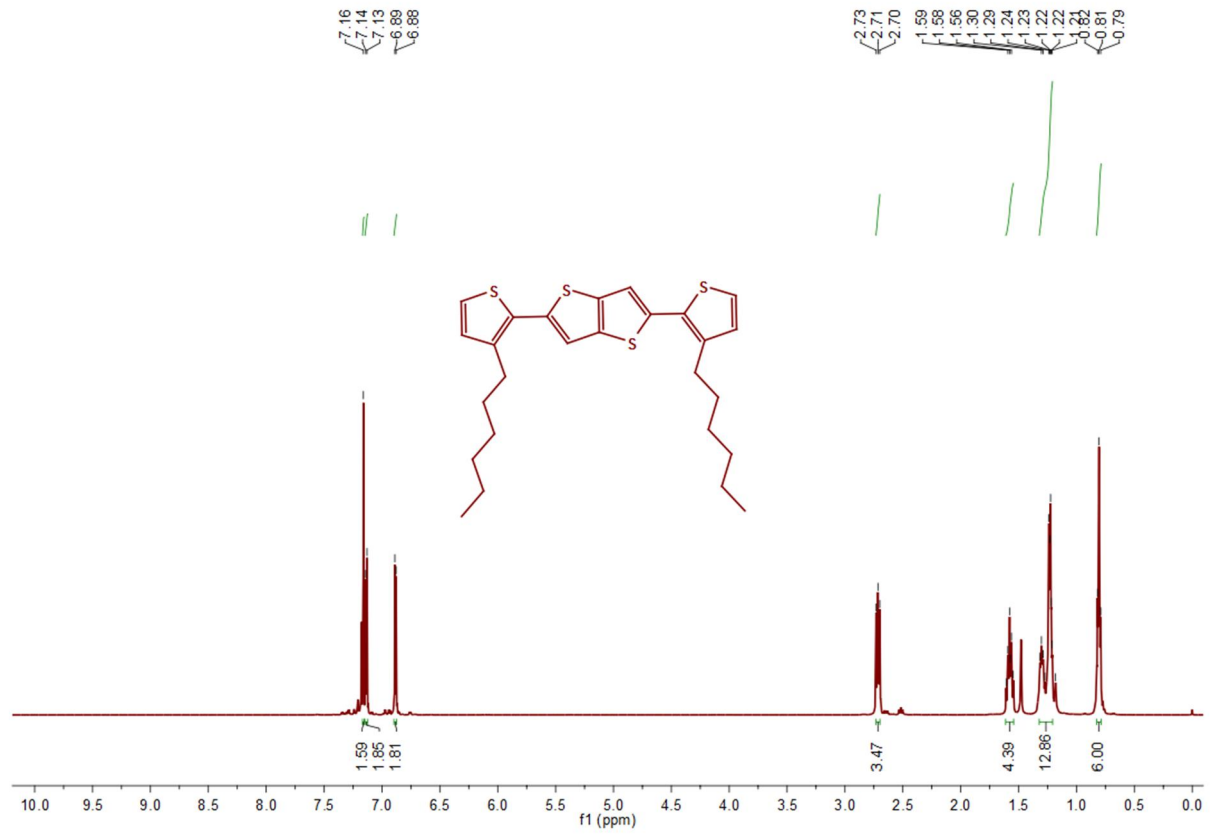


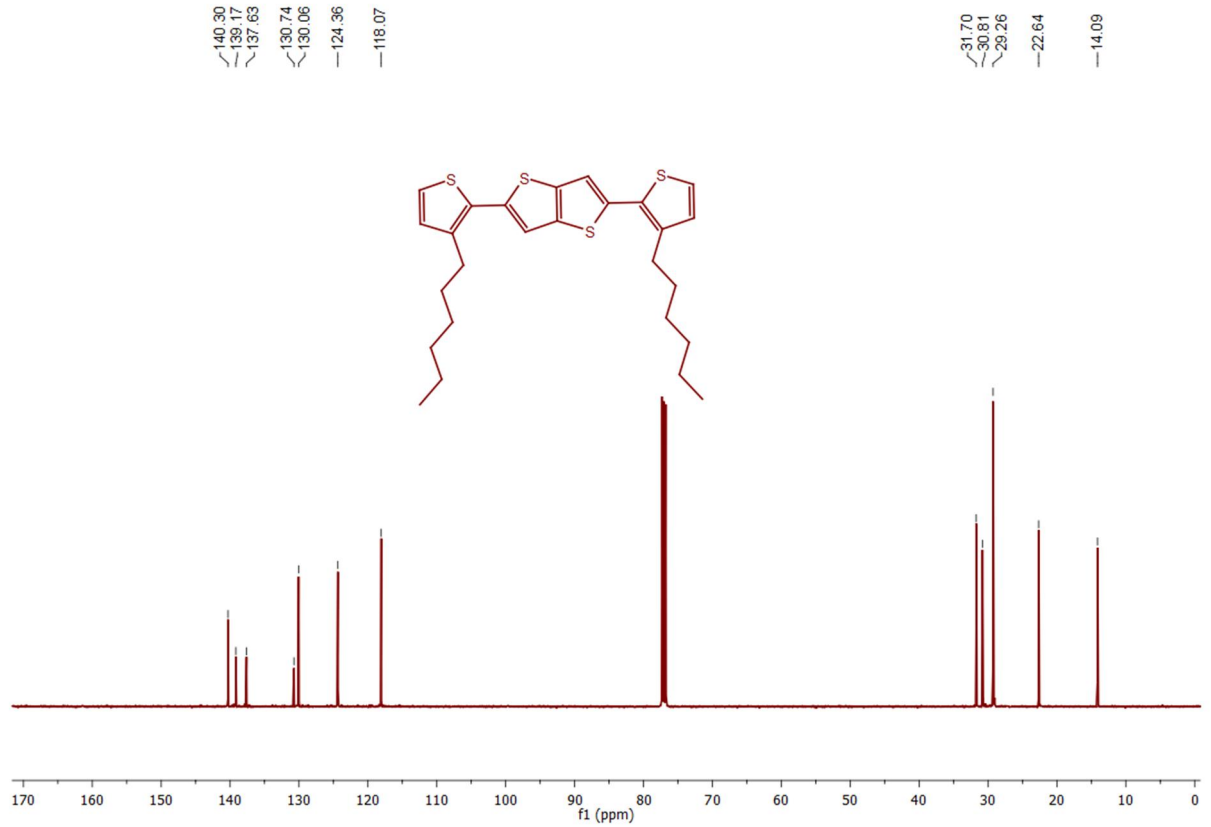
^{1}H & ^{13}C NMR Spectrum of Compound **3f**



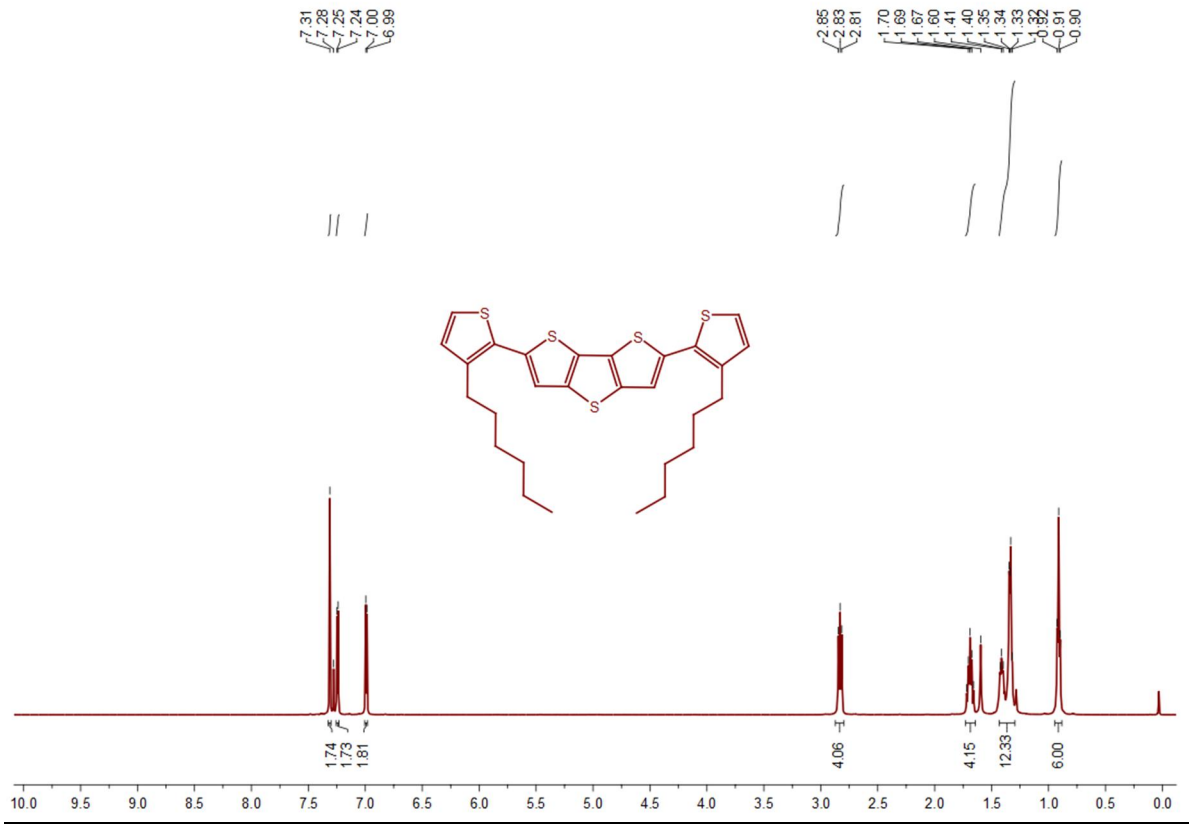


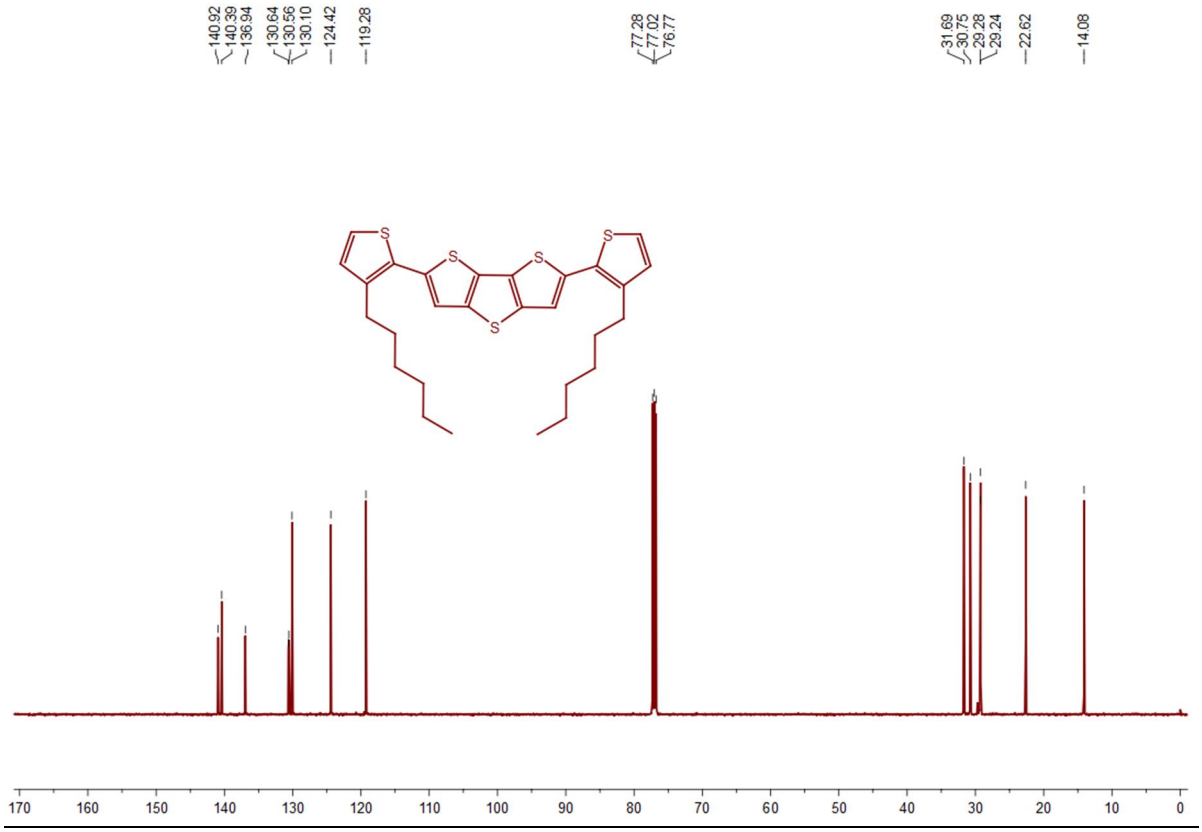
^{1}H & ^{13}C NMR Spectrum of Compound **3g**





^{1}H & ^{13}C NMR Spectrum of Compound **3h**


7.31
7.28
7.25
7.24
7.00
6.99
2.85
2.83
2.81
1.70
1.69
1.67
1.60
1.41
1.40
1.35
1.34
1.33
0.92
0.91
0.90
S
1.74
1.73
1.81
4.06
4.15
12.33
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


140.92
140.39
136.94
130.64
130.56
130.10
124.42
119.28
77.28
77.02
76.77
31.69
30.75
29.28
29.24
22.62
14.08
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

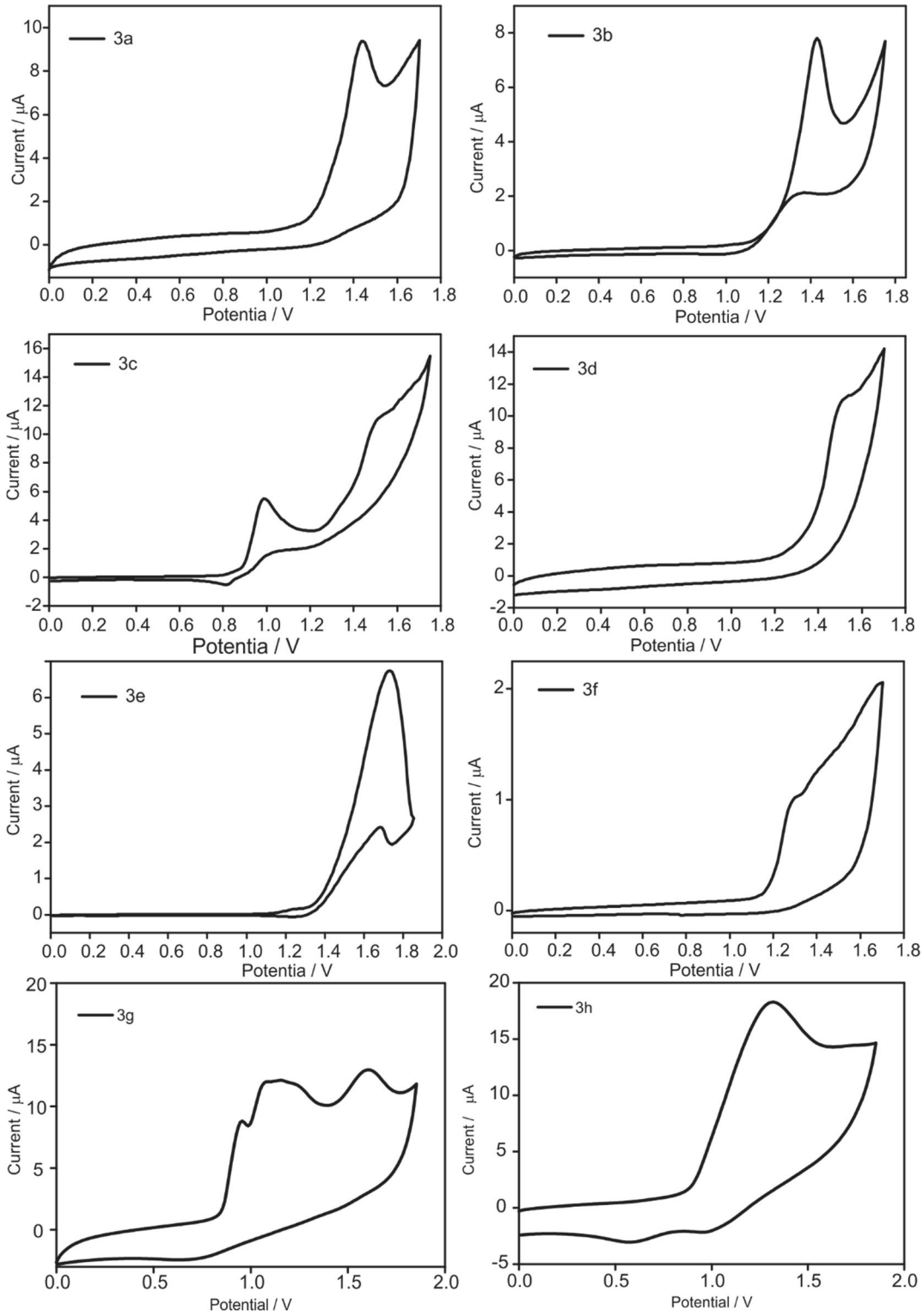


Fig. S1 Cyclic Voltammograms of monomers **3a-h** on GC electrode in 0.1 M TBA.PF_6 in CH_2Cl_2

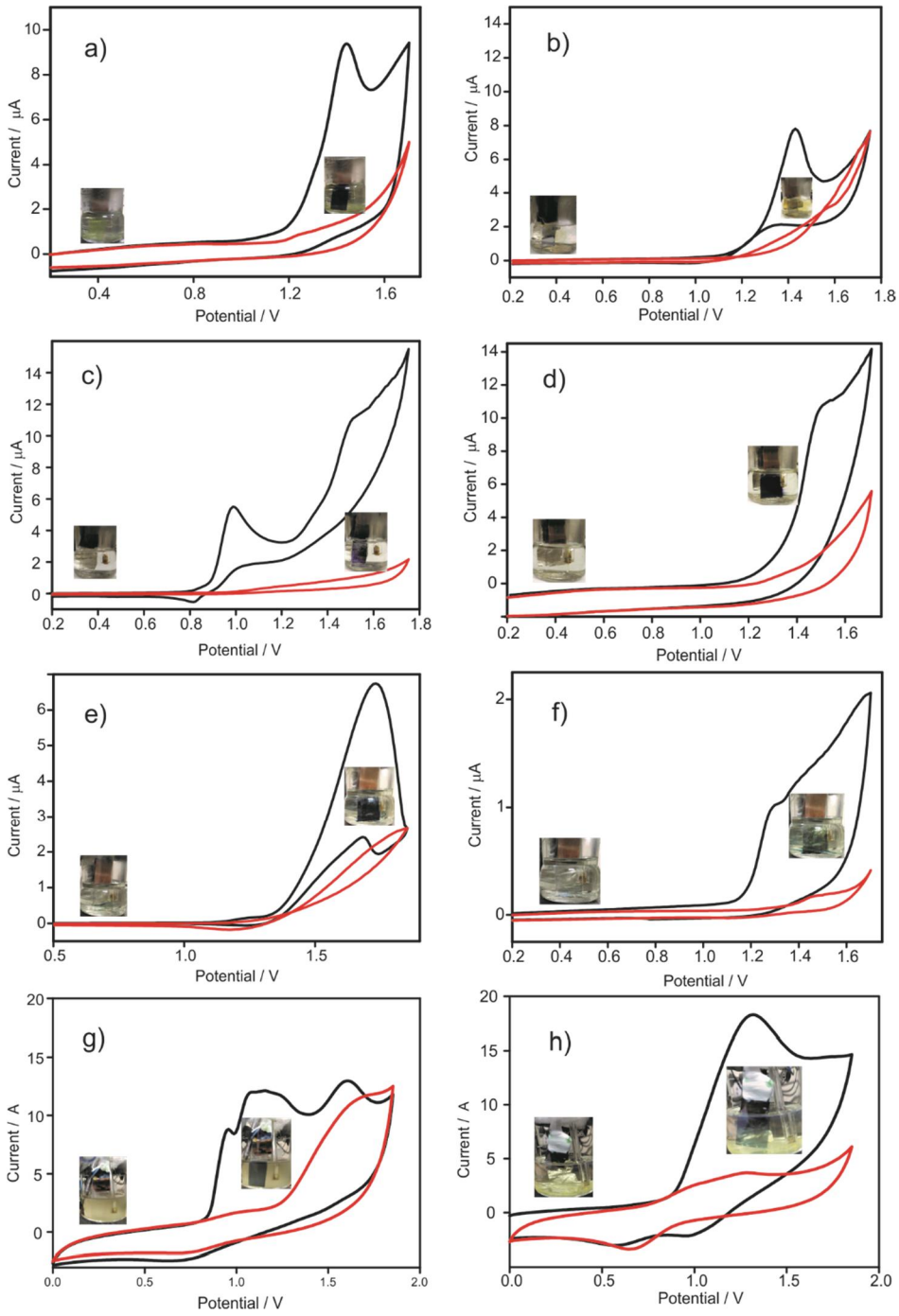


Fig. S2 Cyclic voltammogram of monomers **3a-h** (black) numbered correspondingly and its corresponding electropolymer **4a-h** (red) in 0.1 M TBA.PF_6 in DCM on ITO electrode. Visual color changes upon oxidation and reduction on the ITO electrode is shown as inset.

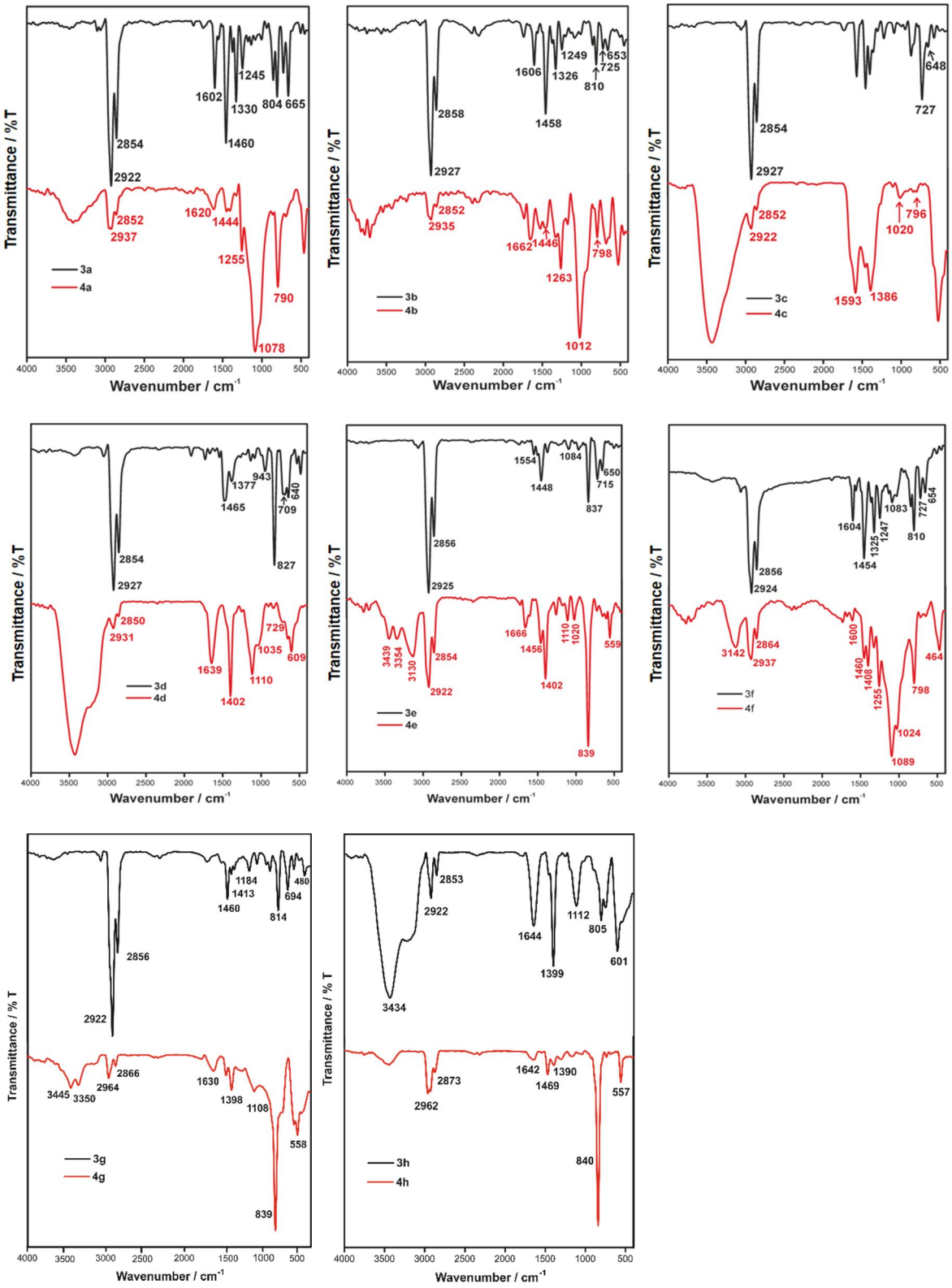
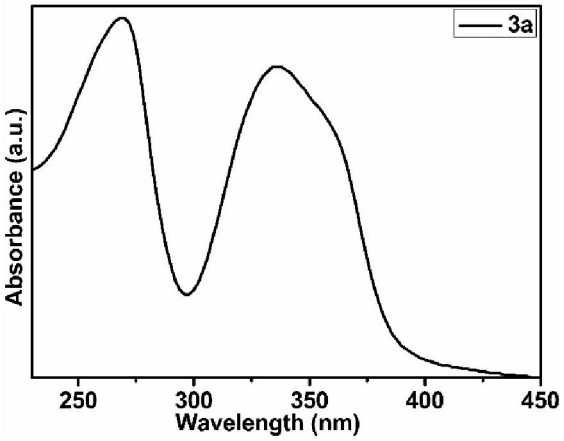
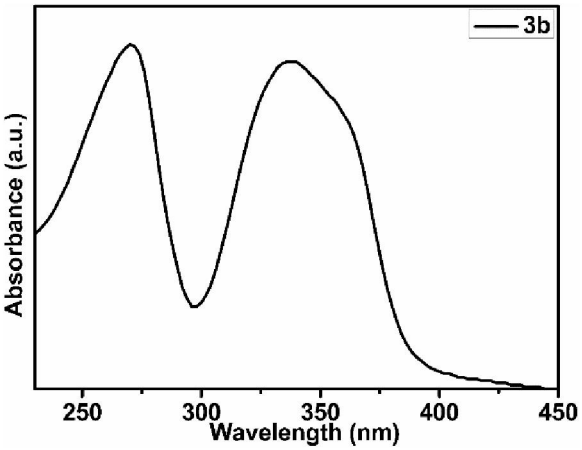
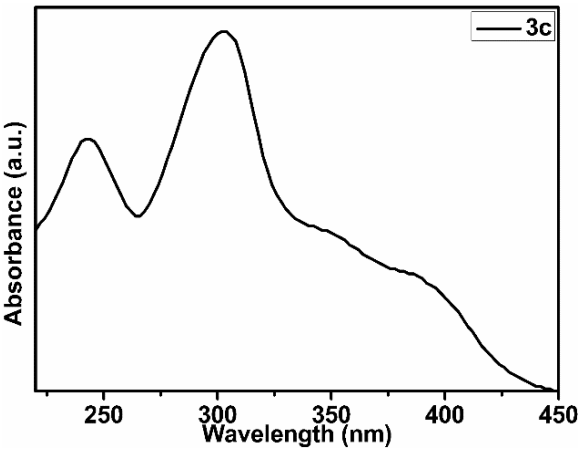
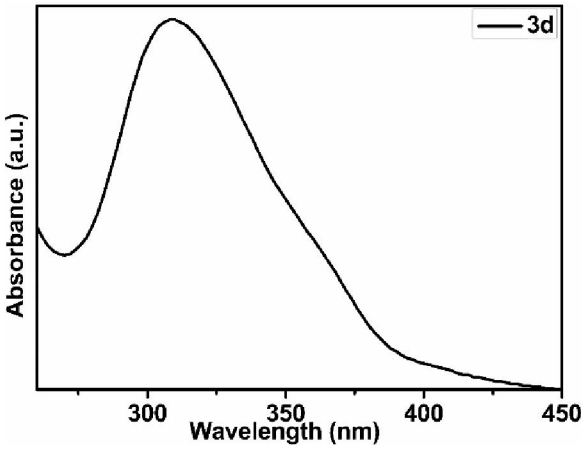


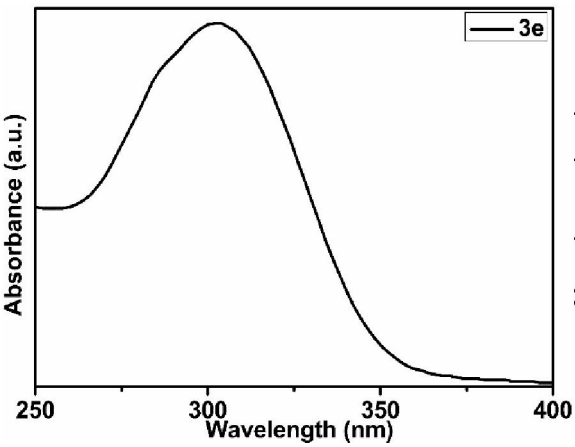
Fig. S3 FTIR spectrum of monomer **3a-3h** (black) and polymer **4a-4h** (red)

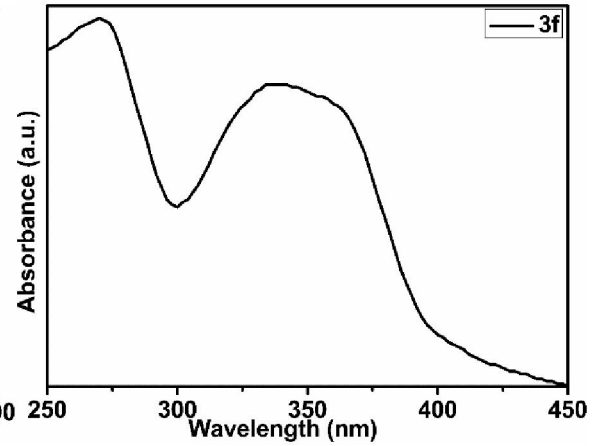

3a
Absorbance (a.u.)
250
300
350
400
450
Wavelength (nm)


3b
Absorbance (a.u.)
250
300
350
400
450
Wavelength (nm)


3c
Absorbance (a.u.)
250
300
350
400
450
Wavelength (nm)


3d
Absorbance (a.u.)
300
350
400
450
Wavelength (nm)


3e
Absorbance (a.u.)
250
300
350
400
Wavelength (nm)


3f
Absorbance (a.u.)
250
300
350
400
450
Wavelength (nm)

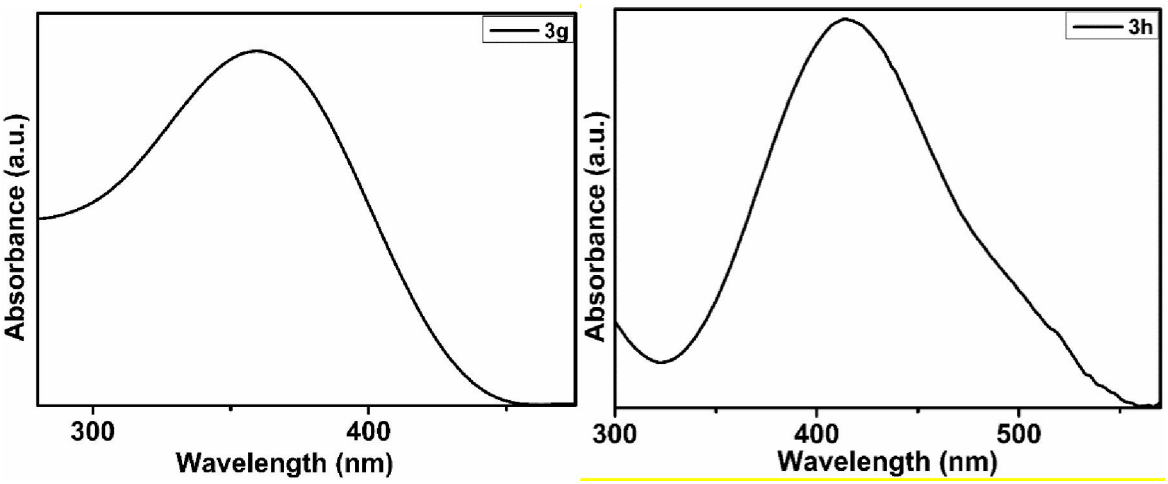
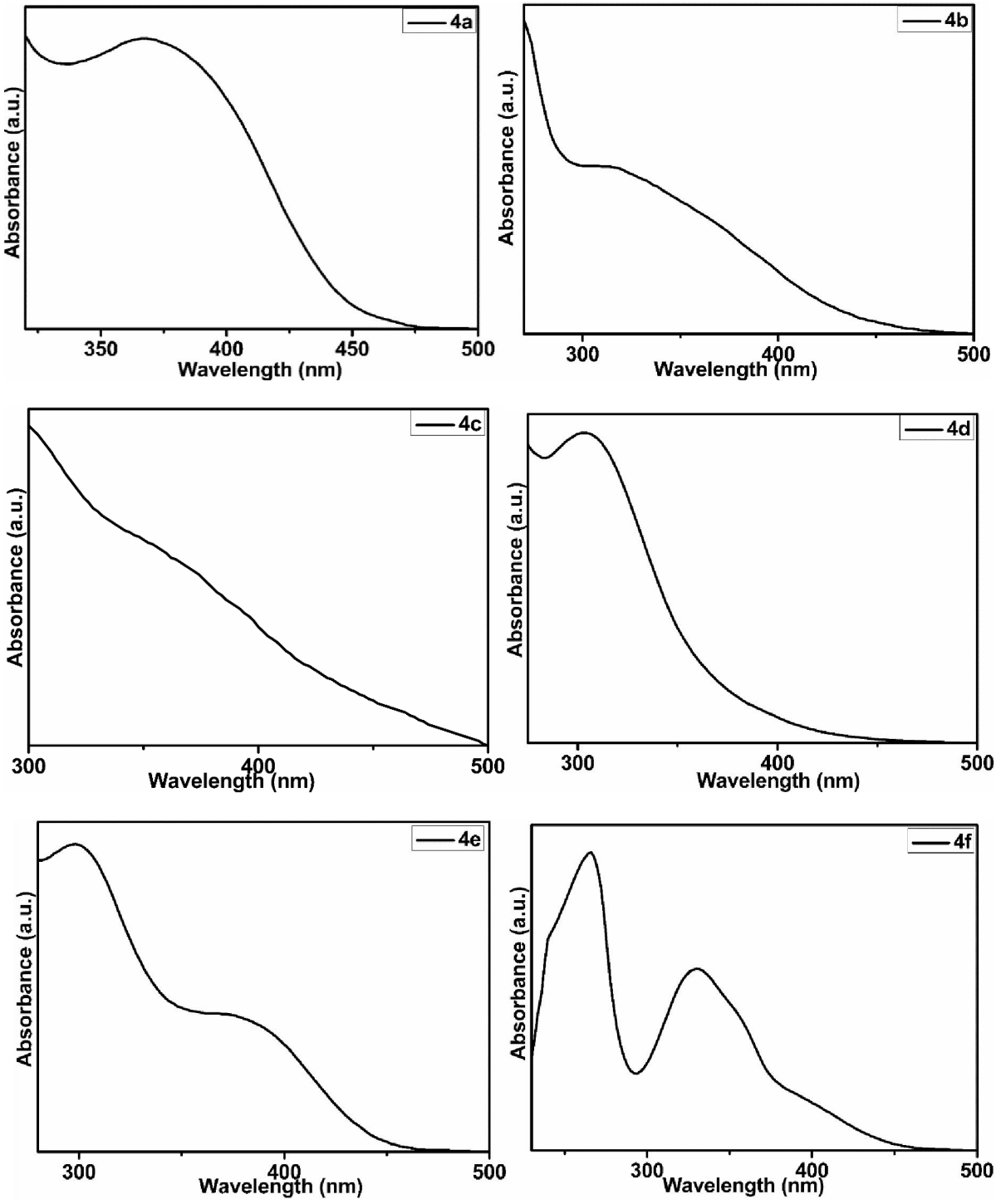


Fig. S4 UV-vis spectra of monomer **3a-3h** as thin film


4a
Absorbance (a.u.)
350
400
450
500
Wavelength (nm)
4b
Absorbance (a.u.)
300
400
500
Wavelength (nm)
4c
Absorbance (a.u.)
300
400
500
Wavelength (nm)
4d
Absorbance (a.u.)
300
400
500
Wavelength (nm)
4e
Absorbance (a.u.)
300
400
500
Wavelength (nm)
4f
Absorbance (a.u.)
300
400
500
Wavelength (nm)

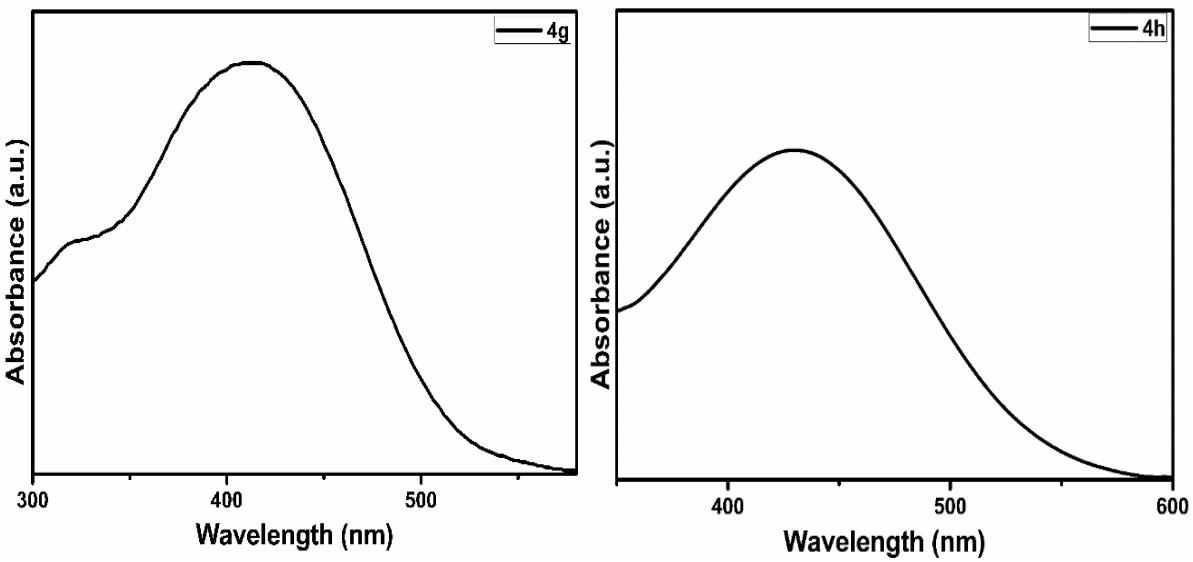


Fig. S5 UV-Vis spectra of Polymer **4a-4h** in 1:1 DCM-THF mixture

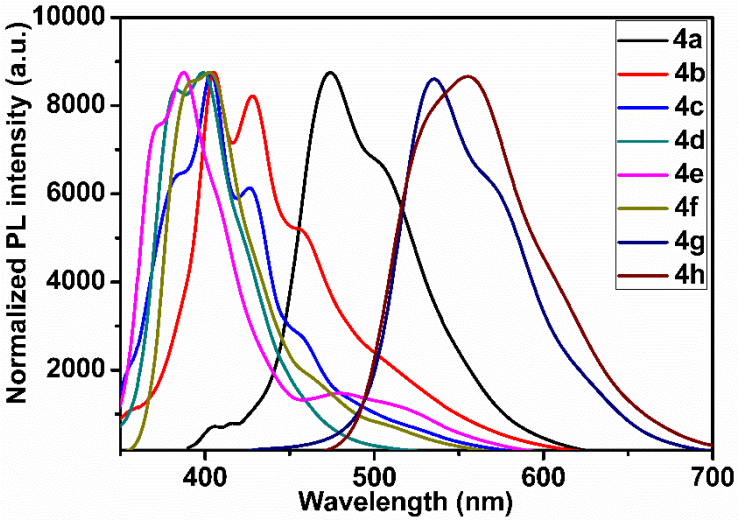
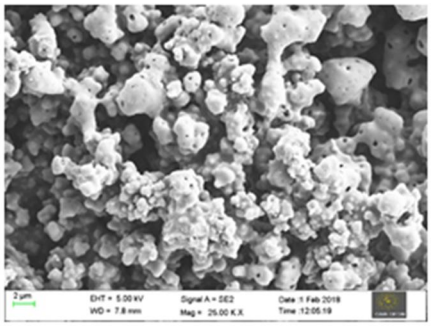


Fig. S6 Photoluminescence spectra of polymer **4a-4h** in 1:1 DCM-THF mixture

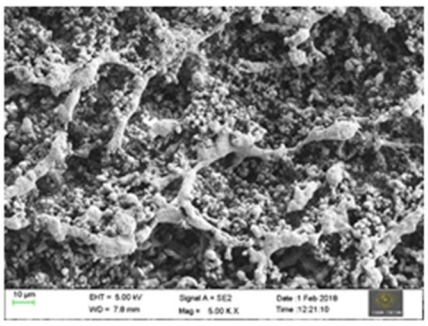
Table S1 Polymers PL data

Compounds	PL-λ_{em} (nm)	Shift (nm)
4a	473	550[a]
4b	405	2900[b]
4c	403	2000[a]
4d	398	3500[b]
4e	387	4100[b]
4f	402	3200[b]
4g	524	5200[a]
4h	546	5000[a]

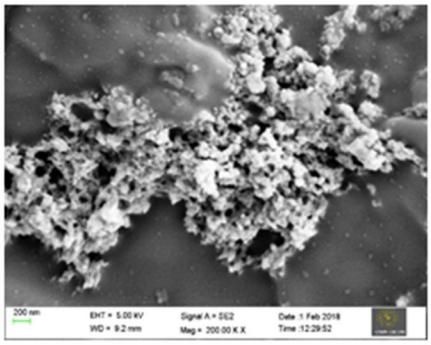
[a]Stokes shift; [b]Anti-Stokes shift



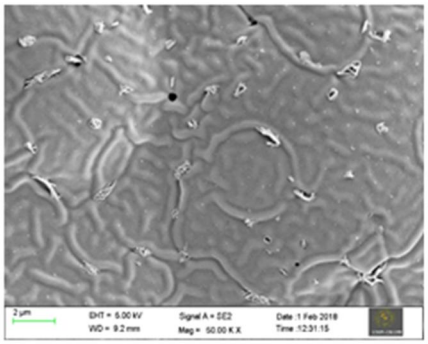
4a



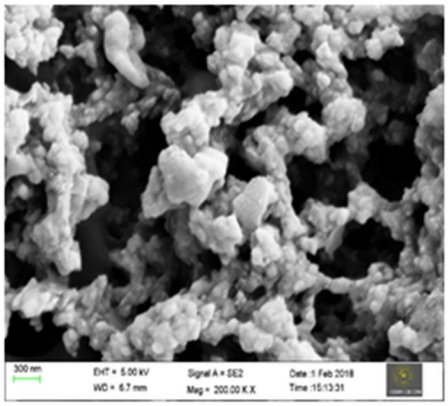
4b

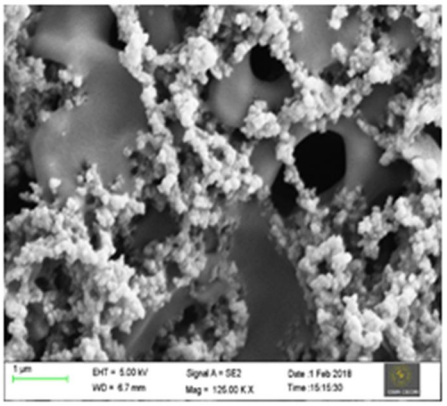


4c

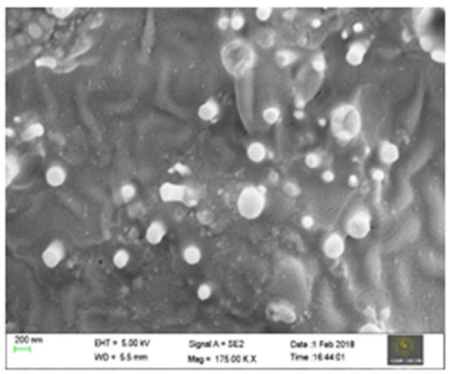


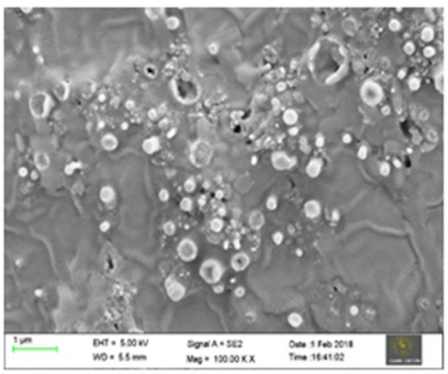
4d





4e





4f

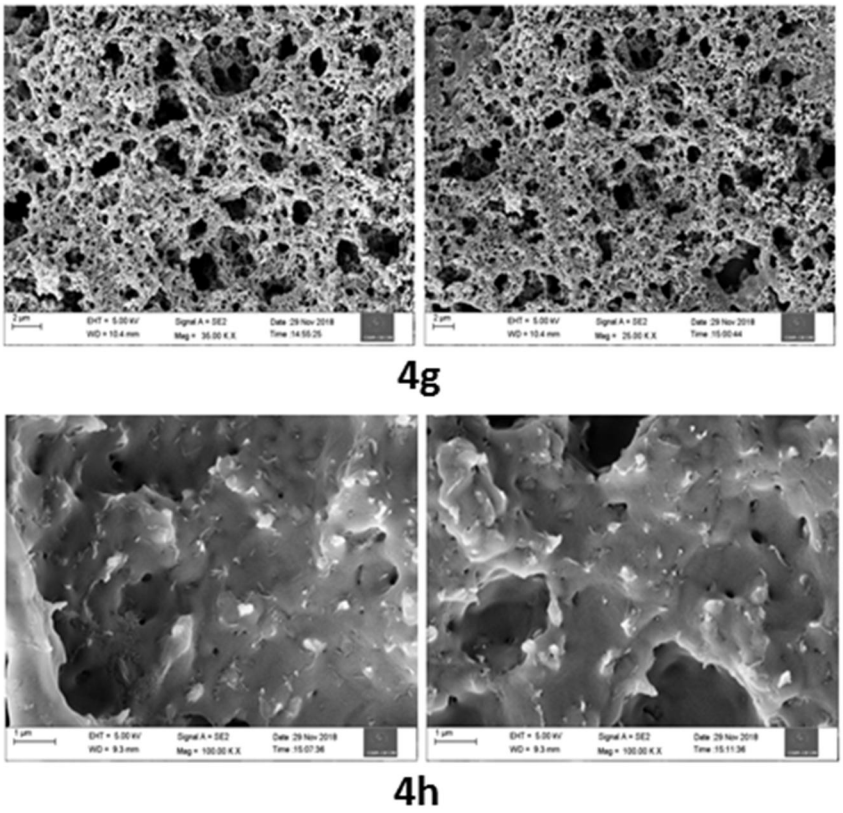
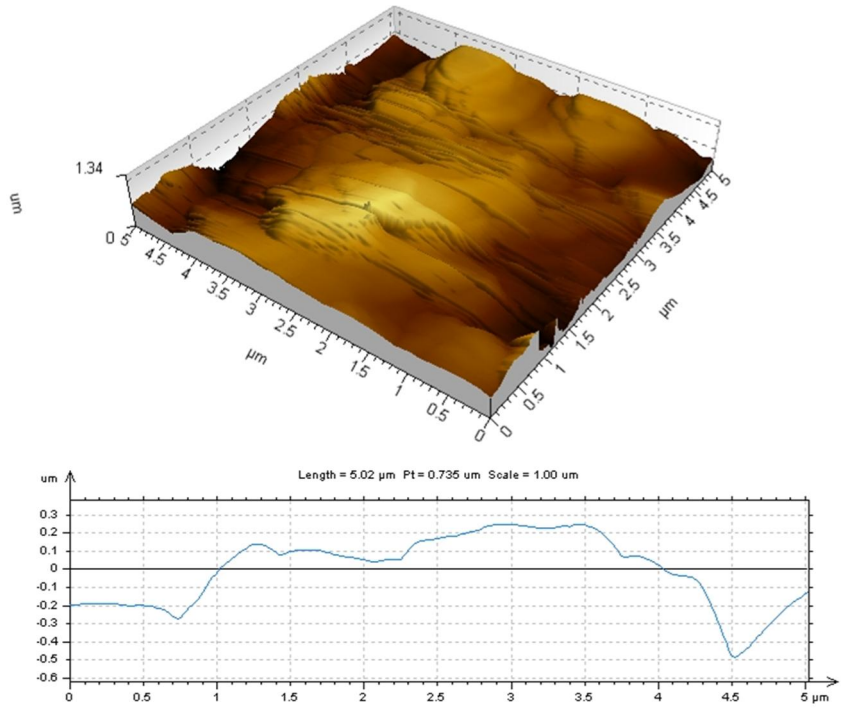
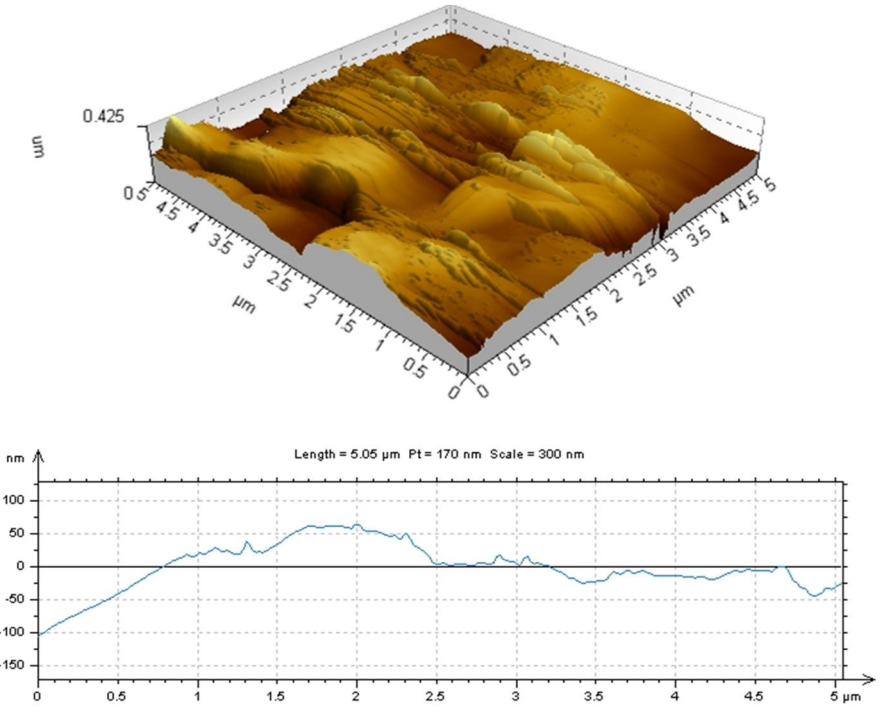


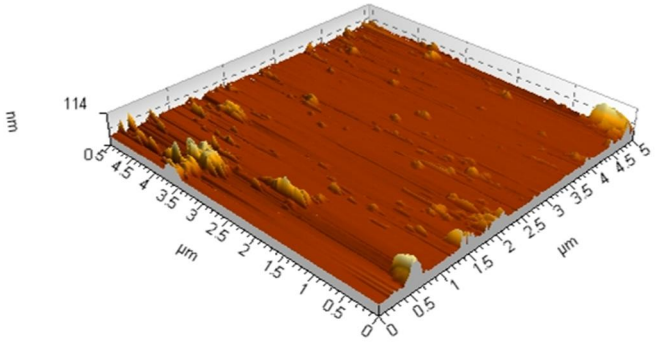
Fig. S7 SEM images of Polymers **4a**-**4h**

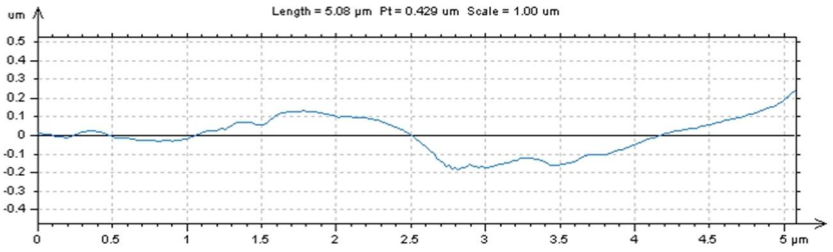

1.34
um
µm
Length = 5.02 µm Pt = 0.735 um Scale = 1.00 um
um
5 µm

4a

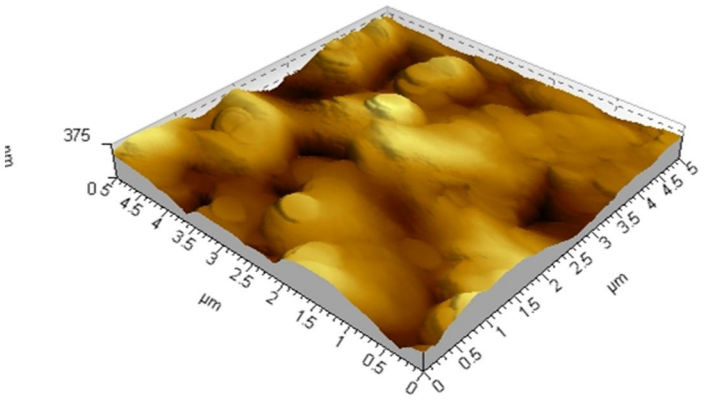

0.425
um
µm
Length = 5.05 µm Pt = 170 nm Scale = 300 nm
nm
5 µm

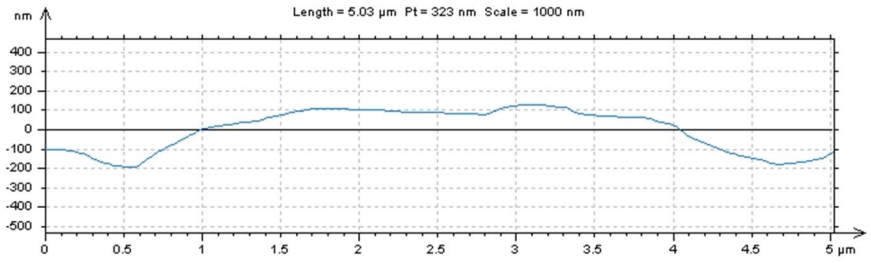
4b


nm
114
0
µm
µm

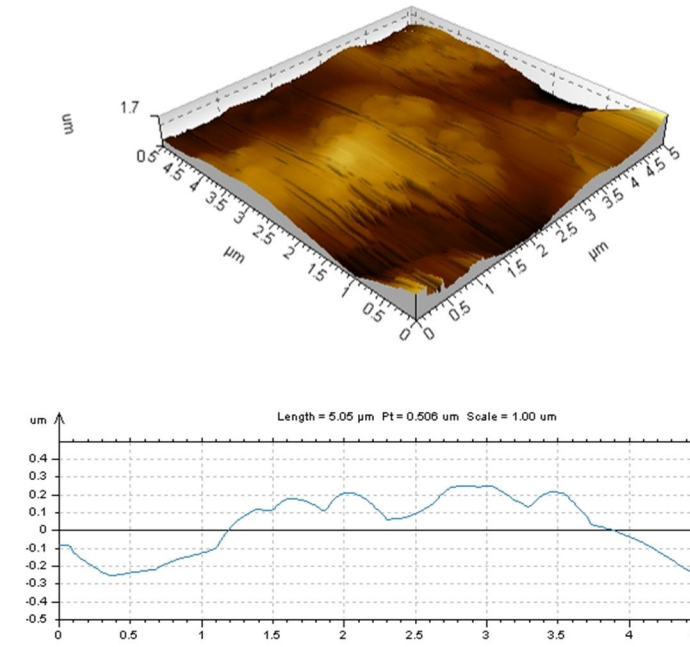

Length = 5.08 µm Pt = 0.429 um Scale = 1.00 um
um
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5 µm

4c

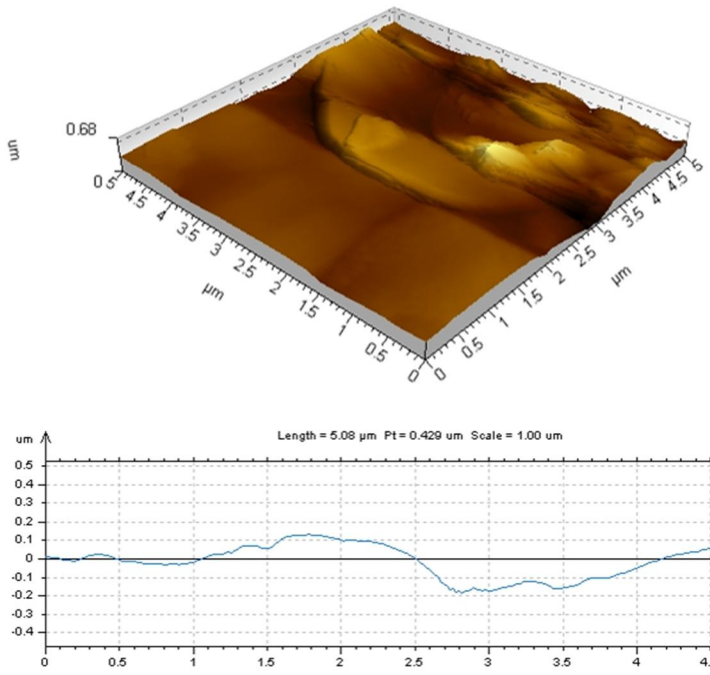

nm
375
0
µm
µm


Length = 5.03 µm Pt = 323 nm Scale = 1000 nm
nm
400
300
200
100
0
-100
-200
-300
-400
-500
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5 µm

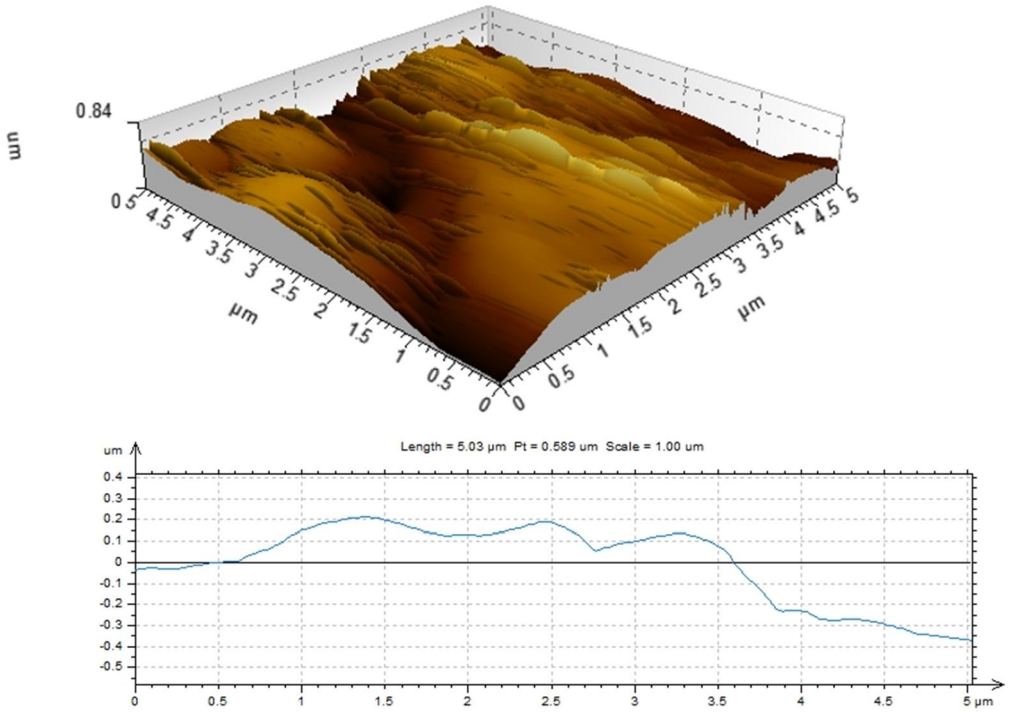
4d


um
1.7
0
μm
μm
Length = 5.05 μm Pt = 0.506 um Scale = 1.00 um
um
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5 μm

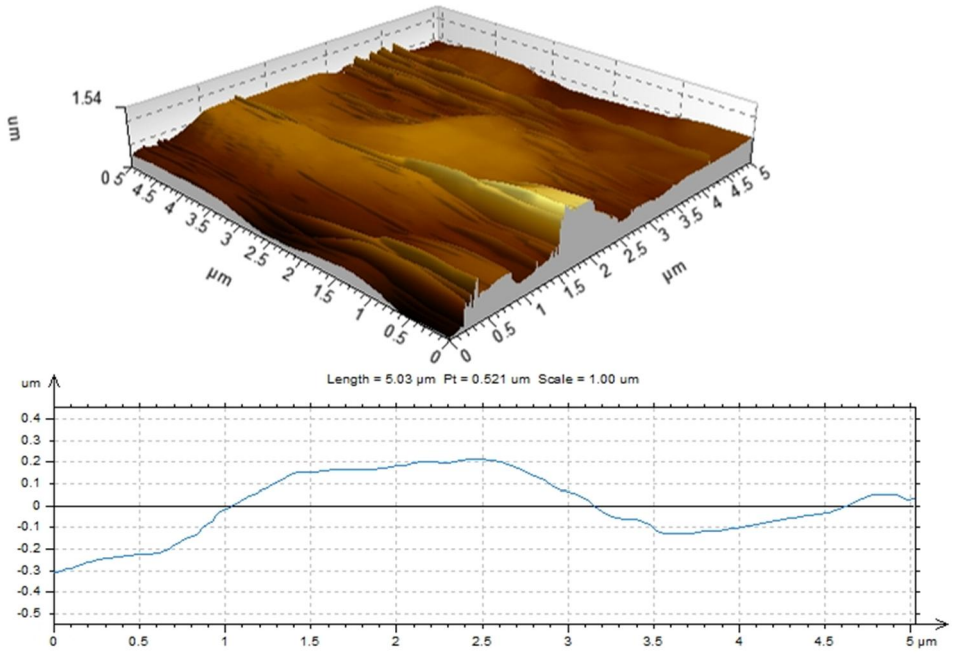
4e


um
0.68
0
μm
μm
Length = 5.08 μm Pt = 0.429 um Scale = 1.00 um
um
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5 μm

4f



4g



4h

Fig S8 AFM image and height profile of polymers **4a**-**4h**

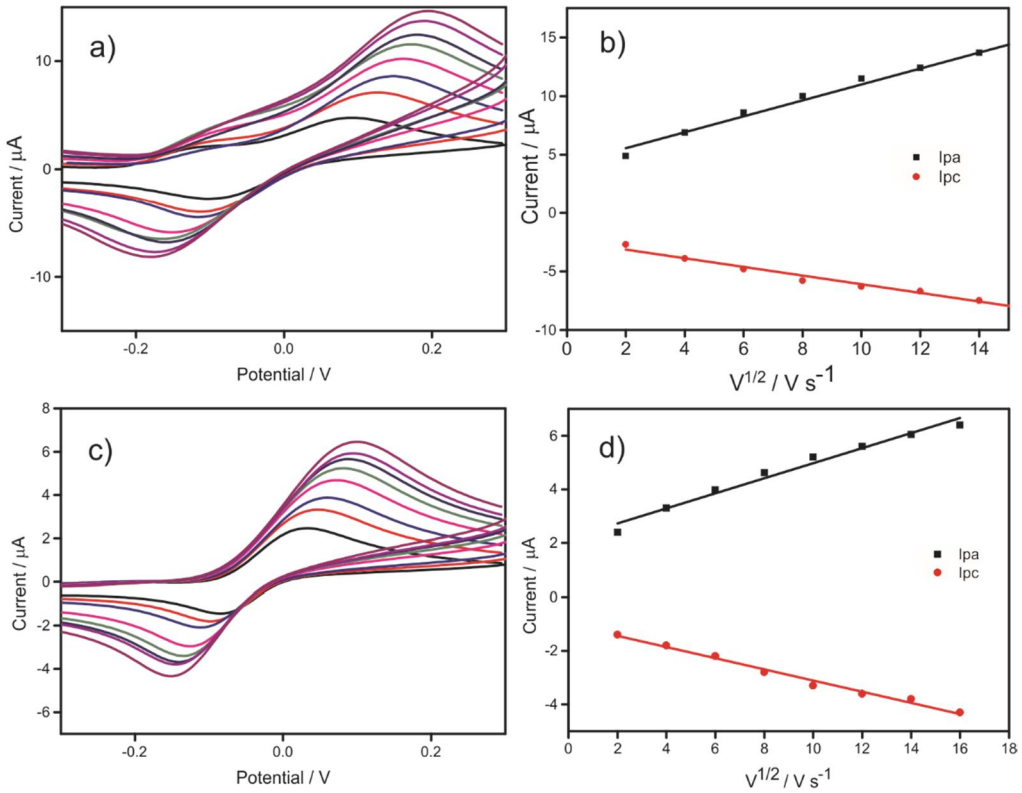


Fig S9 Variations of current *vs* square root of scan rate using polymer **4g** (top) and **4h** (bottom)