Electronic Supplementary Material (ESI) for *New Journal of Chemistry*

A Comprehensive Study of Substituent Effects on Poly(dibenzofulvene)s

Michael Y. Wong*[a] and Louis M. Leung[a]

[a]*Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China. E-mail: myw1011@gmail.com*

Content

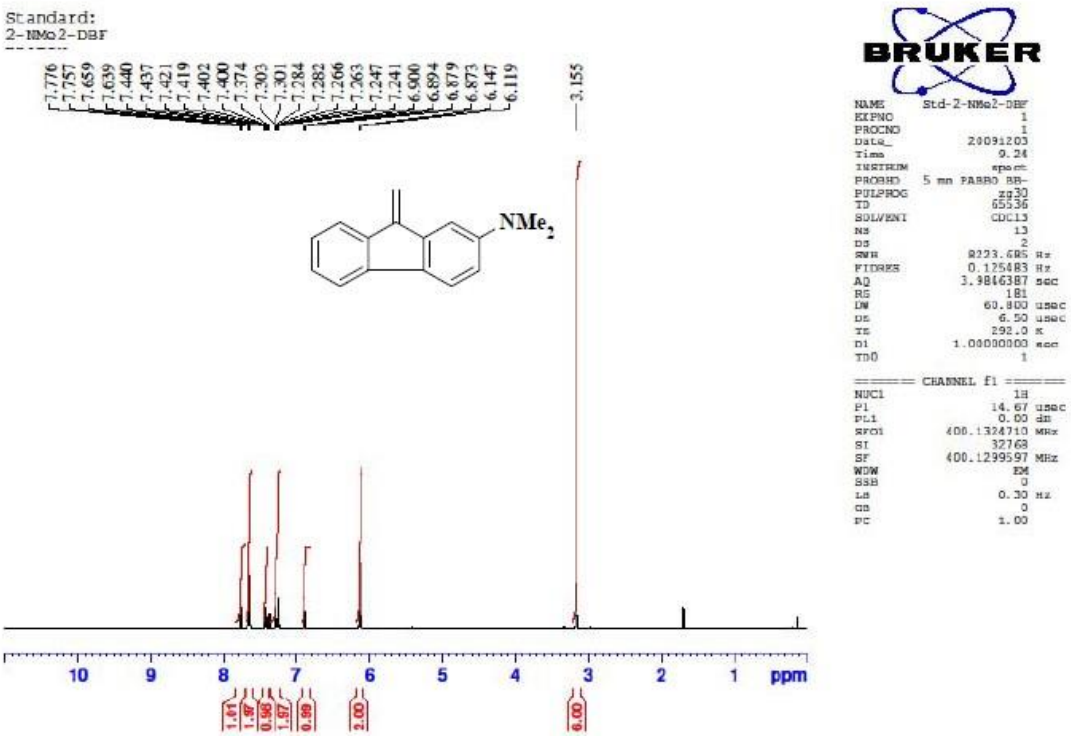

Figure **S1**. ^{1}H NMR spectrum of 2-*N*,*N*-dimethylaminodibenzofulvene in $CDCl_3$.

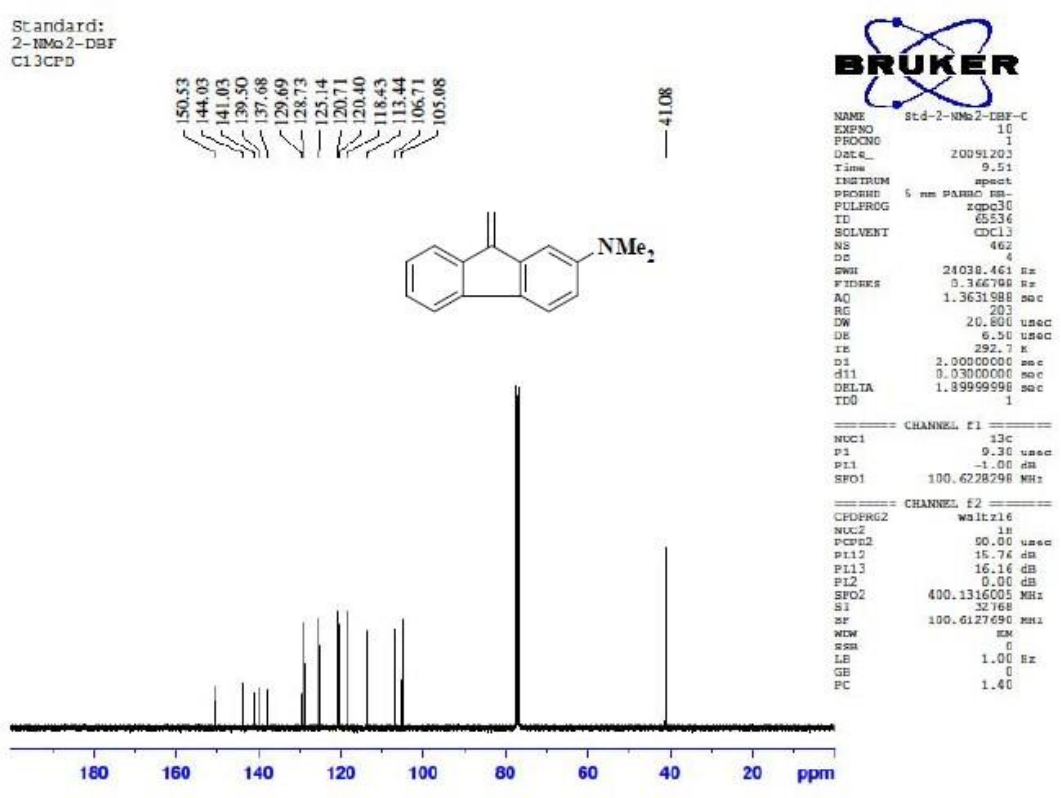

Figure **S2**. ^{13}C NMR spectrum of 2-*N*,*N*-dimethylaminodibenzofulvene in $CDCl_3$.

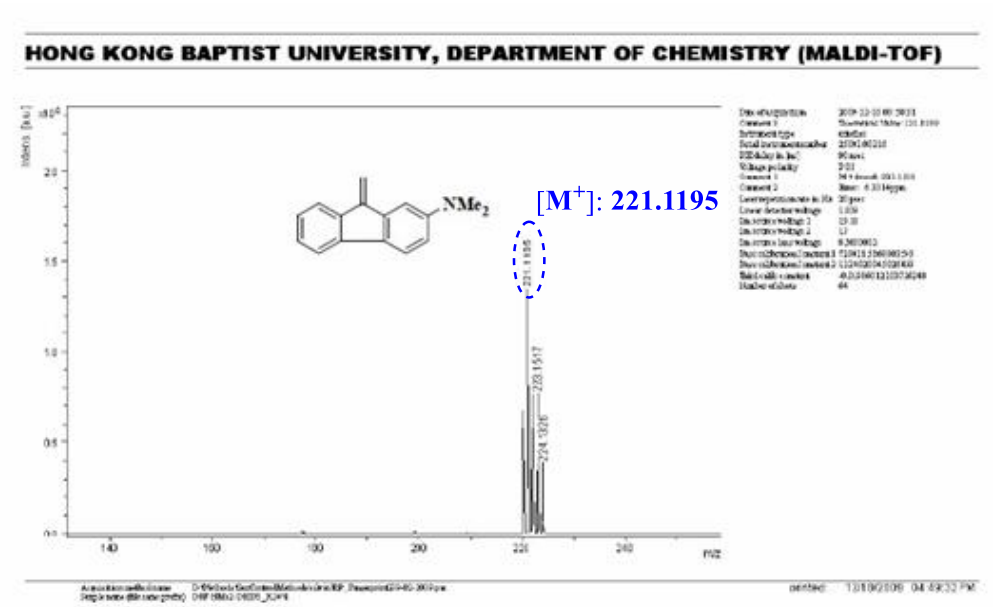

Figure **S3**. HRMS (MALDI-TOF) spectrum of 2-*N*,*N*-dimethylaminodibenzofulvene.

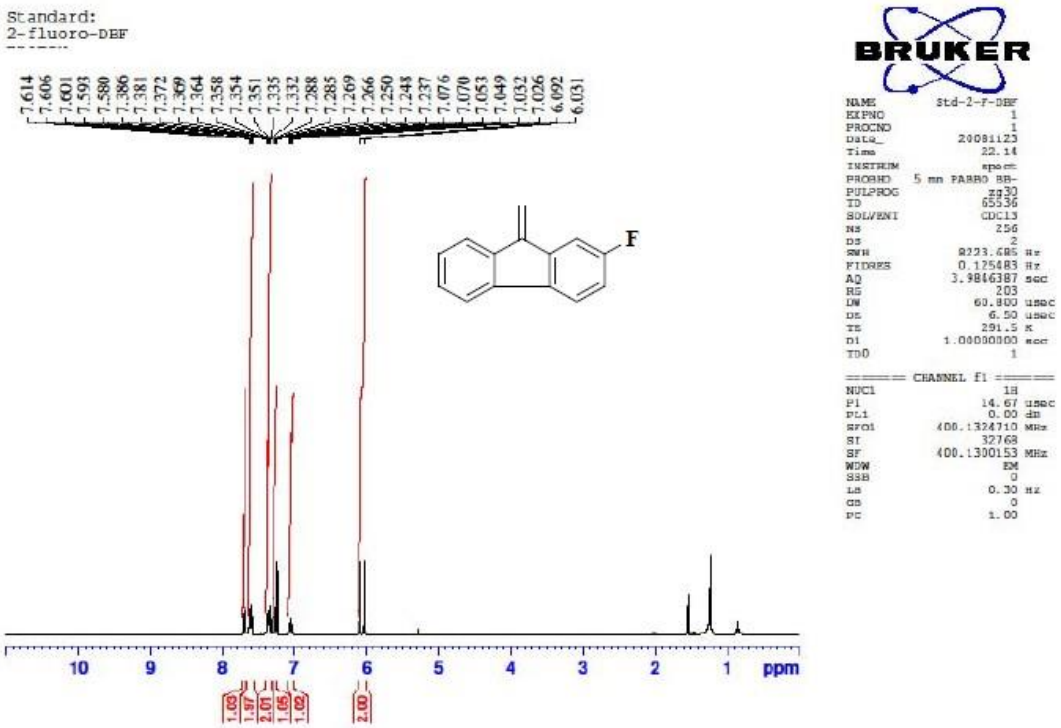

Figure **S4**. ^{1}H NMR spectrum of 2-fluorodibenzofulvene in $CDCl_3$.

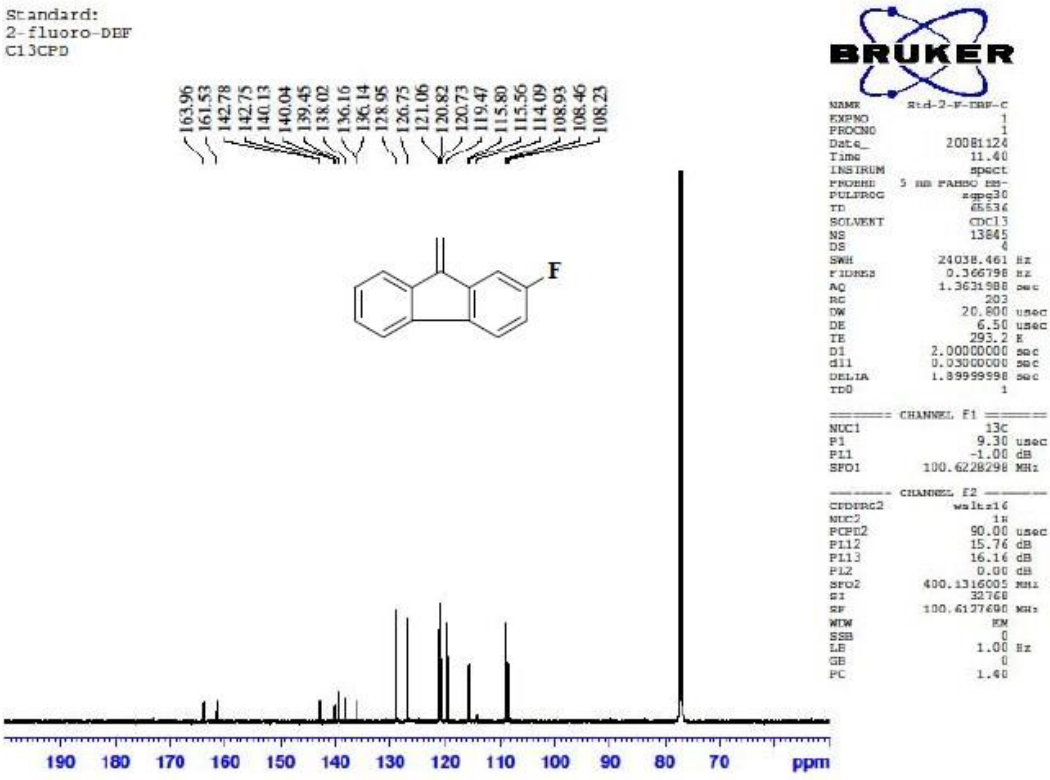

Figure **S5**. ^{13}C NMR spectrum of 2-fluorodibenzofulvene in $CDCl_3$.

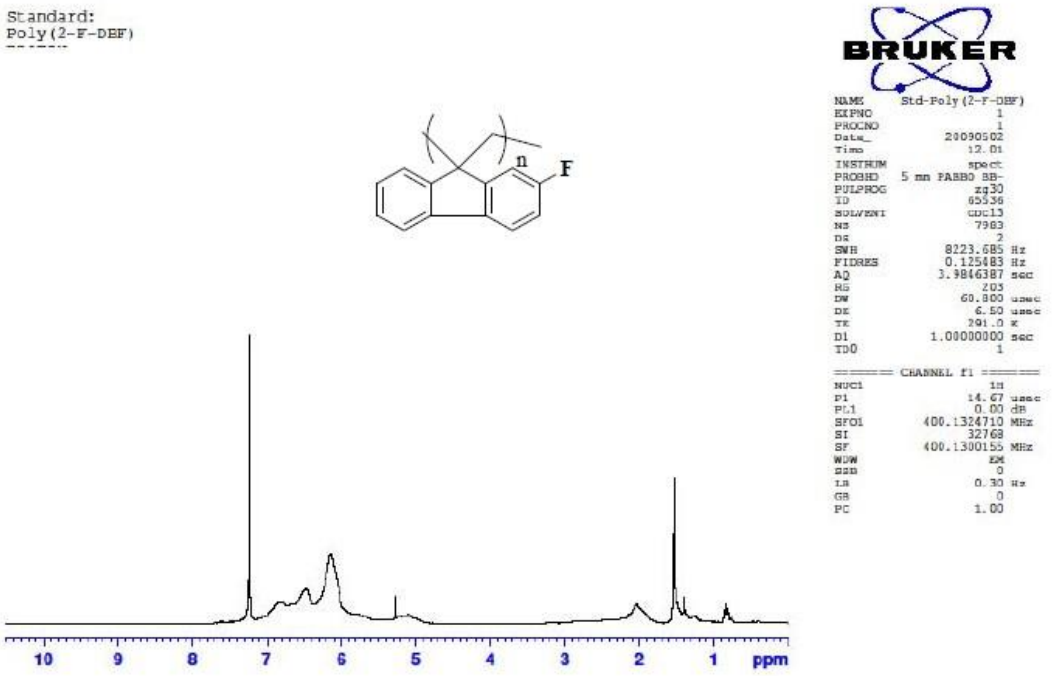

Figure **S6**. ^{1}H NMR spectrum of **poly(FDBF)** in $CDCl_3$.

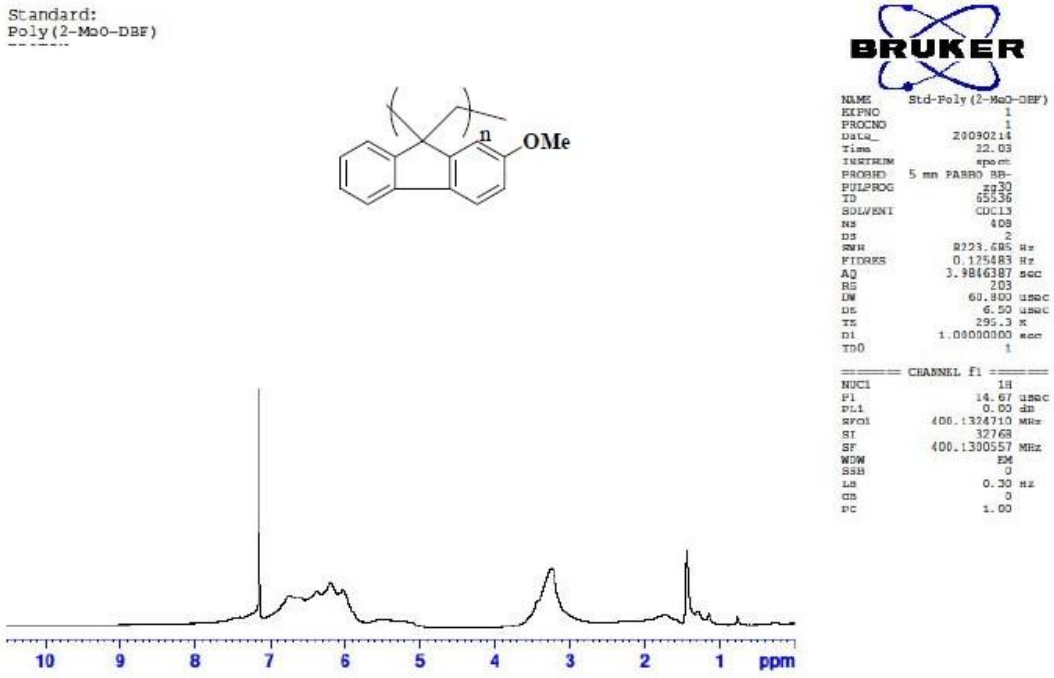

Figure **S7**. ^{1}H NMR spectrum of **poly(MeODBF)** in $CDCl_3$.

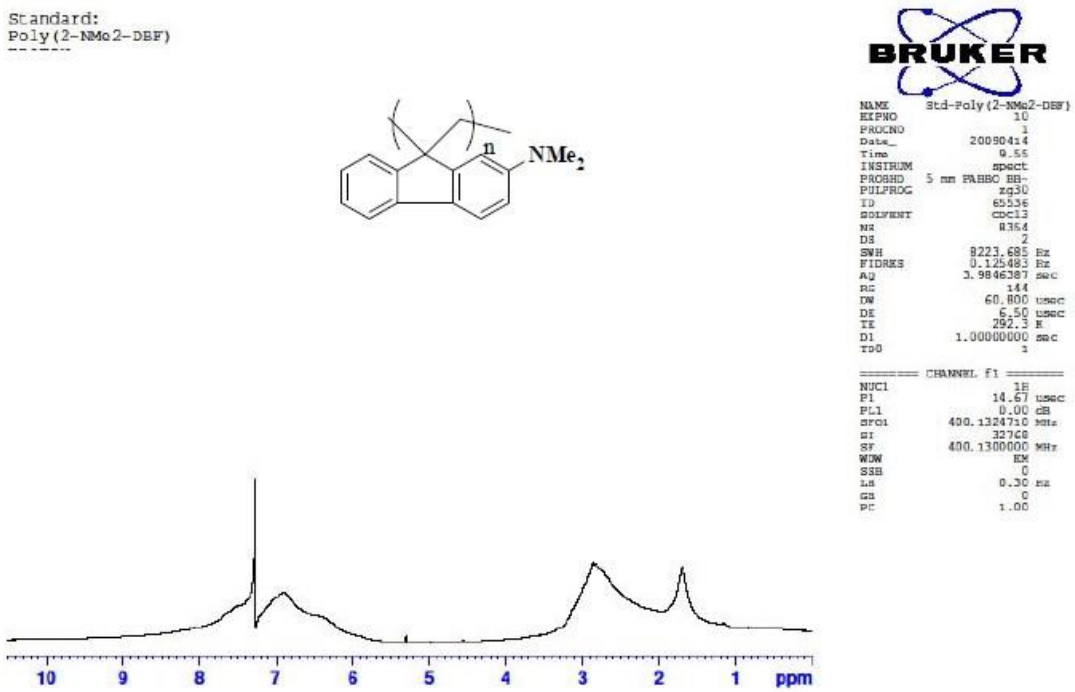

Figure **S8**. ^{1}H NMR spectrum of **poly(NMe2DBF)** in $CDCl_3$.

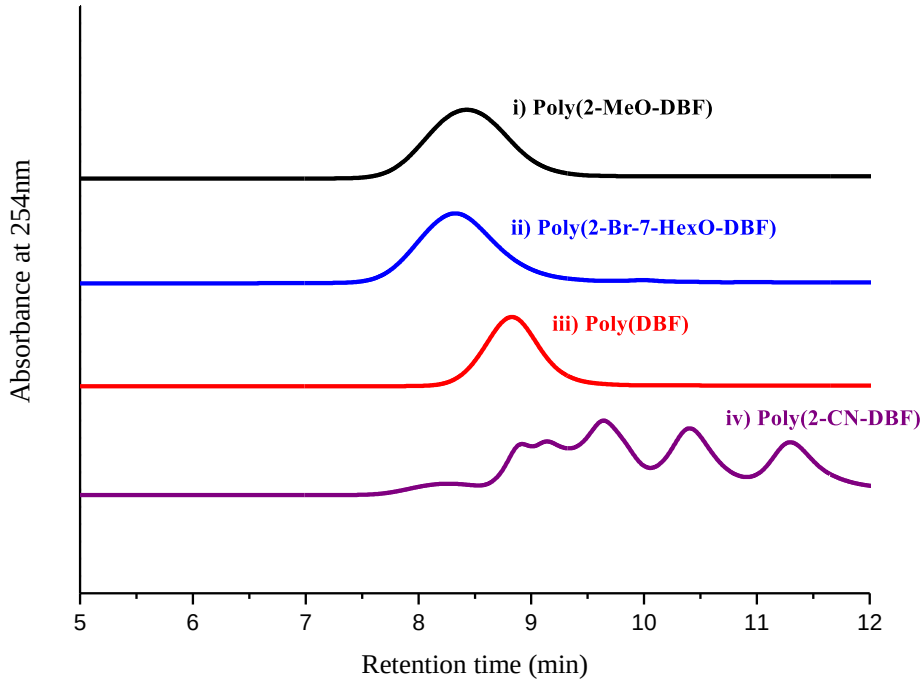

Figure **S9**. GPC traces of some substituted **poly(DBF)**s.

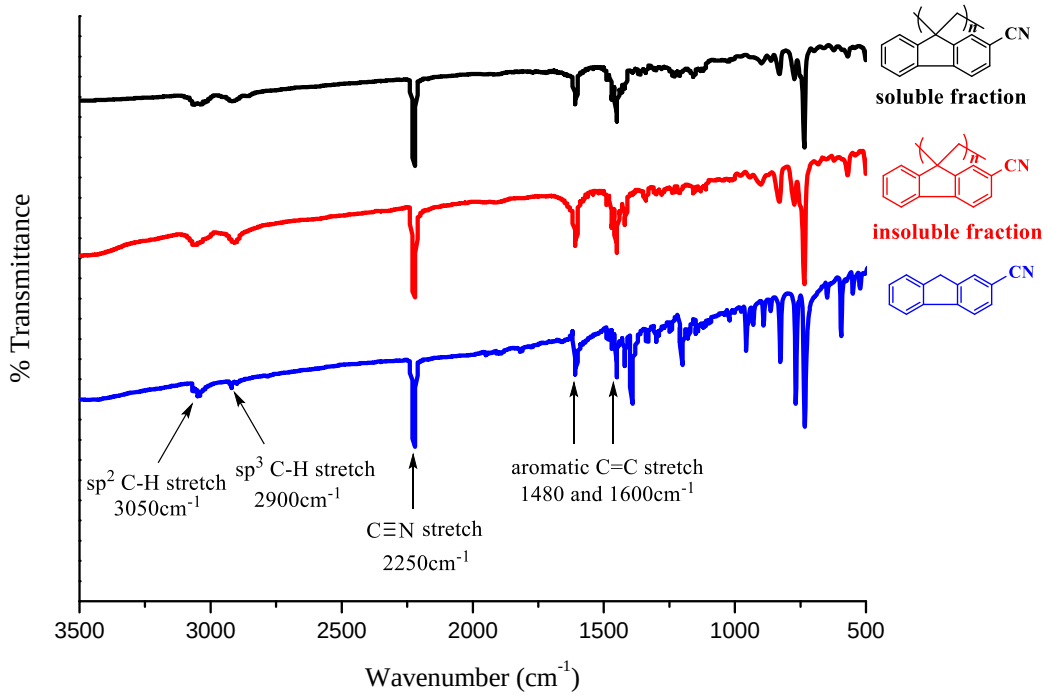

Figure **S10**. Comparison of IR spectra between **poly(CNDBF)** (both soluble and insoluble fractions) and 2-cyanofluorene with peak assignments. The spectra suggest that both fractions contain same chemical composition.

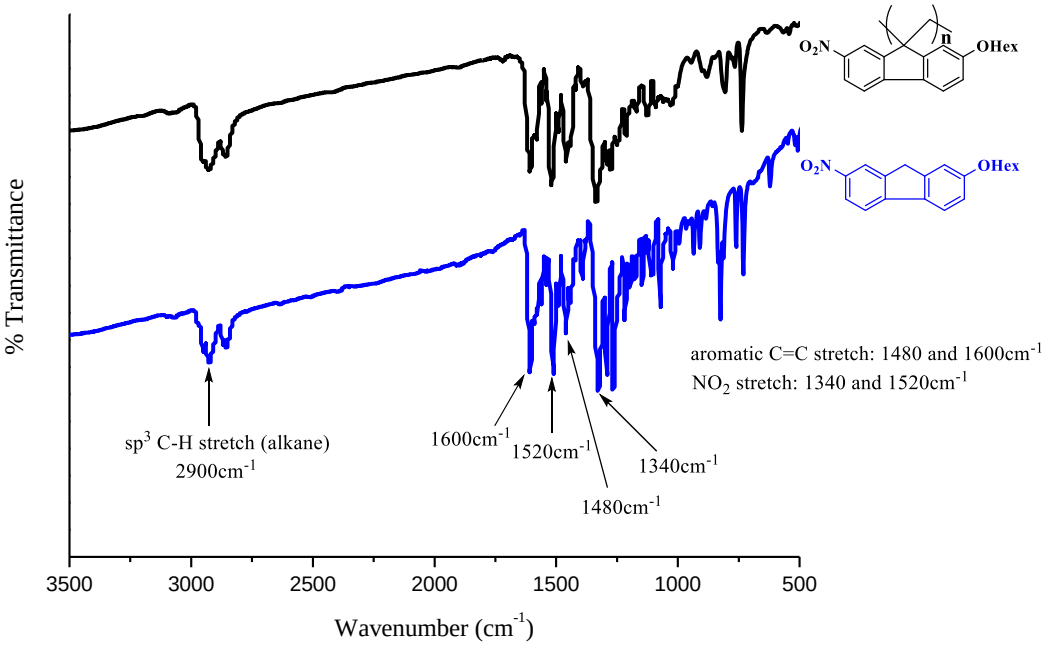

Figure **S11**. Comparison of IR spectra between **poly(NO2HexODBF)** and 2-hexoxy-7-nitrofluorene with peak assignments.

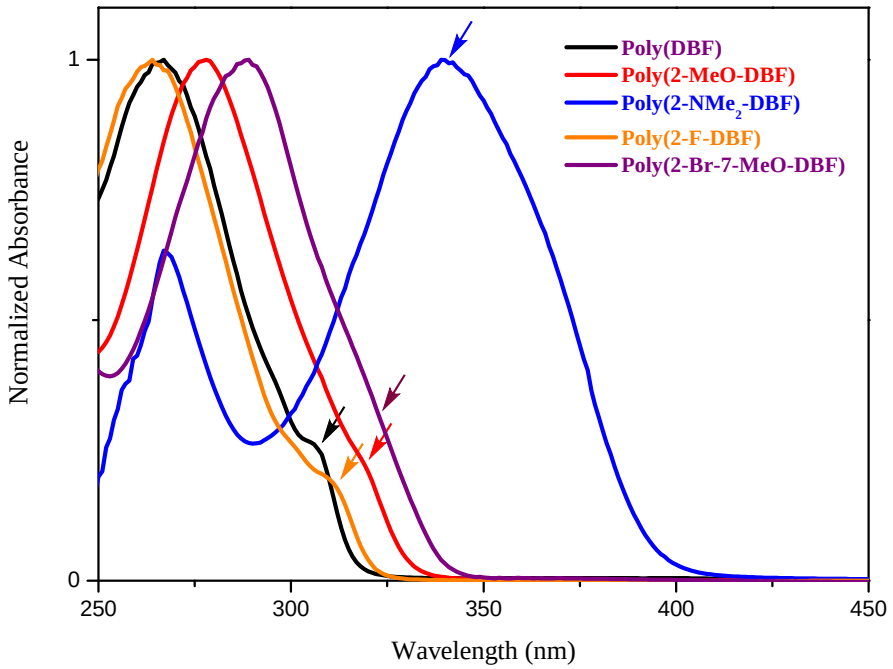

Figure **S12**. Normalized absorption spectra of some substituted **poly(DBF)**s in THF. Arrows indicate the lowest-energy absorption peak wavelengths.

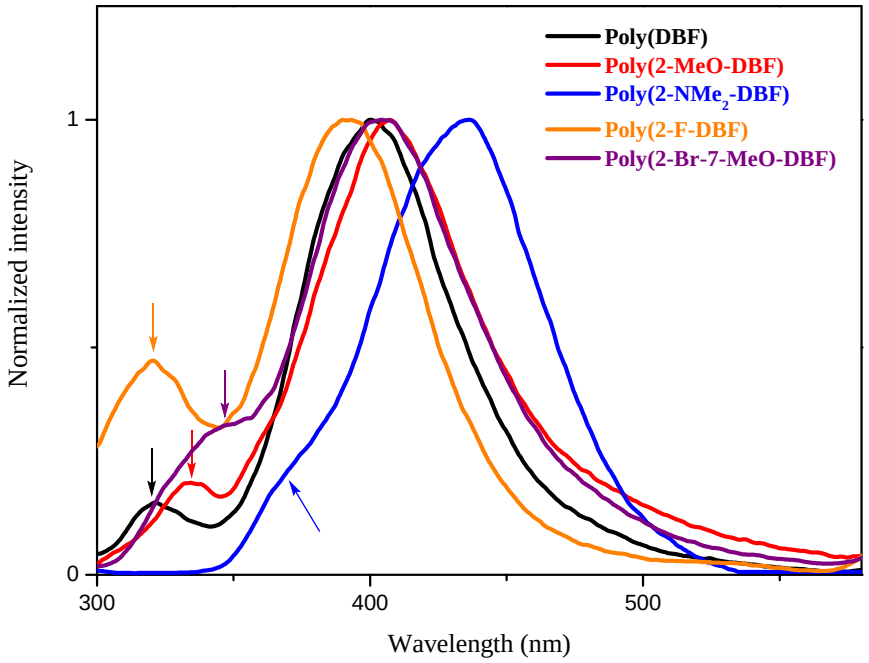

Figure **S13**. Normalized emission spectra of some substituted **poly(DBF)**s in THF. Arrows indicate the defect emissions.

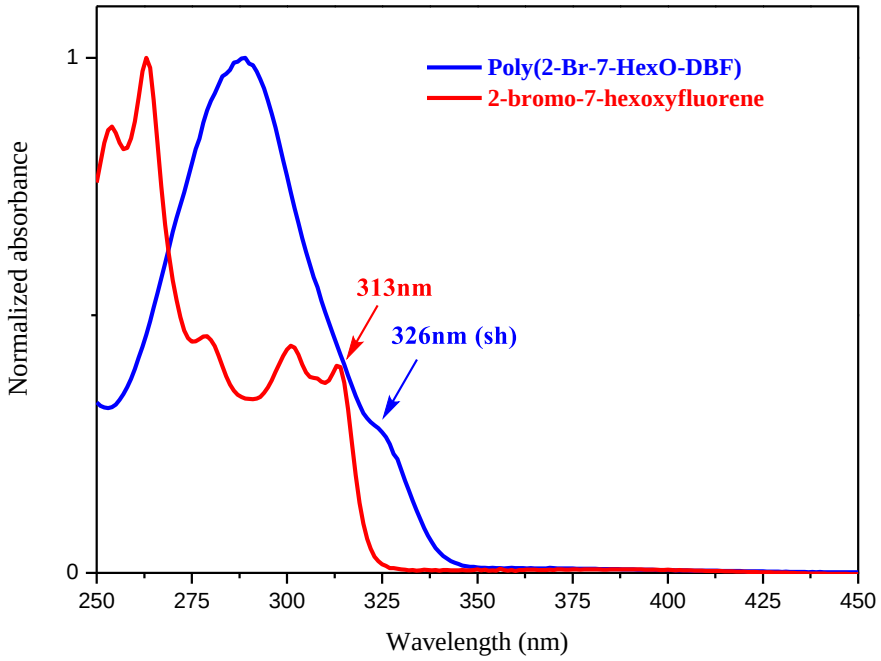

Figure **S14**. Normalized absorption spectra of **poly(BrHexODBF)** and 2-bromo-7-hexoxyfluorene in THF.

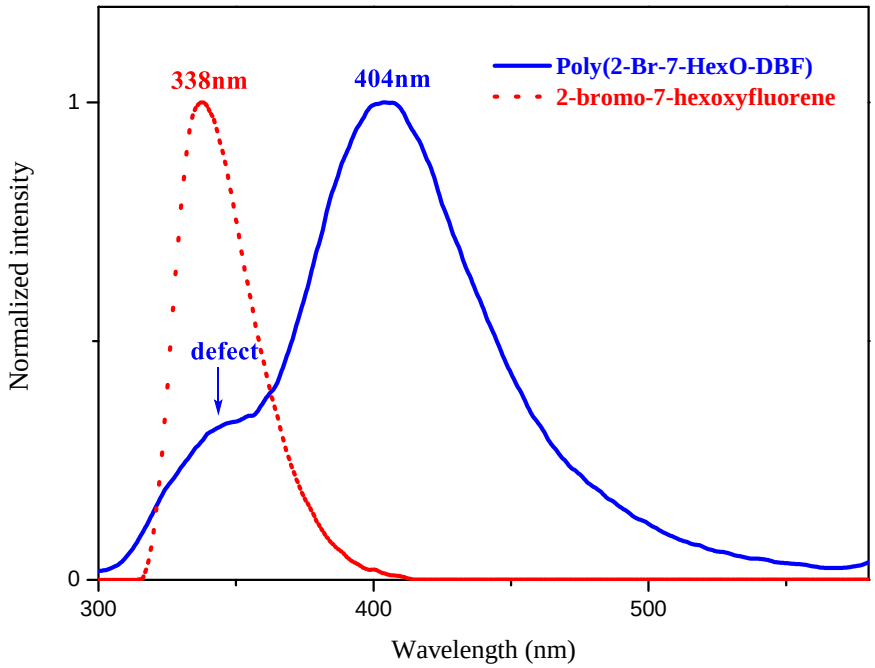

Figure **S15**. Normalized emission spectra of **poly(BrHexODBF)** and 2-bromo-7-hexoxyfluorene in THF. Arrow indicates the emission of defect in the polymer which matches the emission maximum of 2-bromo-7-hexoxyfluorene.

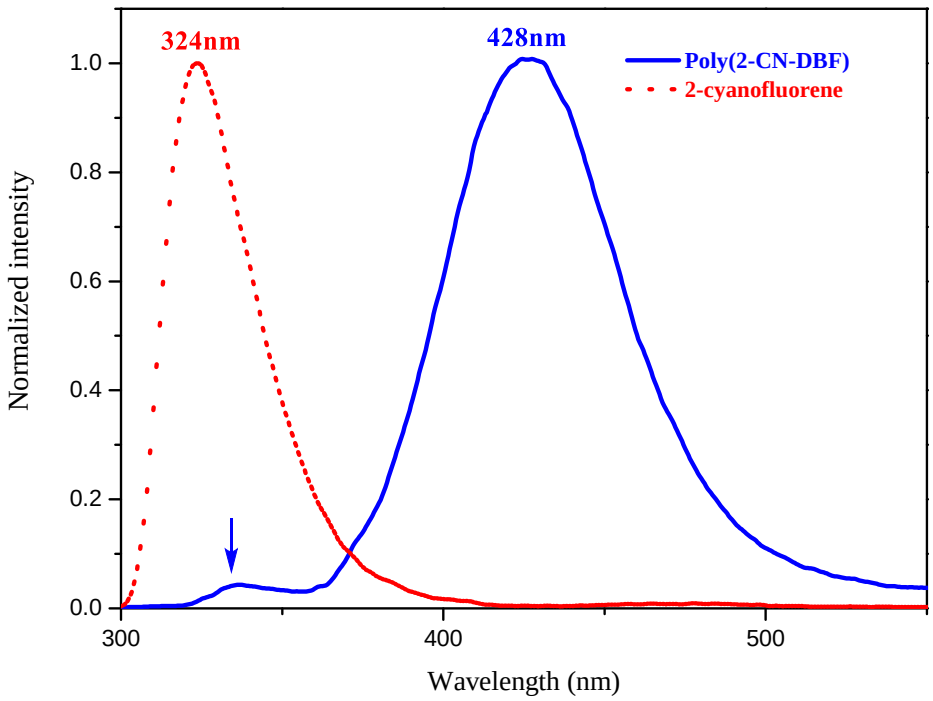

Figure **S16**. Normalized emission spectra of **poly(CNDBF)** and 2-cyanofluorene in THF. The arrow indicates the emission of the stereochemical defect in the polymer which matches the emission maximum of 2-cyanofluorene. Note the excimer emission strongly outweighs that of the defects despite the low molecular weight of the polymer.

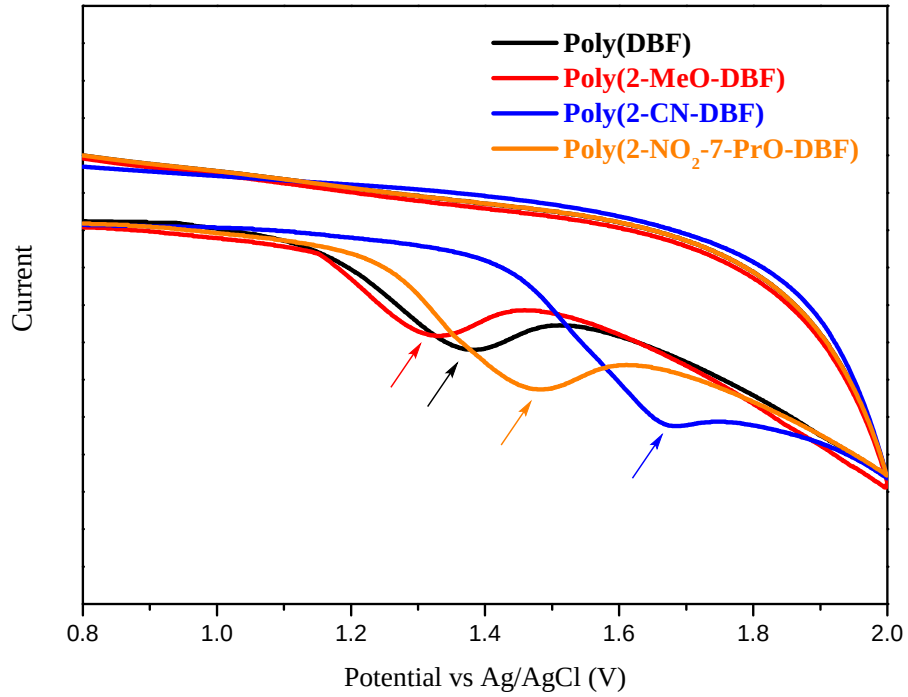

Figure **S17**. Cyclic voltammograms of some substituted **poly(DBF)**s in THF with 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte. Arrows indicate oxidation potentials.

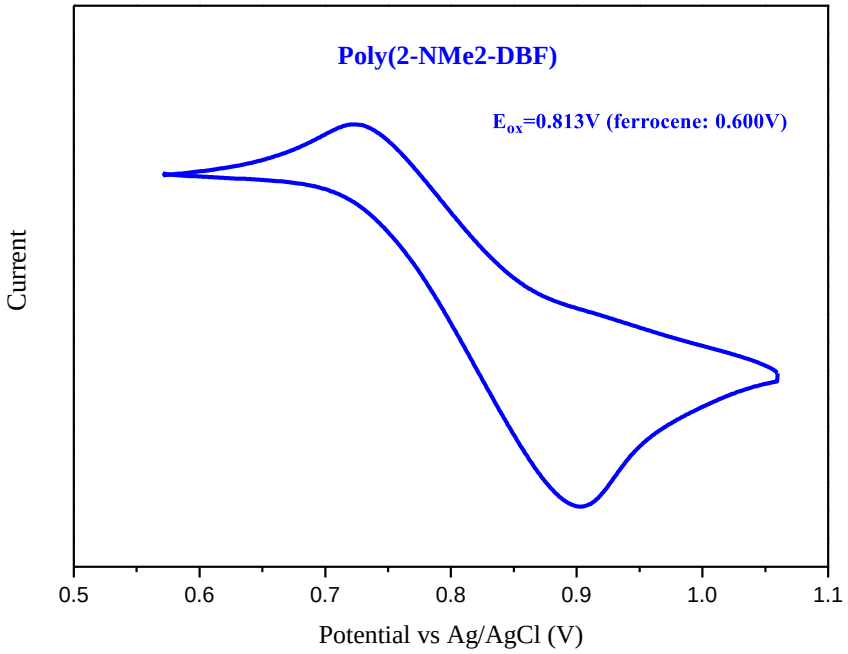

Figure **S18**. Cyclic voltammograms of **poly(NMe2DBF)**s in THF with 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte.

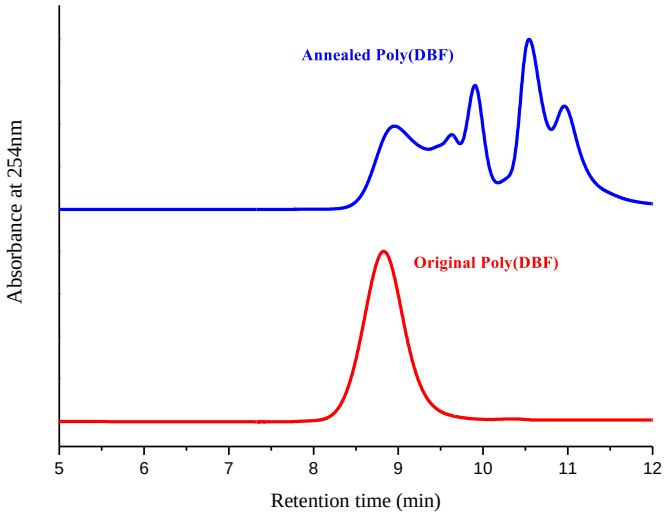

Figure **S19**. GPC traces of **poly(DBF)** after annealing (top, in blue) and before annealing (bottom, in red).

Table **S1**. Electrochemical data of the substituted **poly(DBF)**s.[a]

	HOMO[b] (eV)	LUMO[c] (eV)	ΔE[d] (eV)
Poly(DBF)	-5.66	-1.79	3.87
Poly(MeODBF)	-5.61	-1.96	3.70
Poly(NMe2DBF)	-5.01	-1.90	3.11
Poly(FDBF)	-5.76	-1.91	3.85
Poly(BrDBF)	-5.86	-2.05	3.81
Poly(IDBF)	-5.83	-2.07	3.76
Poly(CNDBF)	-5.93	-2.58	3.35
Poly(NO2DBF)	-6.07	-3.12	2.95
Poly(NO2PrODBF)	-5.75	-3.14	2.61
Poly(NO2HexODBF)	-5.66	-3.07	2.59
Poly(BrMeODBF)	–	–	–
Poly(BrPrODBF)	-5.64	-1.97	3.70
Poly(BrHexODBF)	-5.61	-1.89	3.72
Poly(Br2DBF)	–	–	–

[a.] Performed in degassed THF under N_2 with 0.1 M nBu$_4$NPF$_6$ as the supporting electrolyte. [b.] HOMO energies are obtained with reference to ferrocene internal standard by relation: HOMO = − ($E_{Fc}^{1/2}$ + 4.8) eV. [c.] LUMO energies are estimated from HOMO and bandgap (ΔE) by relation: ΔE= |HOMO|-|LUMO|. [d.] Bandgap is estimated from the absorption onset wavelength.