

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

A Comprehensive Study of Substituent Effects on

Poly(dibenzofulvene)s

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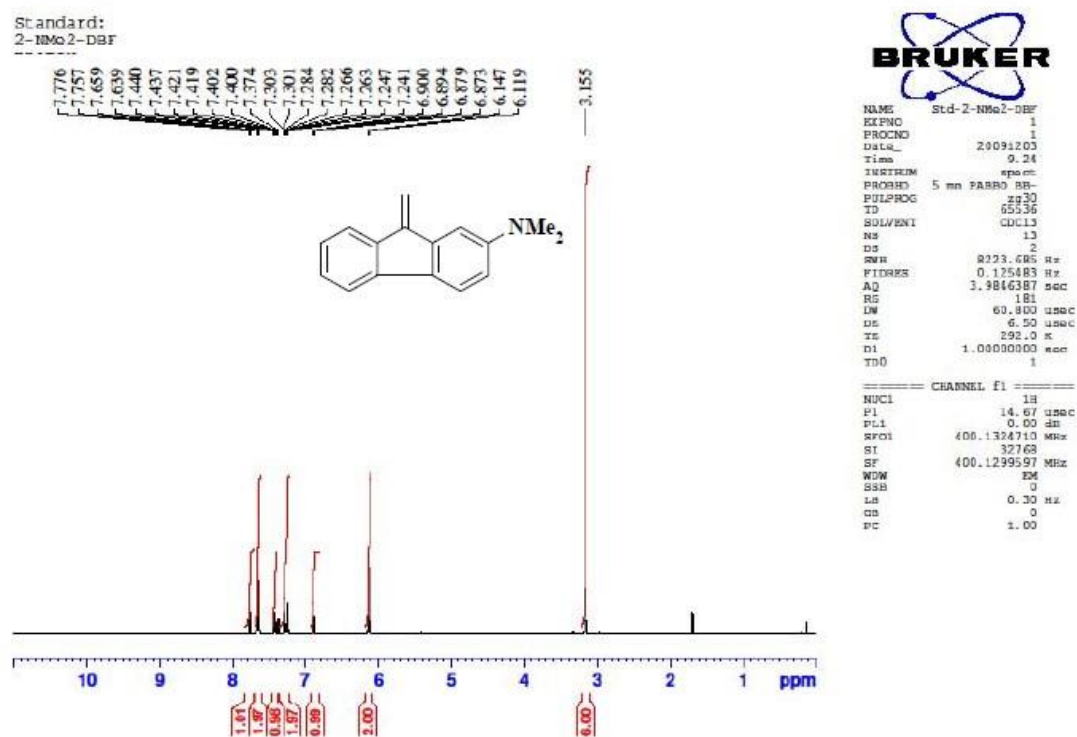


Figure S1. ¹H NMR spectrum of 2-*N,N*-dimethylaminodibenzofulvene in CDCl₃.

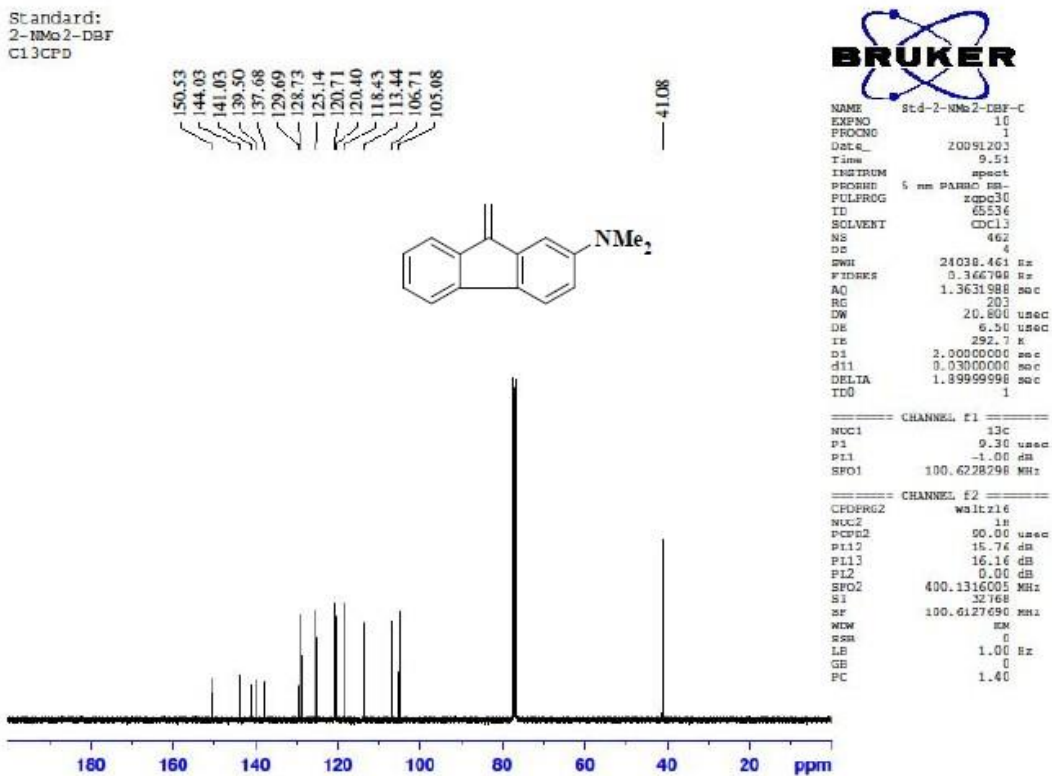


Figure S2. ¹³C NMR spectrum of 2-*N,N*-dimethylaminodibenzofulvene in CDCl₃.

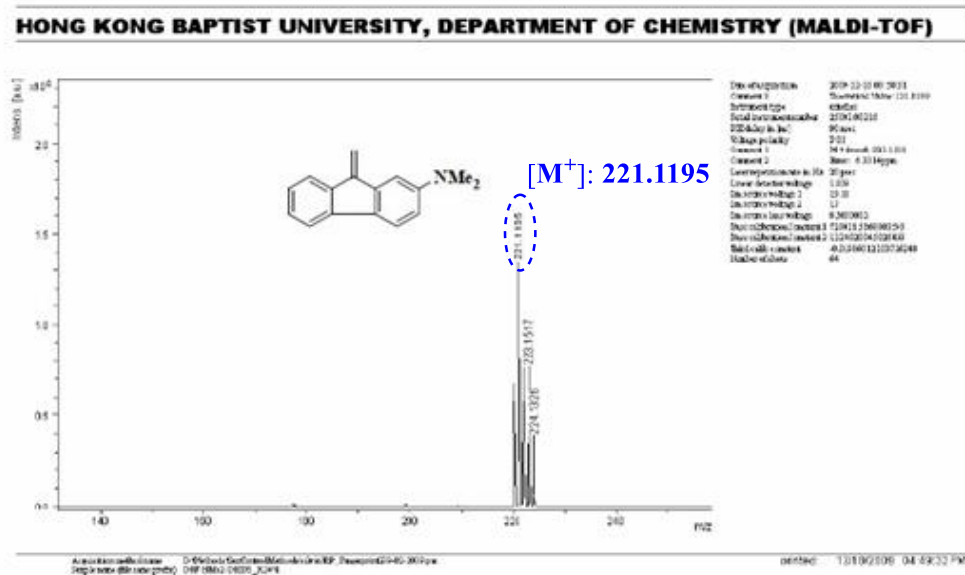


Figure S3. HRMS (MALDI-TOF) spectrum of 2-*N,N*-dimethylaminodibenzofulvene.

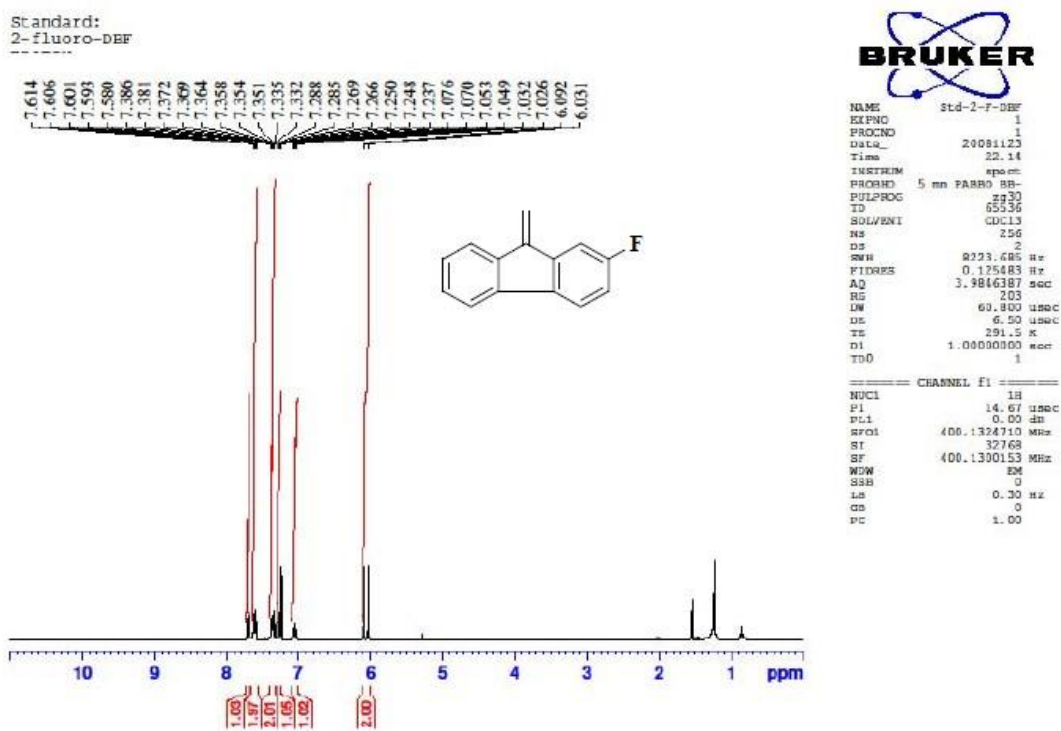


Figure S4. ^1H NMR spectrum of 2-fluorodibenzofulvene in CDCl_3 .

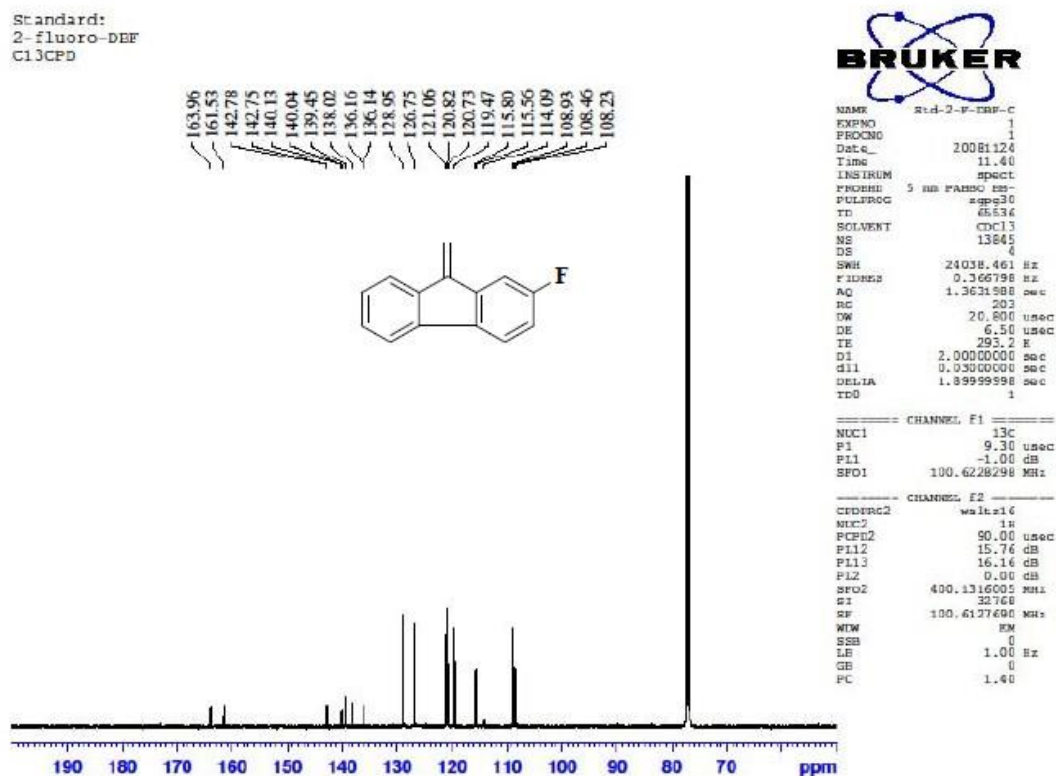
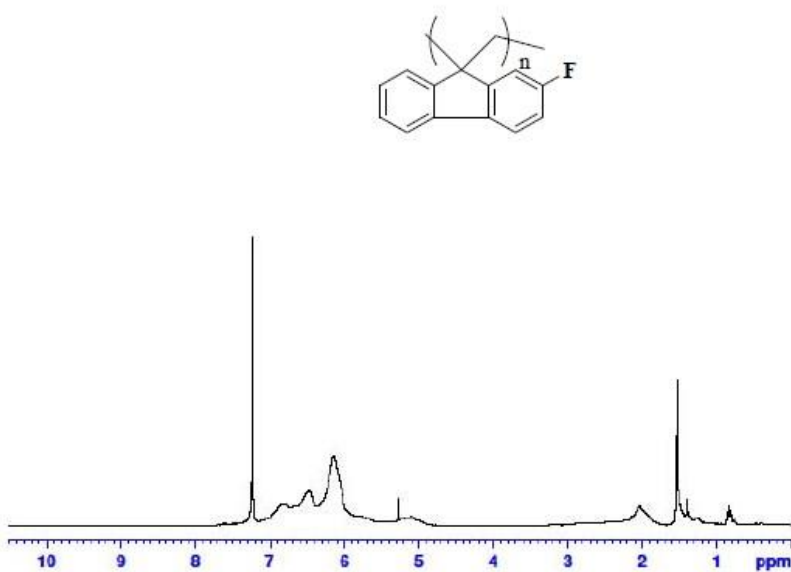


Figure S5. ^{13}C NMR spectrum of 2-fluorodibenzofulvene in CDCl_3 .

Standard:
Poly(2-F-DBF)

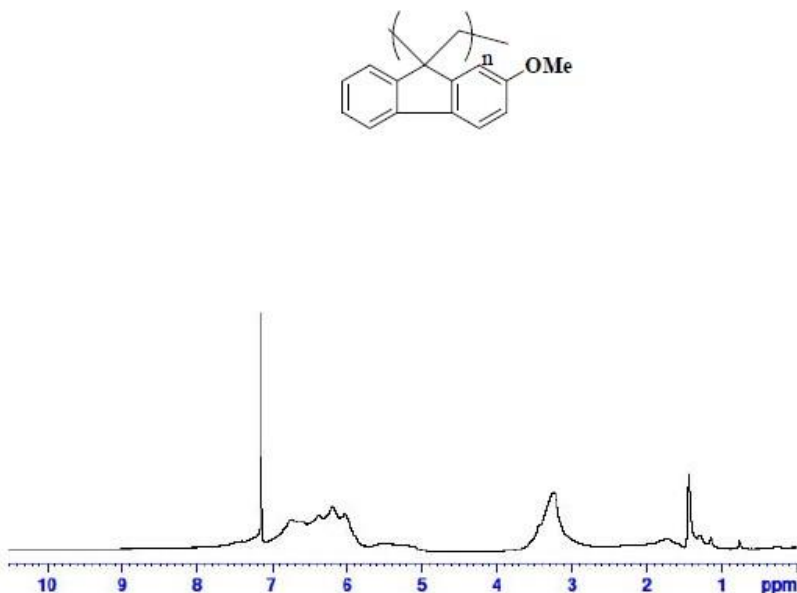


```
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EXPNO     1
PROCNO    1
Date_     20090502
Time      12.01
INSTRUM   spect
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PULPROG   zg30
TD        65536
SOLVENTI  cdcl3
NS        7983
DS        2
SWH        8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846387 sec
RG        203
DW        60.800 usec
DE        6.50 usec
TE        291.0 K
D1        1.00000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      1H
P1        14.67 usec
PL1       0.00 dB
SFO1     400.1324710 MHz
SI        32768
SF        400.1300150 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
```

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

Standard:
Poly(2-MeO-DBF)

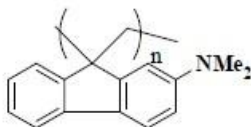


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PROCNO    1
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PULPROG   zg30
TD        65536
SOLVENTI  CDCl3
NS        408
DS        2
SWH        8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846387 sec
RG        203
DW        60.800 usec
DE        6.50 usec
TE        295.3 K
D1        1.00000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      1H
P1        14.67 usec
PL1       0.00 dB
SFO1     400.1324710 MHz
SI        32768
SF        400.1300557 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
```

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

Standard:
Poly(2-NMe2-DBF)



```
NAME Std-Poly(2-NMe2-DBF)
EXPNO 10
PROCNO 1
Date_ 20090414
Time 0.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
ID 65536
SOLVENT cdcl3
NS 8354
DS 2
SWH 9223.695 Hz
FIDRES 0.125483 Hz
AQ 3.984637 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 292.3 K
D1 1.0000000 sec
TD0 1

===== CHANNEL F1 =====
NUC1 1H
P1 14.67 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
```

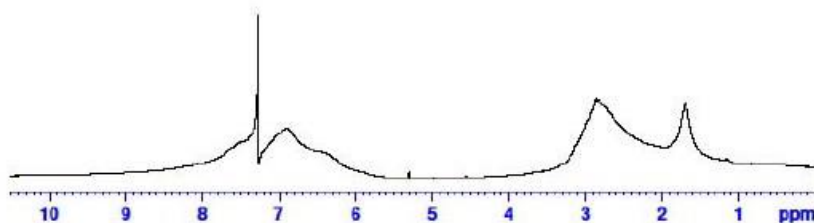


Figure S8. ¹H NMR spectrum of **poly(NMe₂DBF)** in CDCl₃.

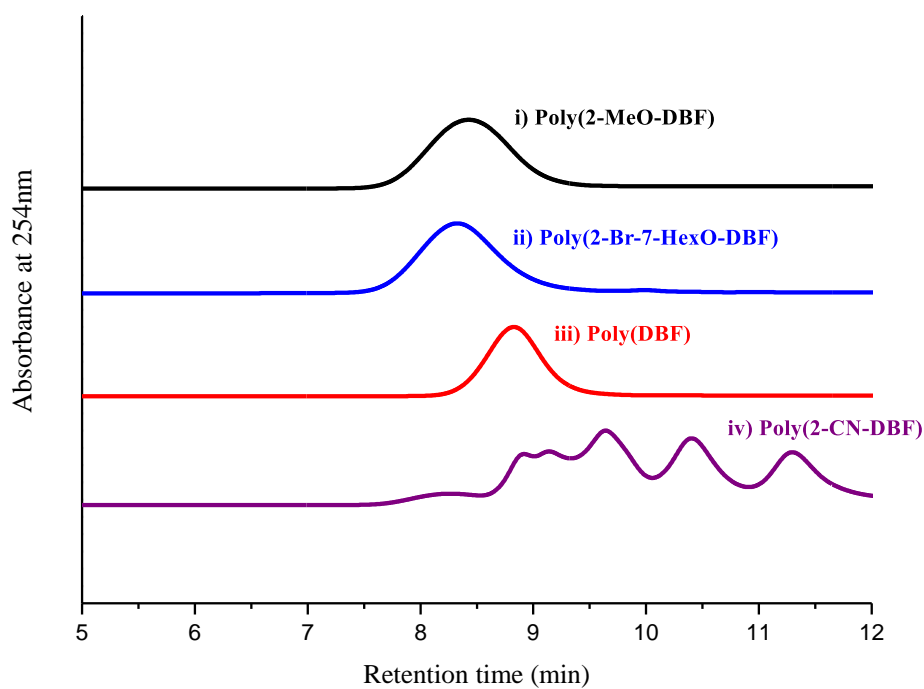


Figure S9. GPC traces of some substituted **poly(DBF)s**.

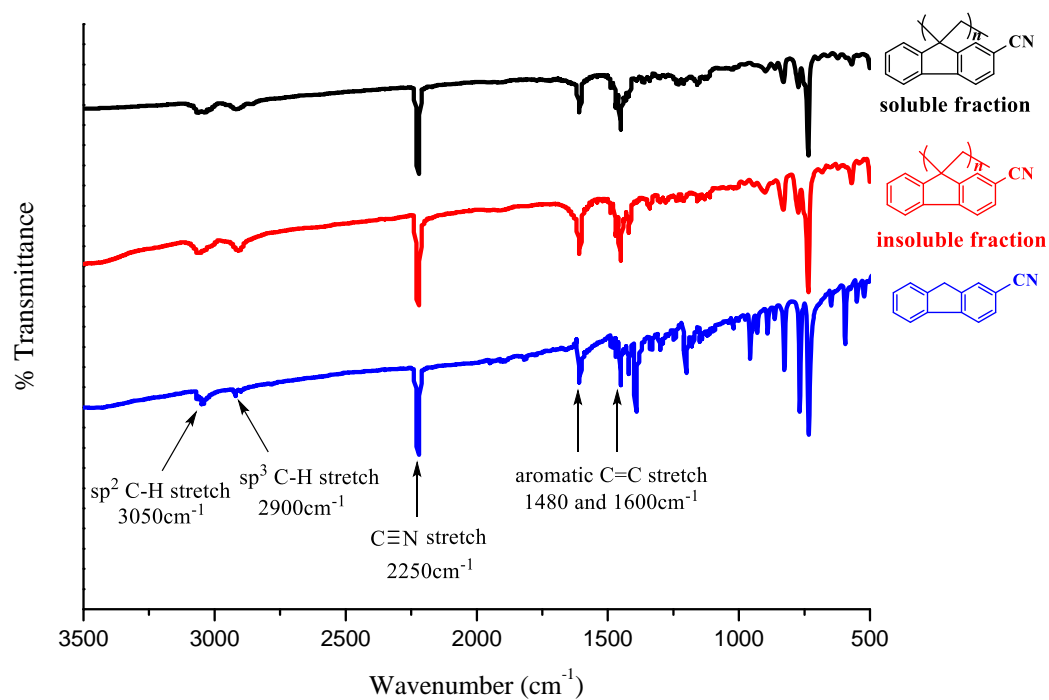


Figure S10. Comparison of IR spectra between **poly(CNDBF)** (both soluble and insoluble fractions) and 2-cyanofluorene with peak assignments. The spectra suggest that both fractions contain same chemical composition.

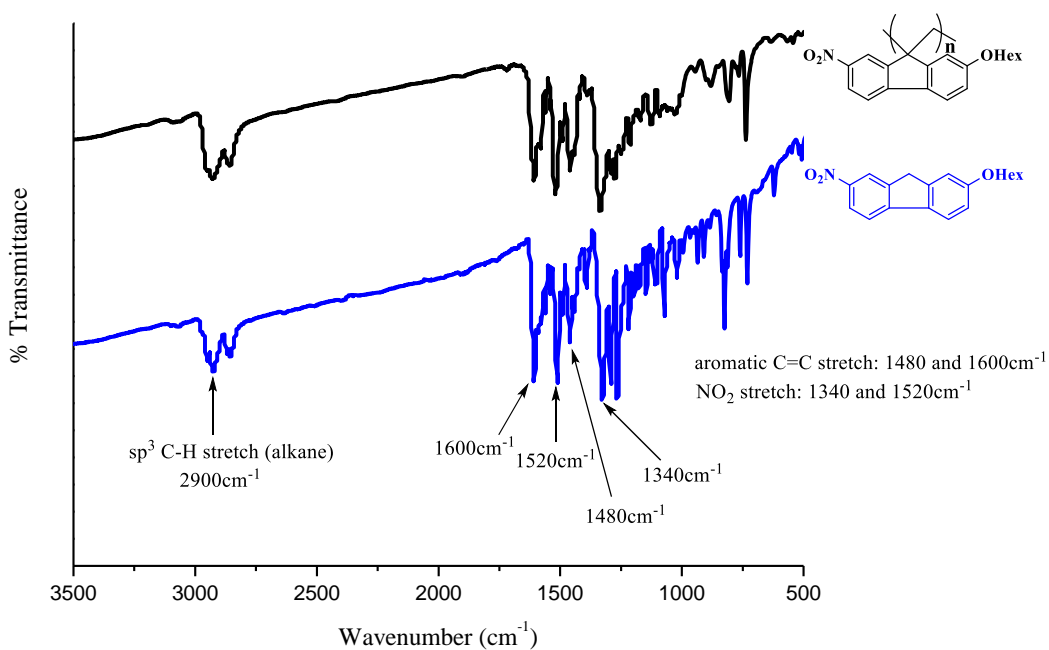


Figure S11. Comparison of IR spectra between **poly(NO₂HexODBF)** and 2-hexoxy-7-nitrofluorene with peak assignments.

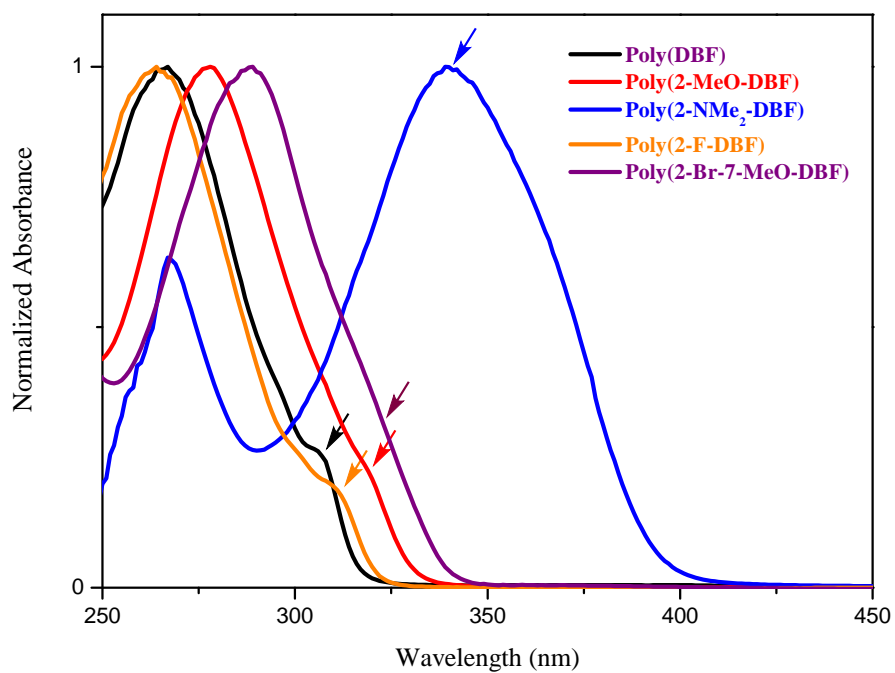


Figure S12. Normalized absorption spectra of some substituted **poly(DBF)**s in THF. Arrows indicate the lowest-energy absorption peak wavelengths.

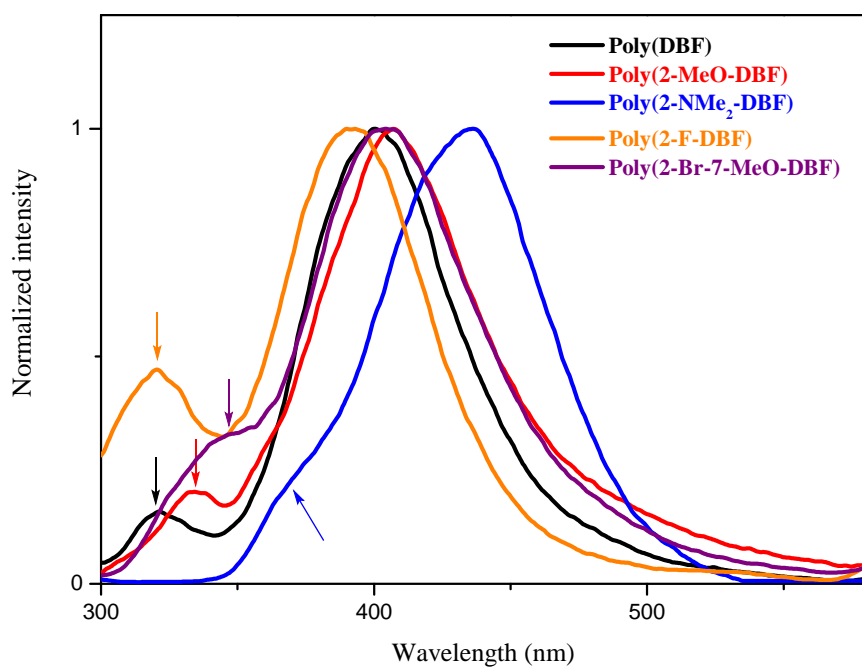


Figure S13. Normalized emission spectra of some substituted **poly(DBF)**s in THF. Arrows indicate the defect emissions.

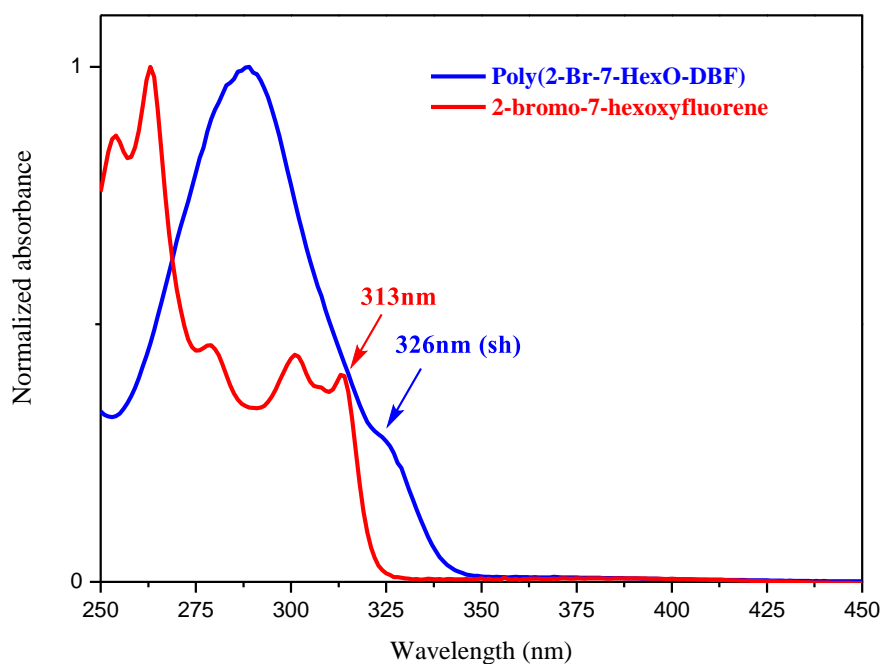


Figure S14. Normalized absorption spectra of **poly(BrHexODBF)** and 2-bromo-7-hexoxyfluorene in THF.

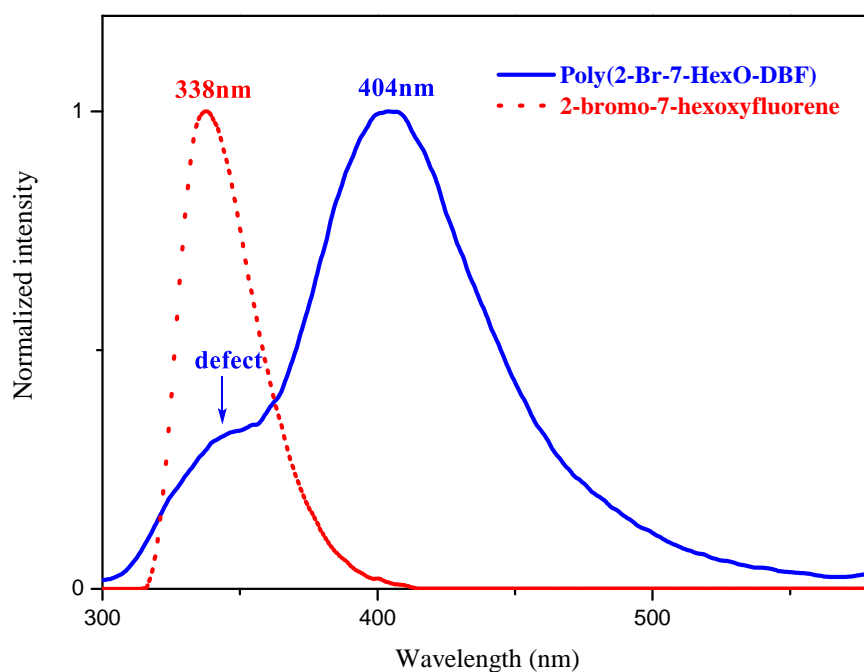


Figure S15. Normalized emission spectra of **poly(BrHexODBF)** and 2-bromo-7-hexoxyfluorene in THF. Arrow indicates the emission of defect in the polymer which matches the emission maximum of 2-bromo-7-hexoxyfluorene.

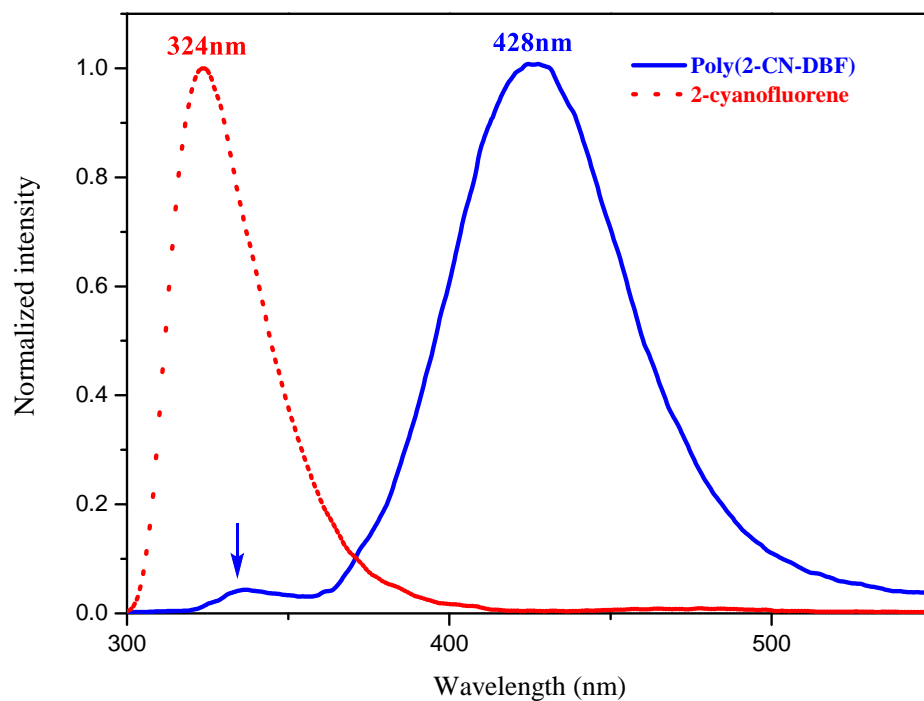


Figure S16. Normalized emission spectra of **poly(CNDBF)** and 2-cyanofluorene in THF. The arrow indicates the emission of the stereochemical defect in the polymer which matches the emission maximum of 2-cyanofluorene. Note the excimer emission strongly outweighs that of the defects despite the low molecular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

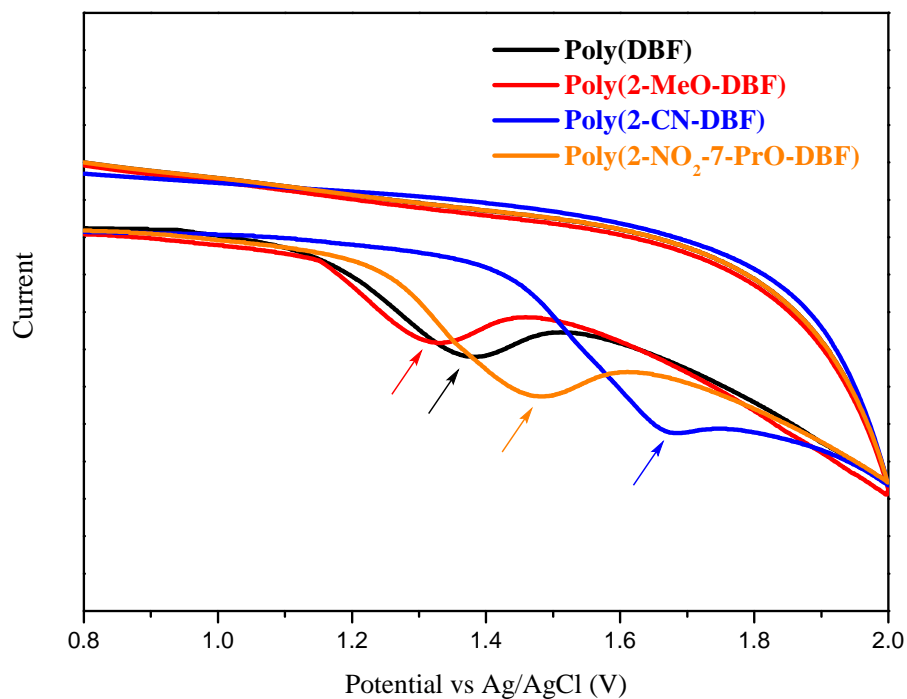


Figure S17. Cyclic voltammograms of some substituted **poly(DBF)s** in THF with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte. Arrows indicate oxidation potentials.

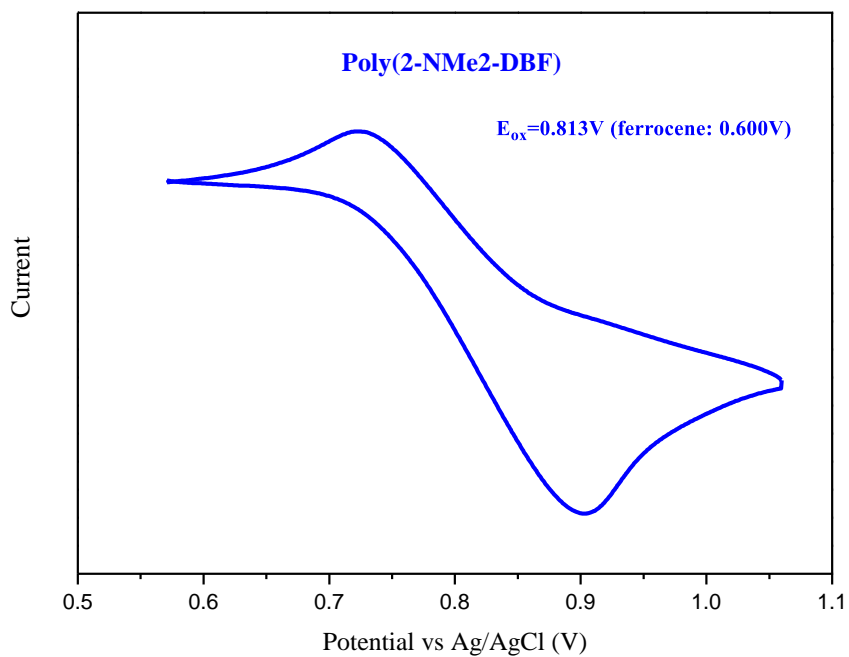


Figure S18. Cyclic voltammograms of **poly(NMe₂DBF)s** in THF with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte.

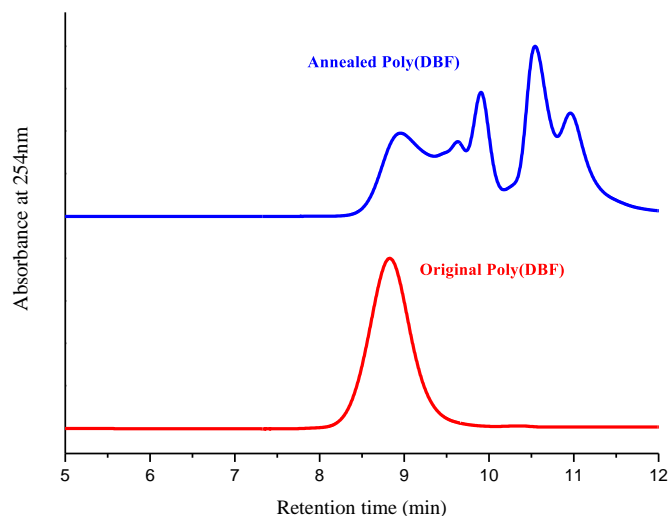


Figure S19. GPC traces of **poly(DBF)** after annealing (top, in blue) and before annealing (bottom, in red).

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 N₂ with 0.1 M *n*Bu₄NPF₆ 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: $\Delta E = |\text{HOMO}| - |\text{LUMO}|$. ^d Bandgap is estimated from the absorption onset wavelength.