Supporting Information for

Facile synthesis and optoelectronic properties of N,N-Difluorenevinylaniline-based Molecules

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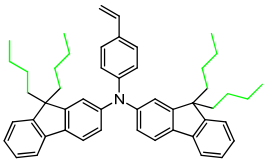
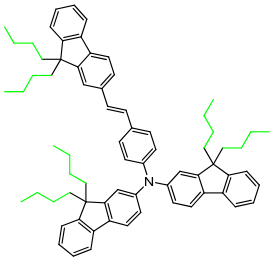
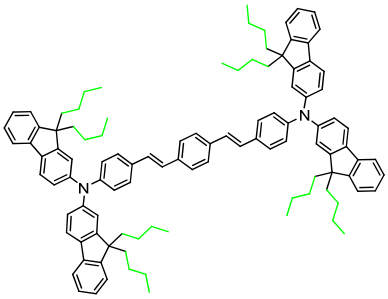
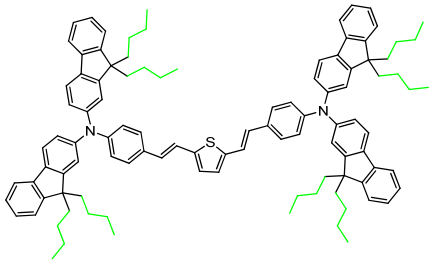
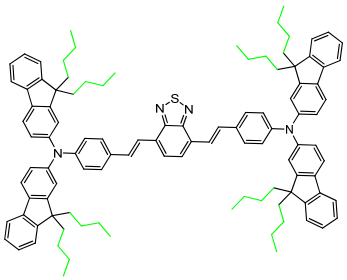
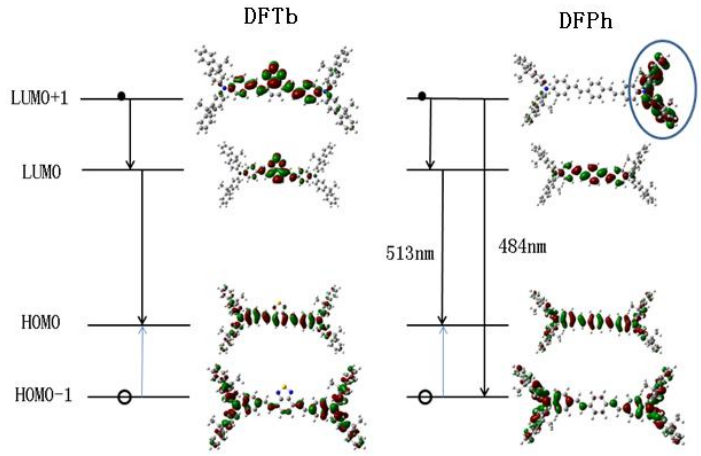
Computational Details

Computations were done with Gaussian 03 program package with different parameters for structure optimization and vibrational analysis. The ground-state geometries were fully optimized by the Becke's three-parameter exchange functional along with the Lee-Yang-Parr correlation functional with the restricted (RB3LYP) at the standard split valence plus polarization function 6-31G(d) basis set. These fully optimized stationary points were further characterized by harmonic vibrational frequency analysis to ensure that real local minima had been found without imaginary vibrational frequency. The C_4H_9 groups in FXs were downsized to CH_3 groups in the model compounds as shown in Table S1 in order to reduce

the computational burden, since the length of alkyl has litter influence on the optoelectronic properties of a single molecule. The various property parameters of FXs such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energies, and energy gap (E_g) were derived from the computed results according to literature publications.

Table S1. The calculated model molecules (in black) of *N*,*N*,-difluorene-anline-based D-π-X-π-D molecules (FXs).

Molecule	Model structure
F	
FF	
DFPh	
DFTh	
DFTb	



Scheme S1. Electroluminescence diagram of dumbbell-shaped FXs.

(For DFPh, a new emission at 484 nm emerged besides the emission at 513 nm in comparison with the PL spectrum in film. We tried to figure out the origin of this phenomenon by DFT calculations (see Figure 6). For dumbbell-shaped molecule DFTb, almost electrons were injected into the LUMO level through LUMO+1 and radiate to HOMO level. For DFPh, another available way exists for photoluminescence. Comparing with LUMO+1 of DFTb which is dominated by the π* orbital contribution of the core, the LUMO+1 of DFPh is mainly dominated by the π* orbital contribution of the periphery due to the week electron receptivity of core. When electrons were injected into periphery, parts of them immediately radiate to the HOMO-1 level which also concentrate on the periphery.)

Nuclear magnetic resonance (NMR) and high resolution mass spectrometry (HRMS) spectra

(1) 1-Nitro-4-vinylbenzene

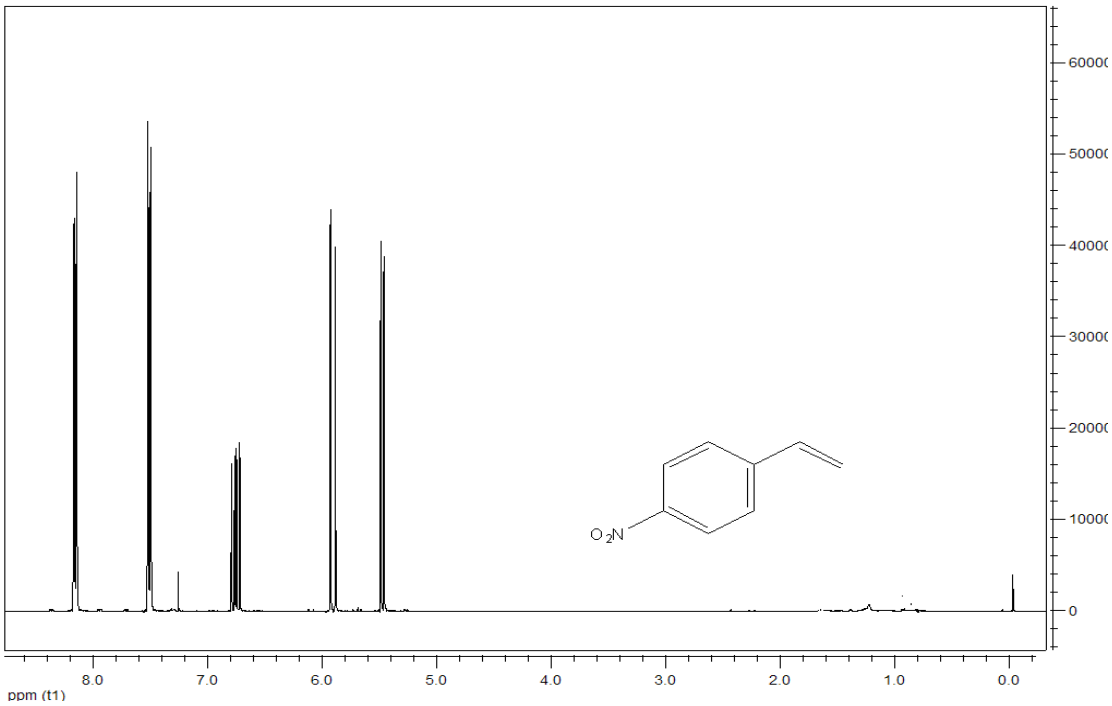


Figure S1. ^{1}H NMR of 1-nitro-4-vinylbenzene in $CDCl_3$.

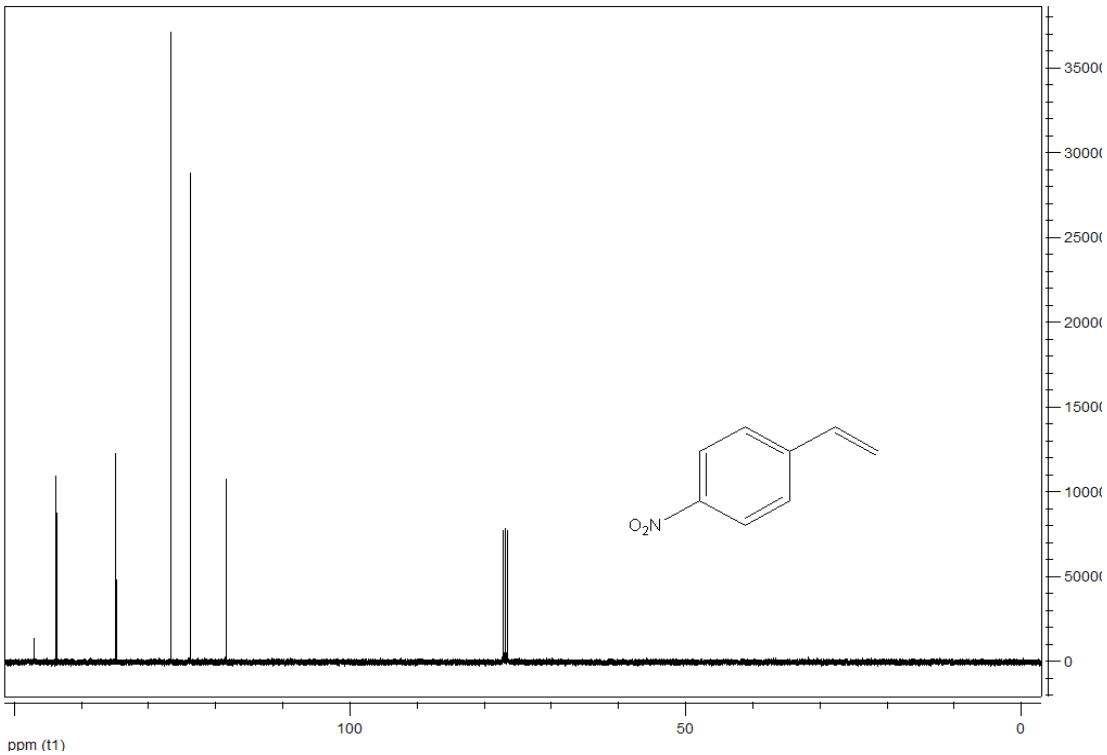


Figure S2. ^{13}C NMR of 1-nitro-4-vinylbenzene in $CDCl_3$.

(2) 4-vinylaniline

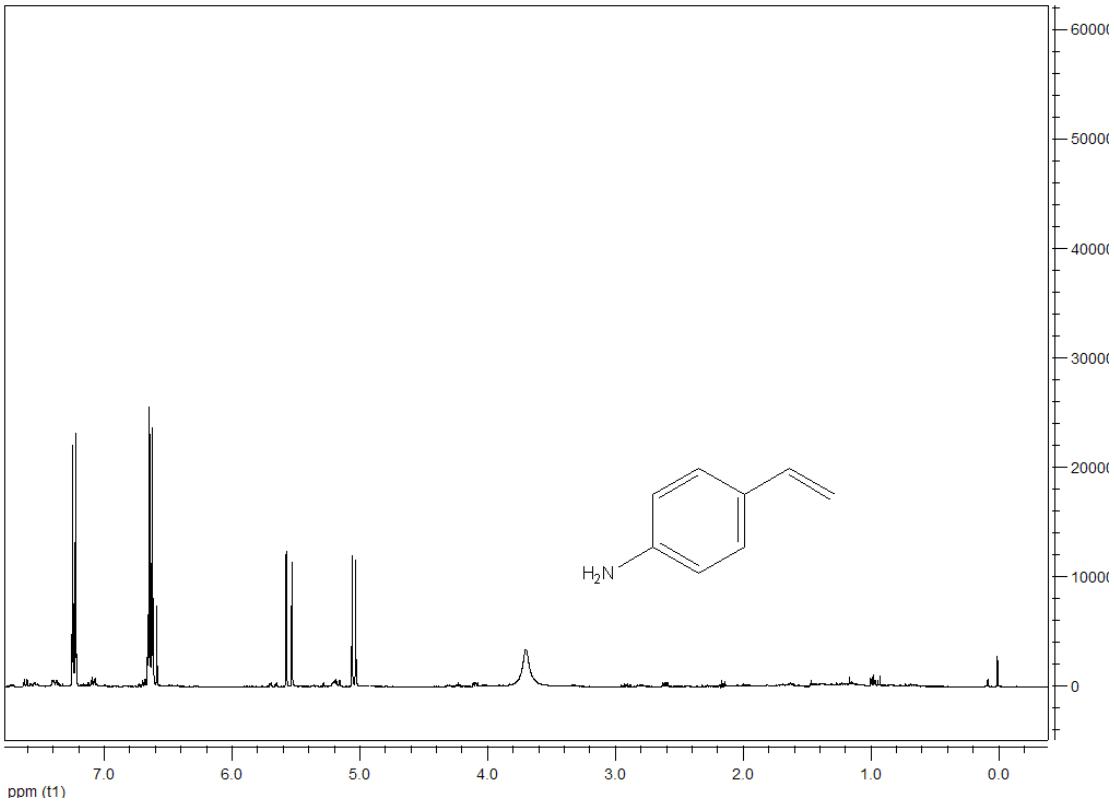


Figure S3. ^{1}H NMR of 4-vinylaniline in $CDCl_3$.

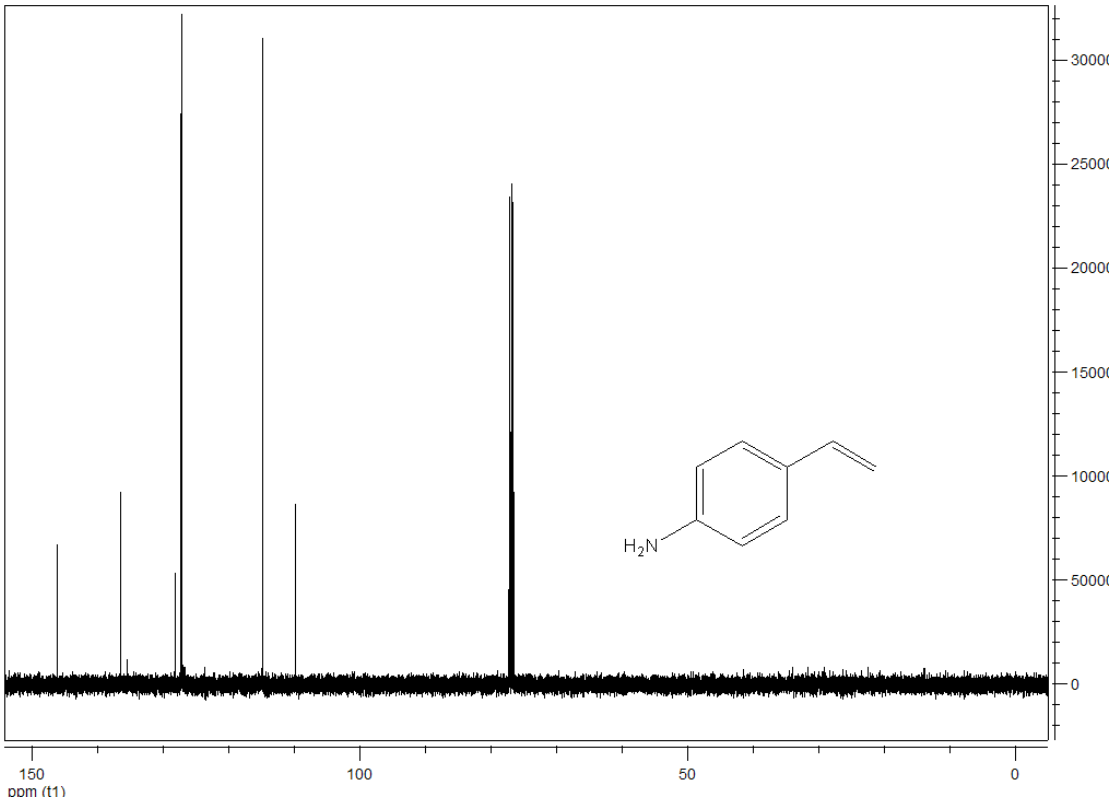


Figure S4. ^{13}C NMR of 4-vinylaniline in $CDCl_3$

(3) 2-bromo-9,9-dibutylfluorene

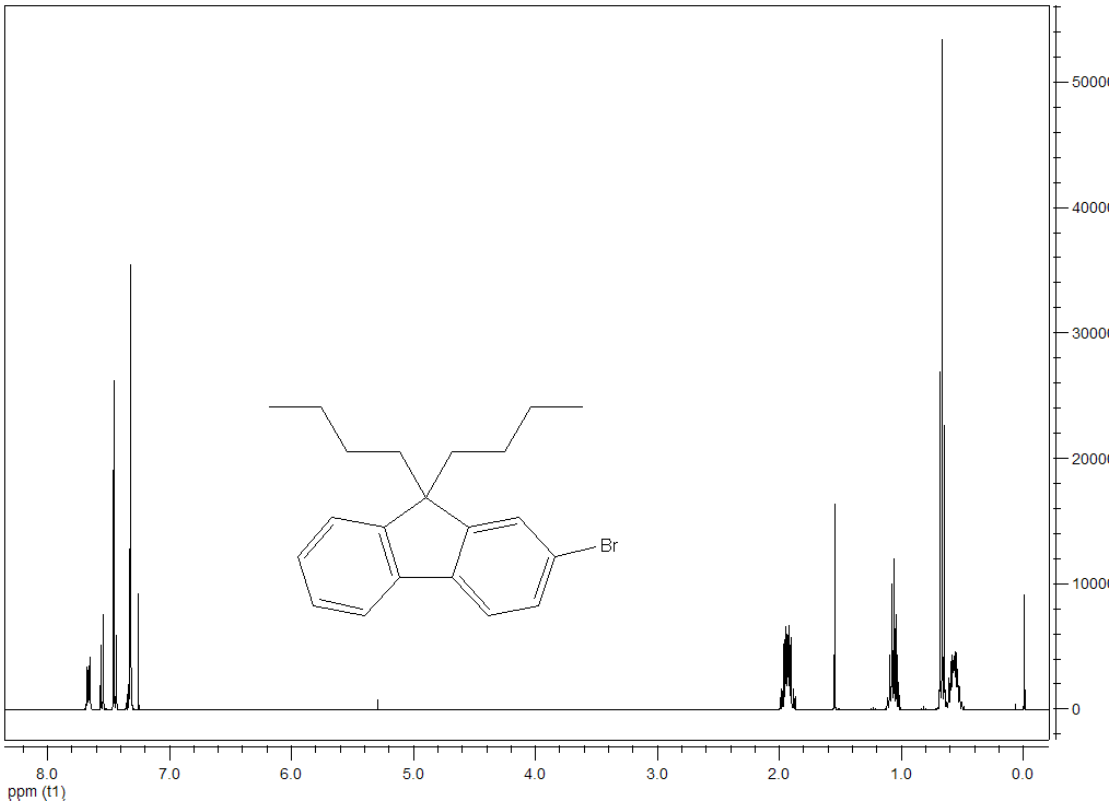


Figure S5. ^{1}H NMR of 2-bromo-9,9-dibutylfluorene in $CDCl_3$.

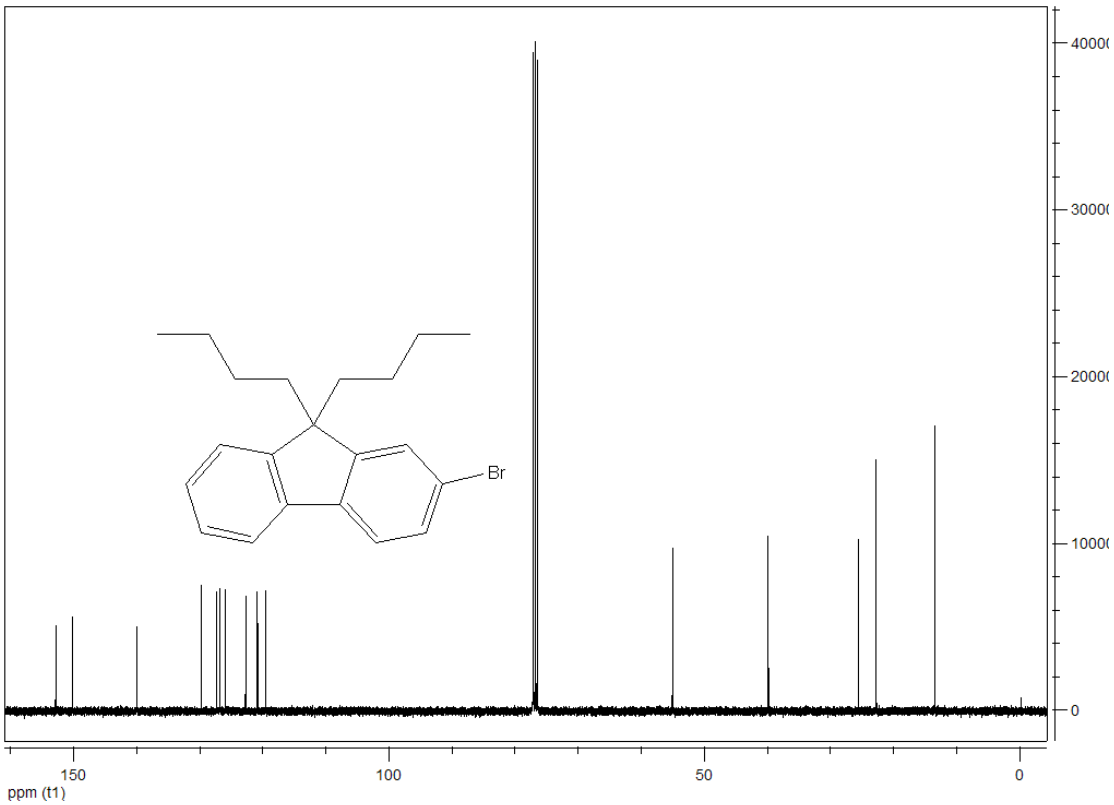


Figure S6. ^{13}C NMR of 2-bromo-9,9-dibutylfluorene in $CDCl_3$.

(4) N,N,-Bis(9,9-dibutyl-fluoren-2-yl)-4-vinylanline (F)

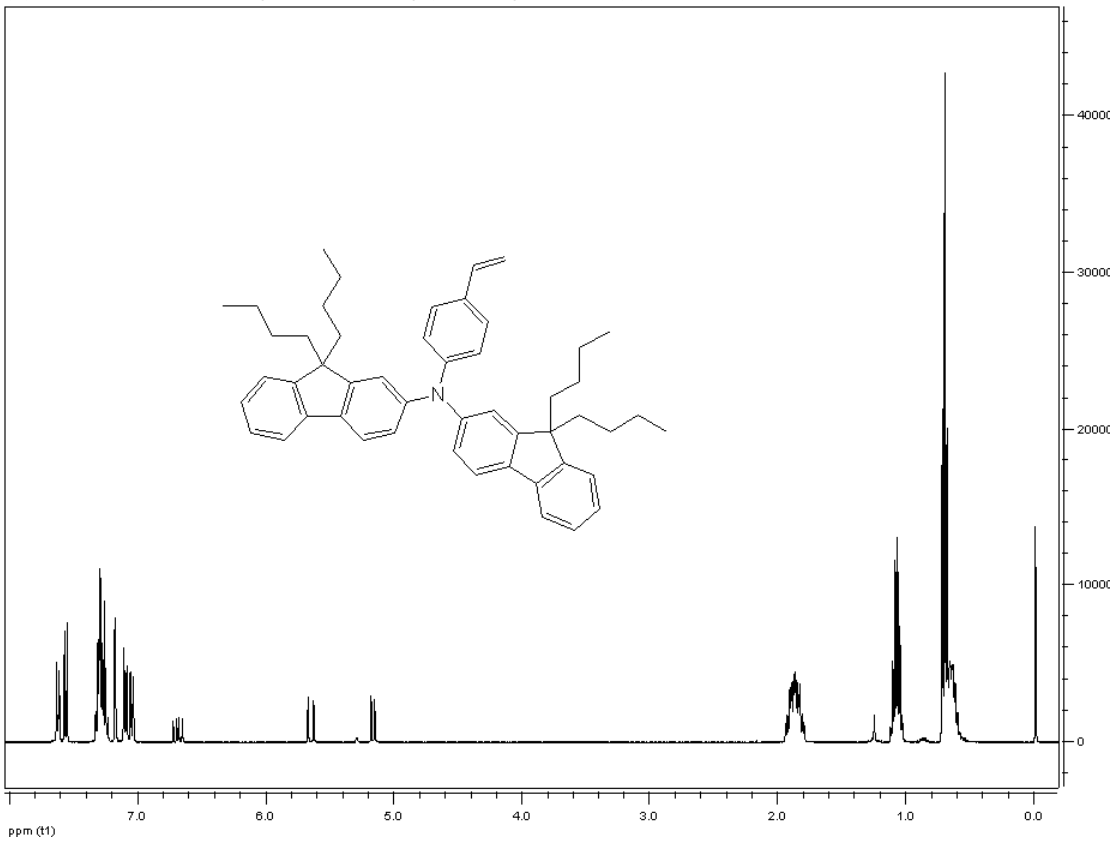


Figure S7. ^{1}H NMR of F in $CDCl_3$.

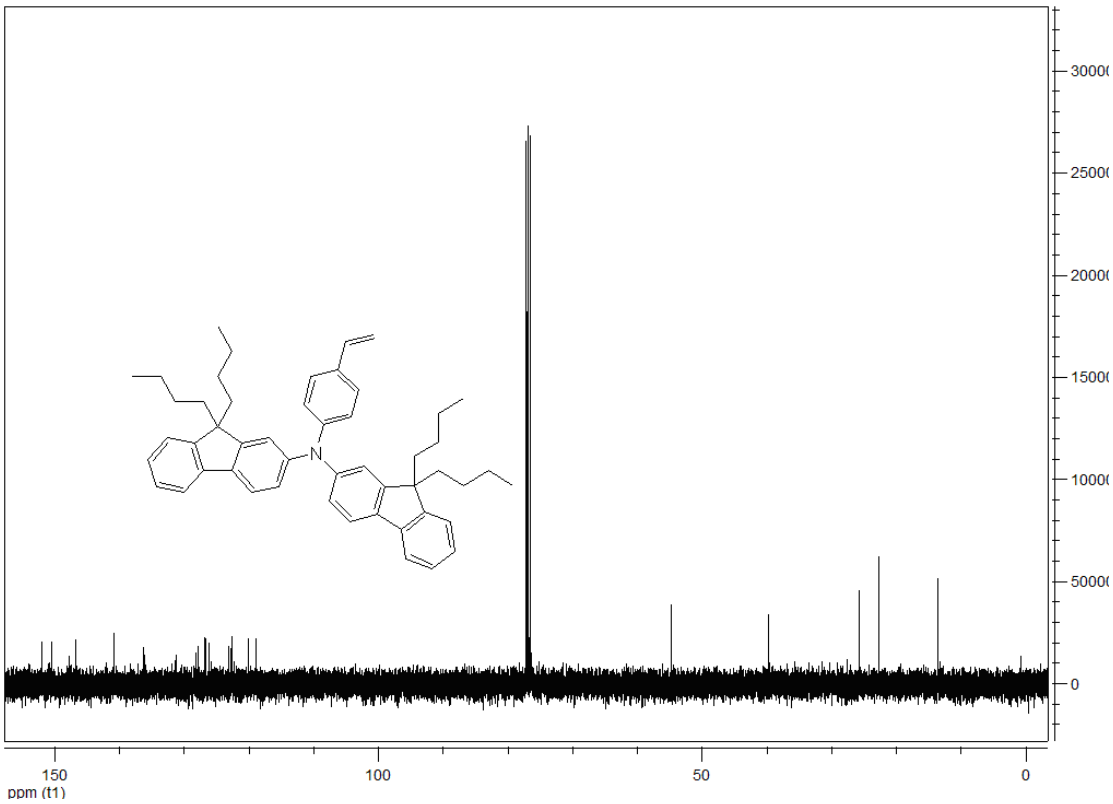


Figure S8. ^{13}C NMR of F in $CDCl_3$.

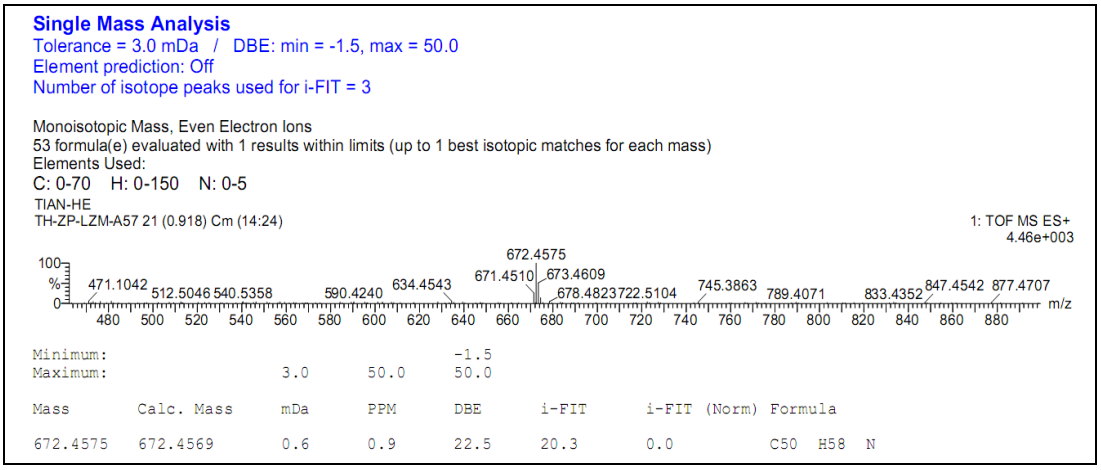


Figure S9. The HRMS spectrum of F.

(5) 1-[N,N-bis (9,9-dibutyl-fluoren-2-yl)]-2-(9,9-dibutyl-fluoren-2-yl)ethene (FF)

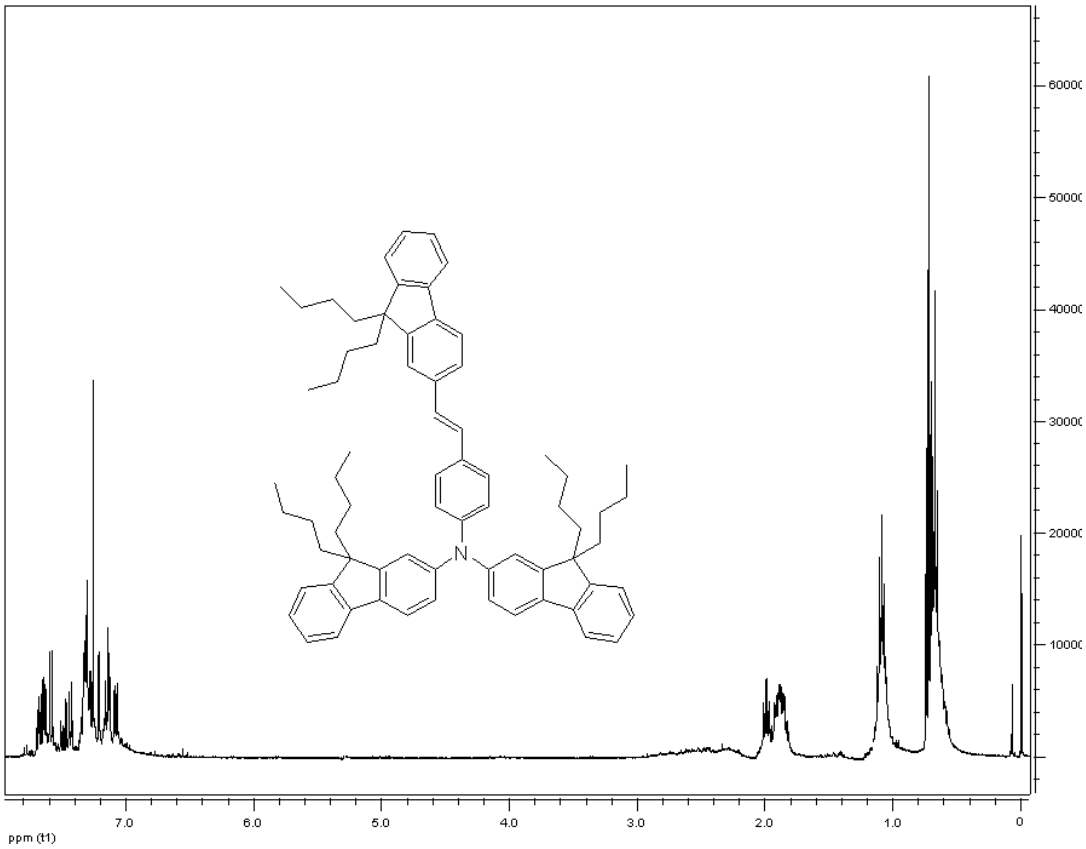


Figure S10. ^{1}H NMR of FF in $CDCl_3$.

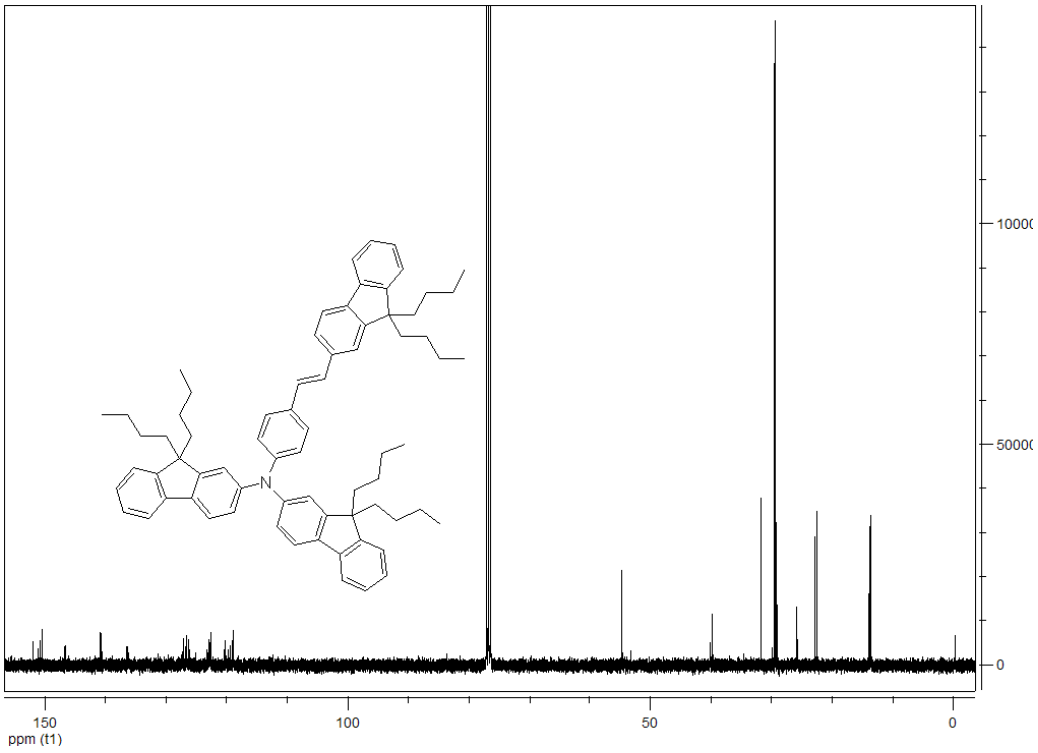


Figure S11. ^{13}C NMR of FF in $CDCl_3$.

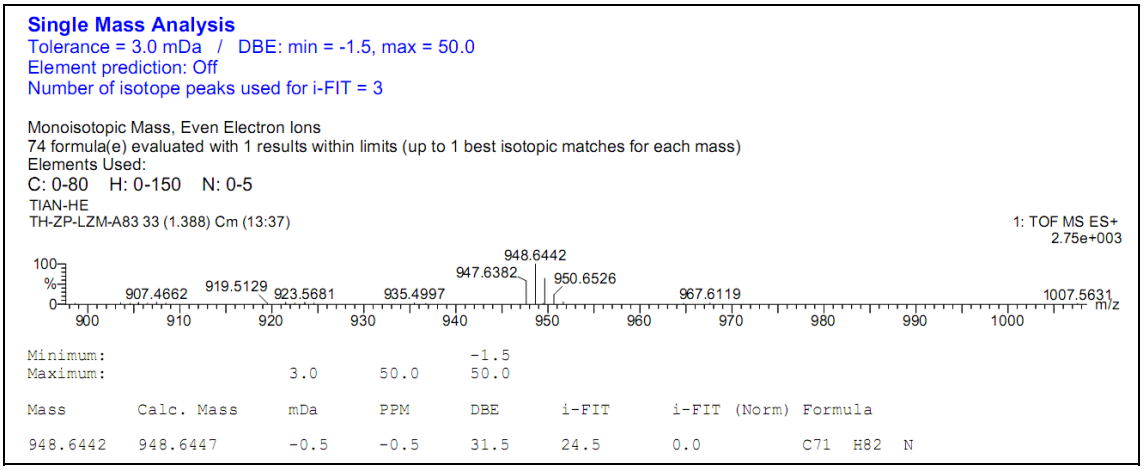


Figure S12. The HRMS spectrum of FF.

(6) 1,4-Bis(4-[N,N-bis(9,9-dibutyl-fluoren-2-yl)aniline]vinyl)benzene (DFPh)

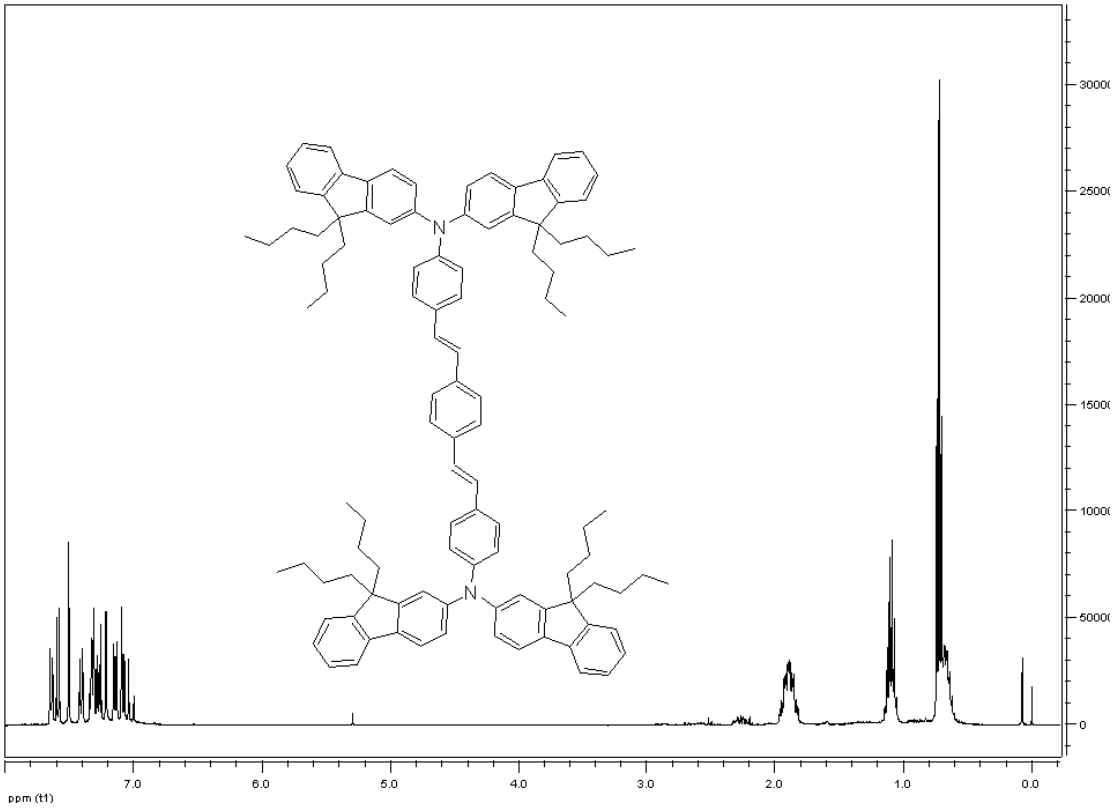


Figure S13. ^{1}H NMR of DFPh in $CDCl_3$.

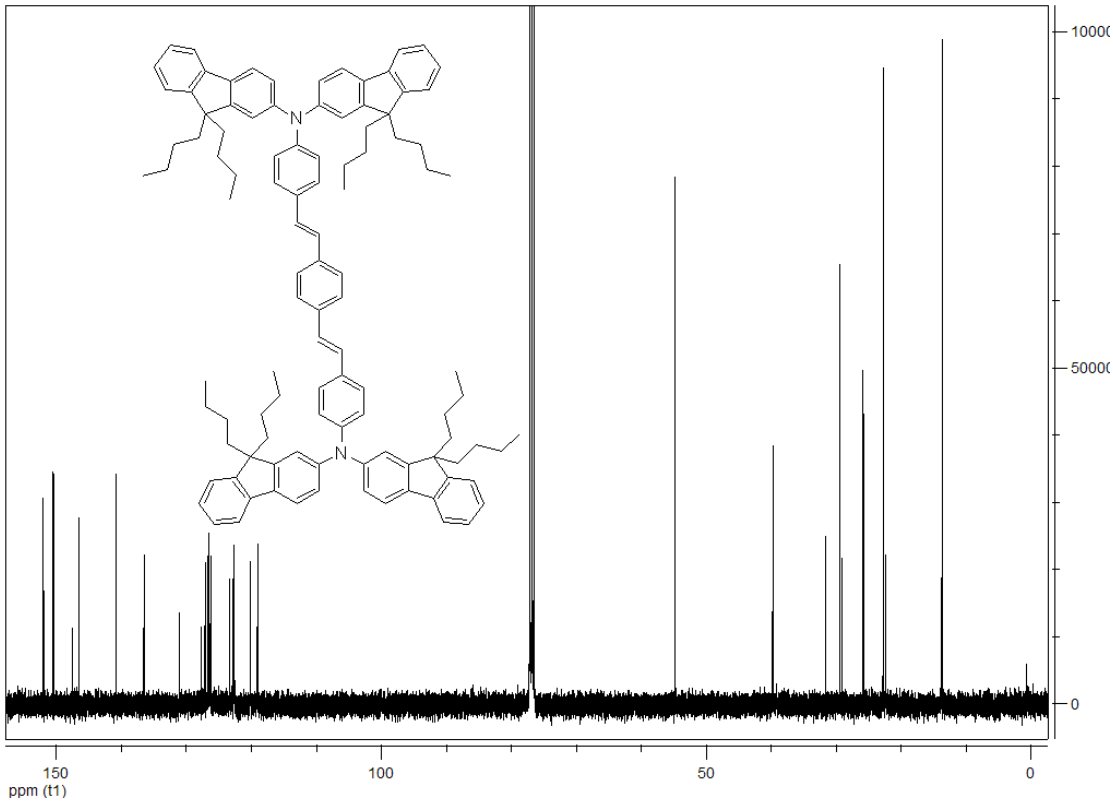


Figure S14. ^{13}C NMR of DFPh in $CDCl_3$.

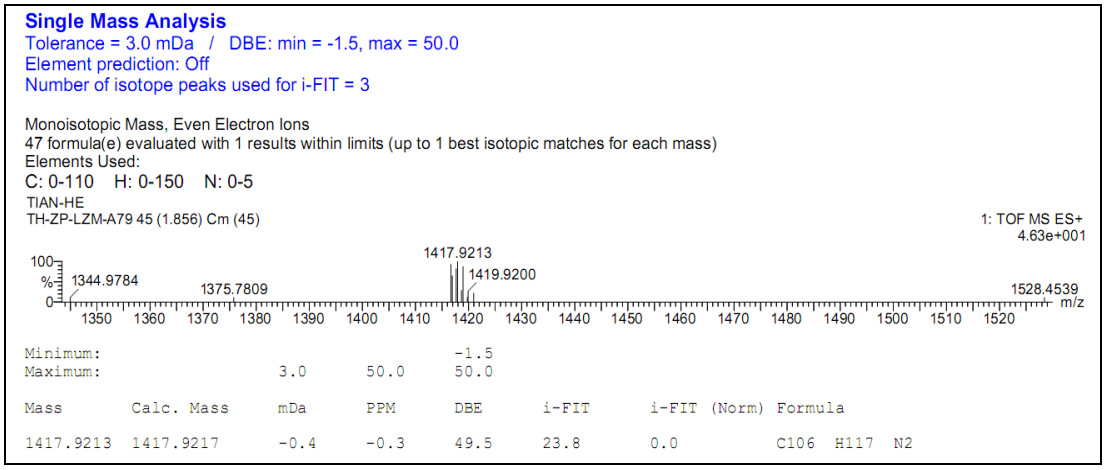


Figure S15. The HRMS spectrum of DFPh.

(7) 2,5-Bis(4-[N,N-bis (9,9-dibutyl-fluoren-2-yl)aniline]vinyl)thiophene (DFTh)

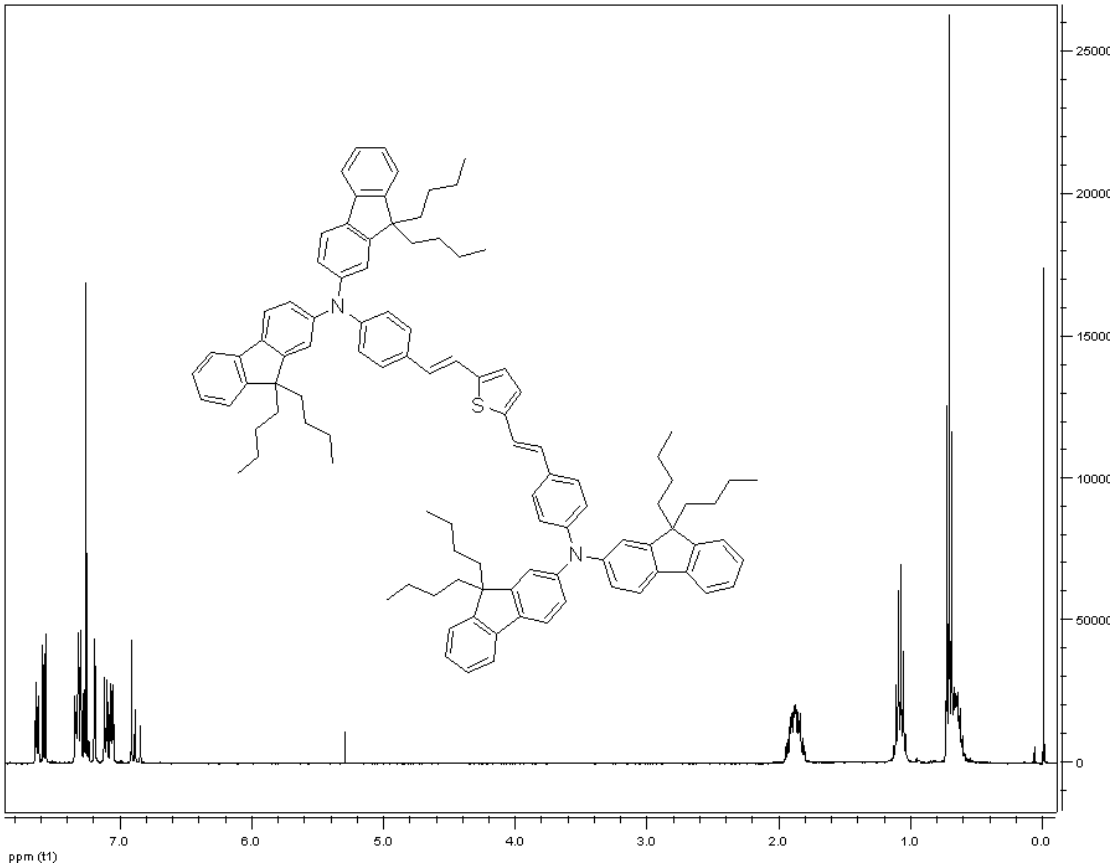


Figure S16. ^{1}H NMR of DFTh in $CDCl_3$.

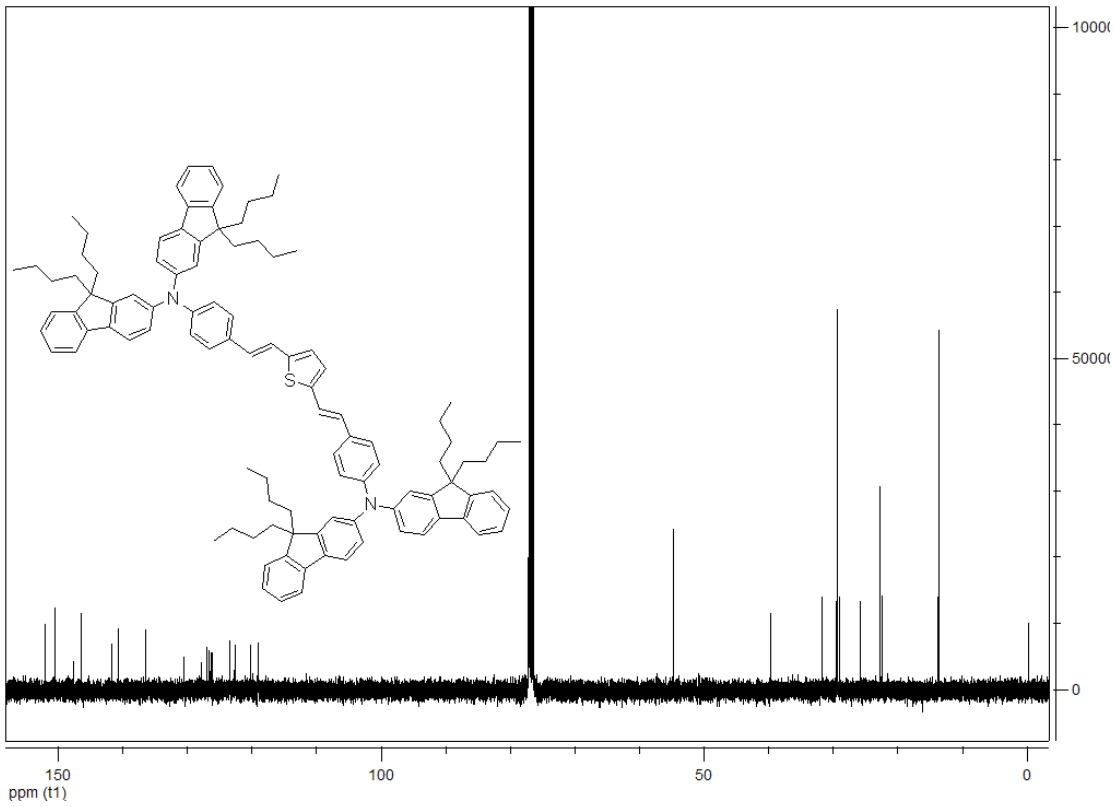
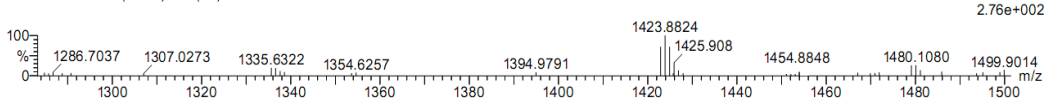


Figure S17. ^{13}C NMR of DFTh in $CDCl_3$.

Single Mass Analysis
Tolerance = 20.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 29-104 H: 0-130 N: 0-2 S: 0-1
TIAN-HE
TH-LZM-A97-3 57 (1.847) Cm (57)

1: TOF MS ES+
2.76e+002



Minimum:				-1.5					
Maximum:		20.0	5.0	100.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
1423.8824	1423.8781	4.3	3.0	48.5	14.1	0.0	C104	H115	N2 S

Figure S18. The HRMS spectrum of DFTh.

(8) 4,7-Bis(4-[N,N-bis(9,9-dibutyl-fluoren-2-yl)aniline]vinyl)benzothiadiazole (DFTb)

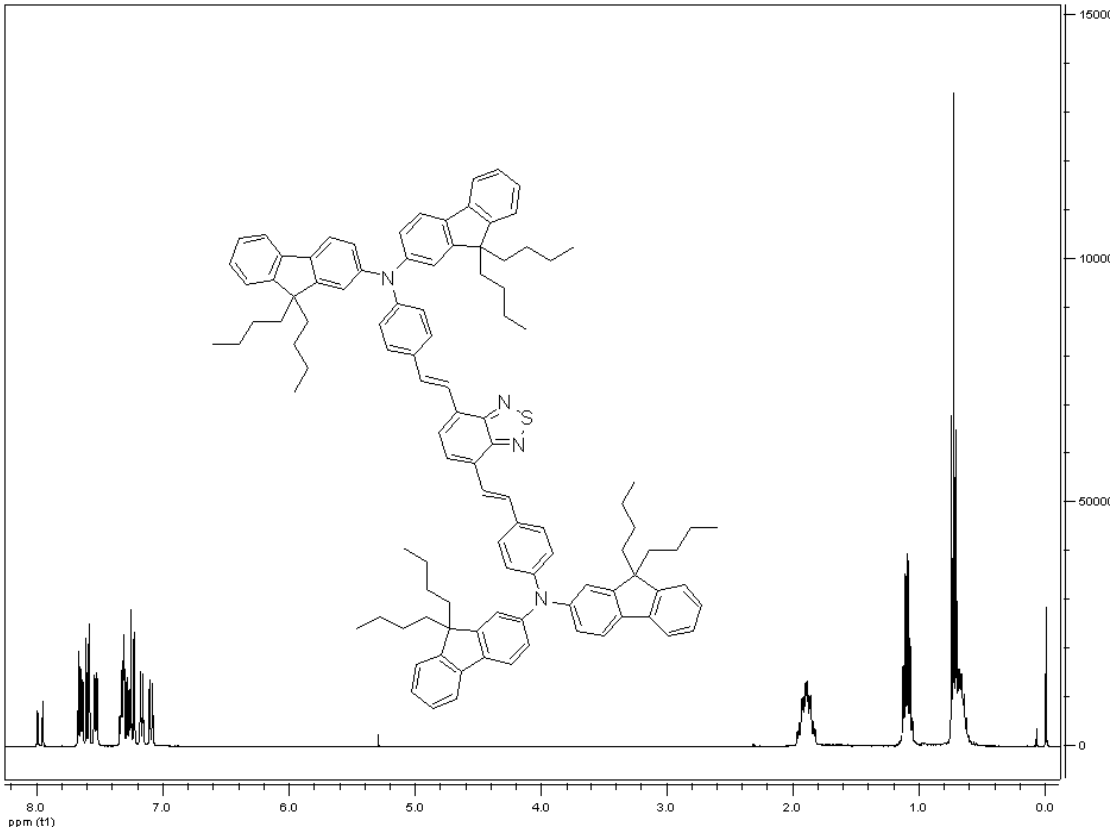


Figure S19. ^{1}H NMR of DFTb in $CDCl_3$.

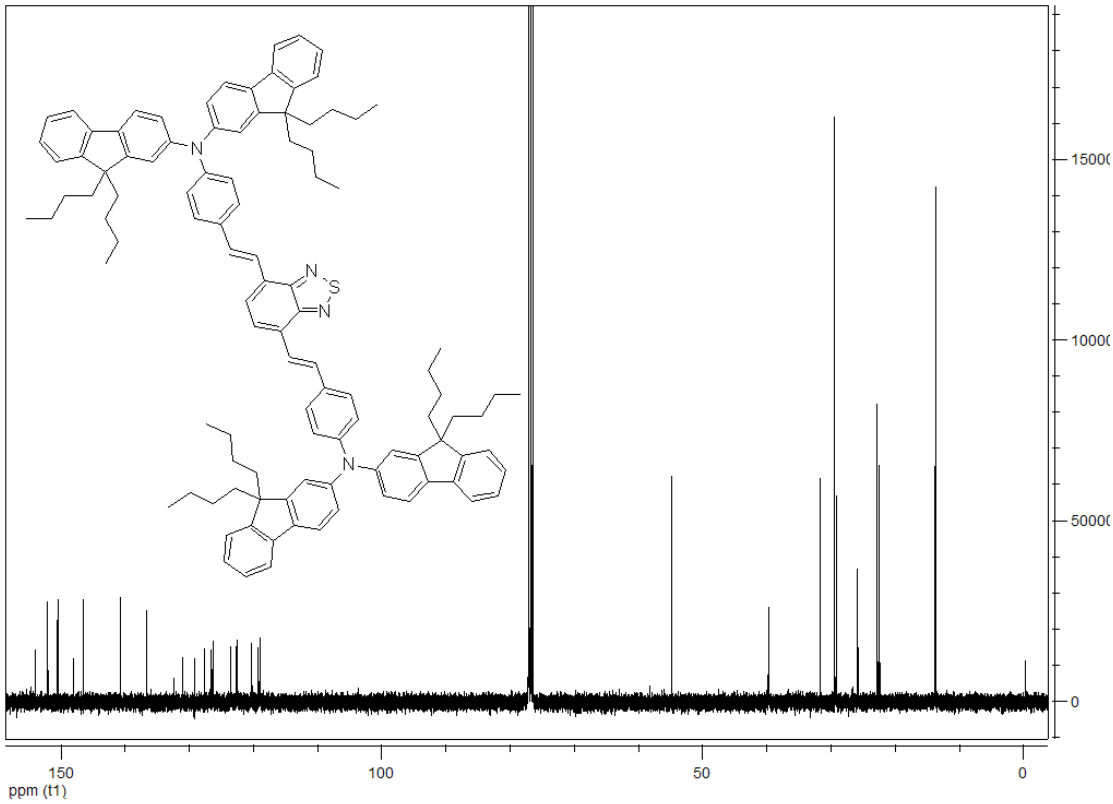


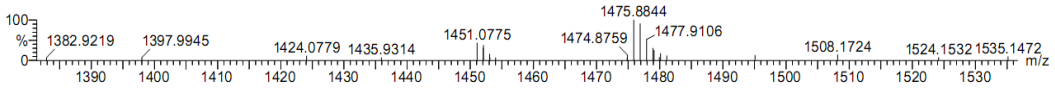
Figure S20. ^{13}C NMR of DFTb in $CDCl_3$.

Single Mass Analysis
Tolerance = 20.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 29-106 H: 0-130 N: 0-4 S: 0-1

TIAN-HE
TH-LZM-A91-3 41 (1.356) Cm (41:42)

1: TOF MS ES+
1.21e+002



Minimum:				-1.5				
Maximum:		20.0	5.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
1475.8844	1475.8842	0.2	0.1	51.5	11.9	0.0	C106 H115 N4 S	

Figure S21. The HRMS spectrum of DFTb.

Fluorescence Decay Profiles

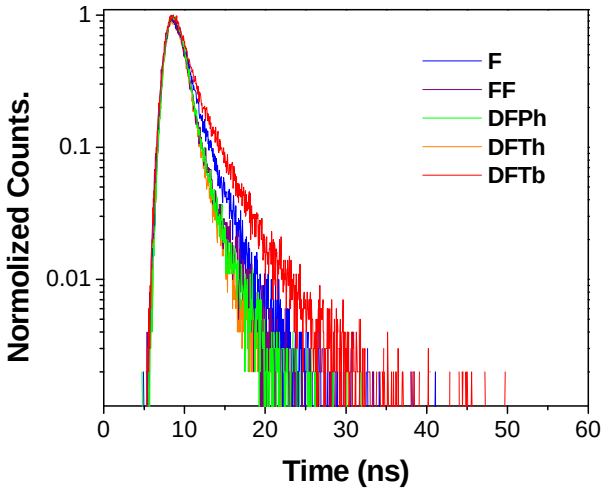


Figure S22. Fluorescence decay profiles of FXs in film excited at 370 nm.

Cyclic Voltammograms of FXs

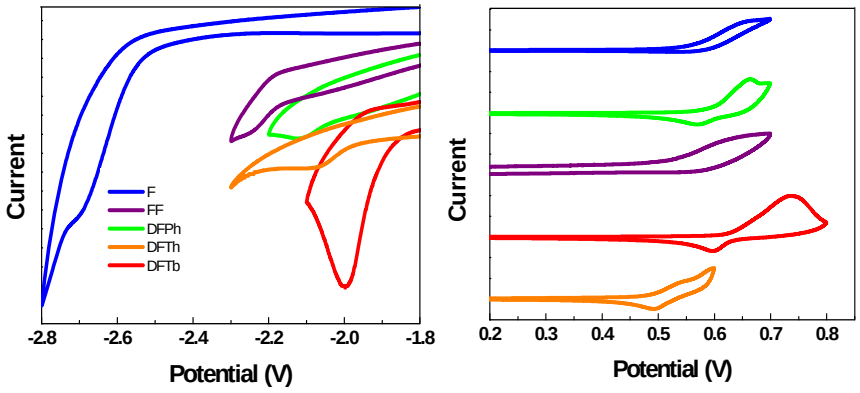


Figure S23. Cyclic Voltammograms of FXs in thin solid films.

Current density-voltage-brightness plots of FXs

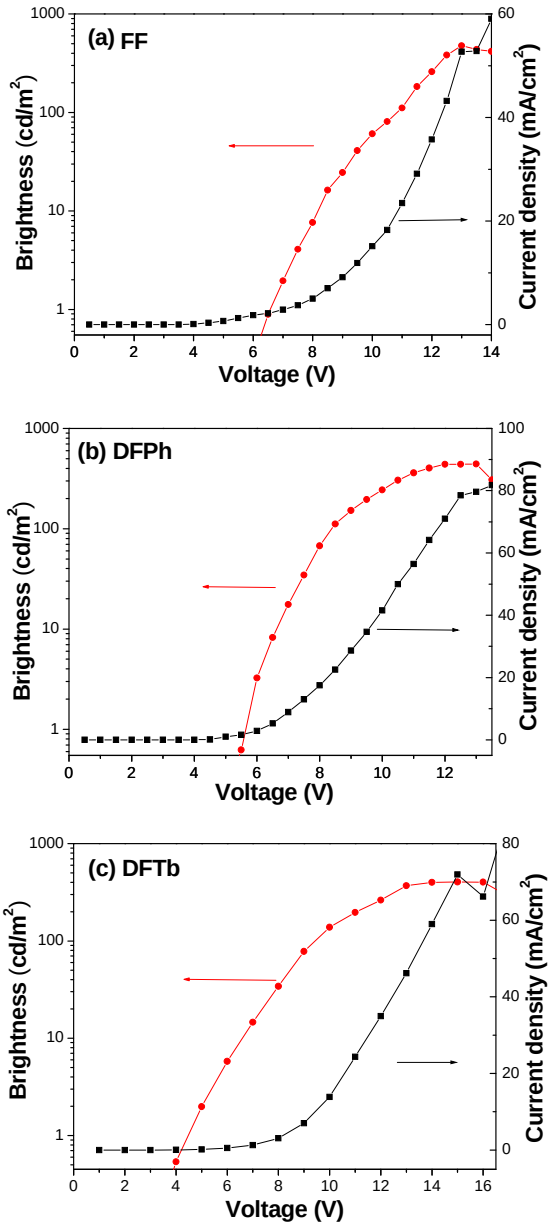


Figure S24. Current density-voltage-brightness plots of FXs.