

Supplementary Information

Photophysical and electroluminescence characteristics of polyfluorene derivatives with triphenylamine

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Material

The monomer M1, M2, M3 and conjugate polymer C1, C2, C3 were synthesized based on our previous work.[1-3] *N*-(4-aminophenyl)-*N*-phenyl-1-aminopyrene was prepared according to reported procedure.[4] 1-Bromo4-iodobenzene, bis(dibenzylideneacetone)palladium (Pd(dba)₂), 1,1'-bis(diphenylphosphino)ferrocene (DPPF), 4-Isopropylaniline, sodium *tert*-butoxide and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) were purchased from Acros Organics. Anhydrous potassium carbonate (K₂CO₃) was purchased from Fisher Chemical. 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester was purchased from Sigma-Aldrich Chemical. Tetrabutylammonium perchlorate (TBAP) was obtained from TCI and recrystallized from ethyl acetate twice before being dried in a vacuum prior to use. The solvents (analytical grade) were purchased from Merck. Tetrahydrofuran and toluene were distilled from sodium/benzophenone (deep purple) under nitrogen before use. All other reagents were used as received.

Synthesis of *N,N*-bis(4-bromophenyl)-1,4-phenylenediamine (M6)

1 equiv of 4-isopropylaniline, 2 equiv of 1-bromo4-iodobenzene, 0.02 equiv of Pd(dba)₂, 0.02 equiv of 1,10-bis(diphenylphosphino)ferrocene, 2 equiv of sodium tert-butoxide, and dry toluene were charged in a three-necked flask and kept under nitrogen atmosphere. The mixture was heated and stirred to reflux for 6 h. After the completion of the reaction, the solvent was removed under reduced pressure, and the residue was extracted with dichloromethane/ water. The collected organic layer was dried over MgSO₄ overnight and then filtered to remove MgSO₄. The solvent from the filtrate was then removed using vacuum distillation, and the residue was purified by silica gel column chromatography (dichloromethane : n-hexane = 1:3) to obtain products. (Yield : 85 %). ¹H NMR (600 MHz, CDCl₃, Me₄Si): δ (ppm) = 1.27 (6H, H₁) , 2.89 (1H, H₂) , 6.94 (4H, H₅) , 7.00 (2H, H₄) , 7.14 (2H, H₃), 7.33 (4H, H₆). ¹³C NMR (150 MHz, CDCl₃, Me₄Si): δ (ppm) = 146.7 (C₁₀), 144.73 (C₇), 144.42 (C₈), 132.21 (C₆), 127.49 (C₃), 125.01 (C₅), 124.92 (C₄), 114.98 (C₉), 33.51 (C₂), 23.98 (C₁).

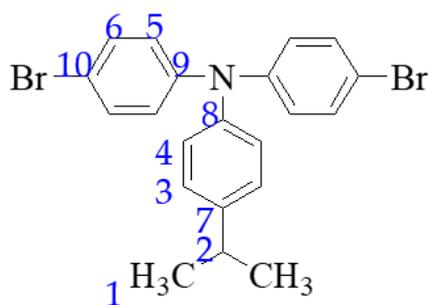


Figure S1. Structure of M6 monomer

General procedure of Suzuki coupling polymerization

The 1 equiv of dibromo monomers, 1 equiv of diboronic ester monomer and 0.02 equiv of Pd(PPh₃)₄ were dissolved in degassed toluene in a three-neck round-bottom flask with a condenser. The 2 M aqueous solution of K₂CO₃ was added to the mixture. The resulting solution was stirred at 105 °C for 48 h under the flow of nitrogen. After cooling, the solution was extracted with toluene/water for three times. The organic layer was separated, concentrated by rotary evaporator and precipitated in excess methanol. The products was filtrated and further purified by Soxhlet extraction with acetone for 48 h.

Synthesis of conjugate polymer (C6)

C6 was synthesized according to the procedure described above. (Yield : 81 %). The structure of C6 (Fig. S2) is verified by NMR (Fig. S3). The cyclic voltammograms of C6 is shown in Fig. S4.

^1H NMR (600 MHz, CDCl_3 , Me_4Si): δ (ppm) = 0.65-0.85 (20H, H_{19} , H_{25}), 1.07-1.20 (20H, H_{20} , H_{21} , H_{22} , H_{23} , H_{24}), 1.28 (6H, H_1), 2.02 (4H, H_{18}), 2.92 (m, 2H, H_2), 7.13-7.95 (4H, H_3 , H_4), 7.23 (d, 4H, H_5), 7.54-7.62 (8H, H_6 , H_{12} , H_{15}), 7.73-7.76 (2H, H_{13}). ^{13}C NMR (150 MHz, CDCl_3 , Me_4Si): δ (ppm) = 14.05 (C_{25}), 22.59 (C_{24}), 23.83 (C_{19}), 24.07 (C_1), 29.21 (C_{22} , C_{23}), 30.05 (C_{21}), 31.78 (C_{20}), 33.56 (C_2), 40.49 (C_{18}), 55.21 (C_{17}), 119.88 (C_{13}), 120.92 (C_{15}), 123.82 (C_5), 124.96 (C_3), 125.49 (C_{12}), 127.24 (C_4), 127.75 (C_6), 135.50 (C_{10}), 139.39 (C_{11}), 139.74 (C_{14}), 144.15 (C_8), 145.10 (C_7), 147.05 (C_9), 151.64 (C_{16}).

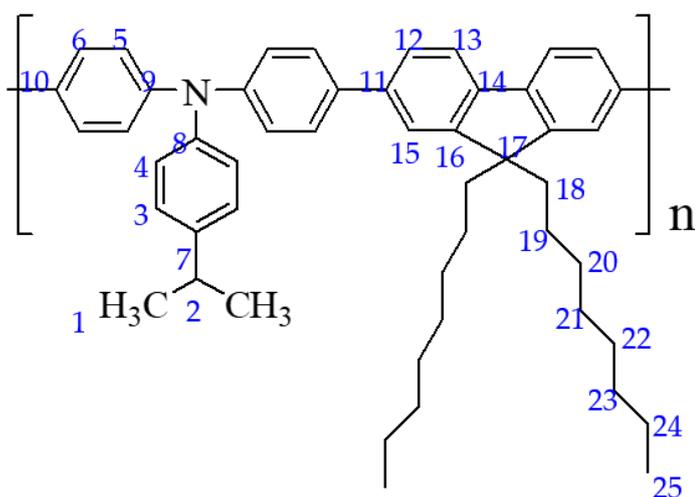


Figure S2. Structure of conjugate polymer C6

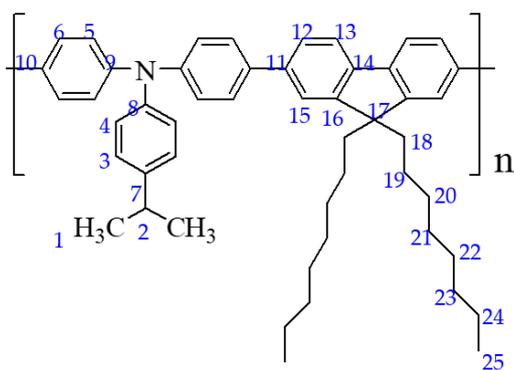
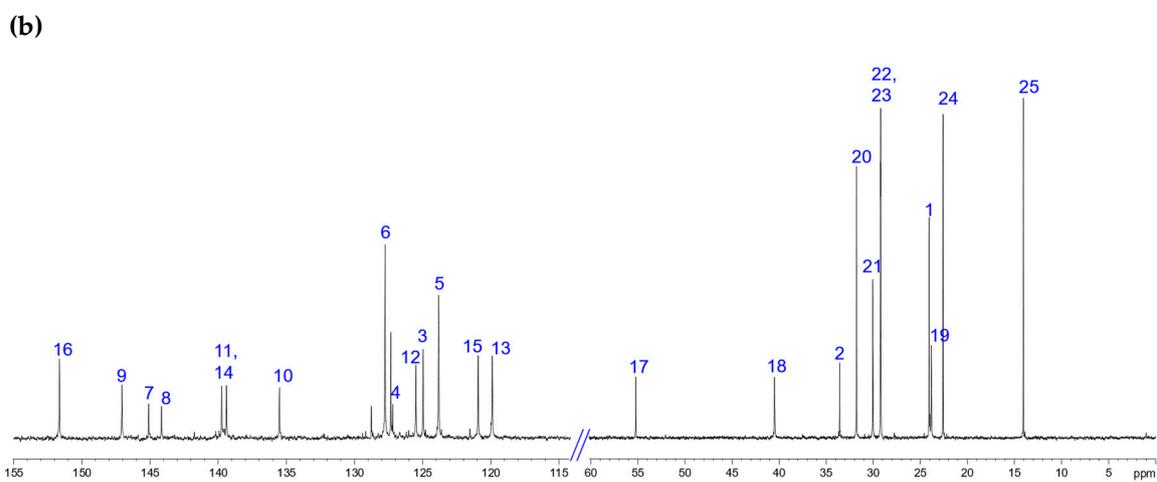
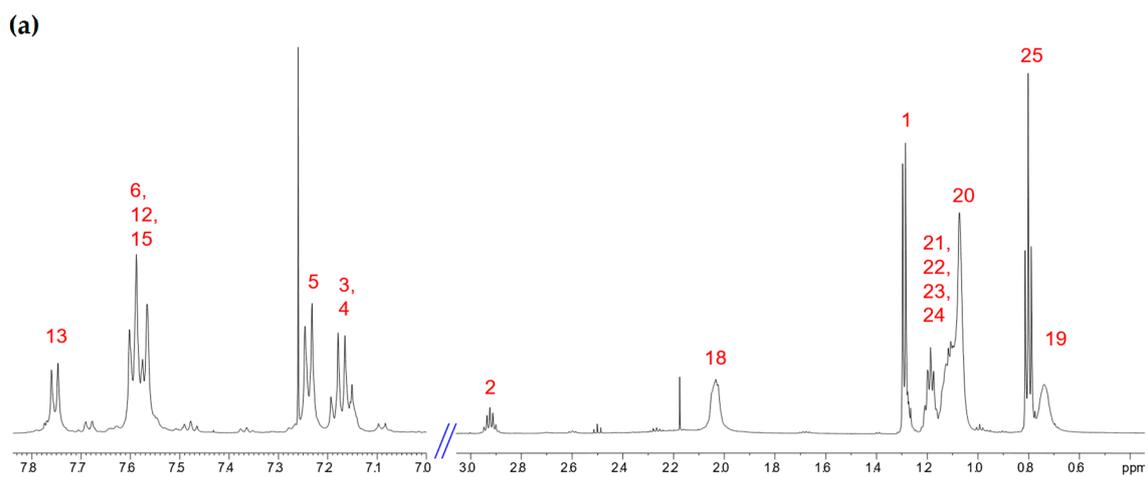


Figure S3. NMR Spectra of C6 (a) ^1H NMR (b) ^{13}C NMR

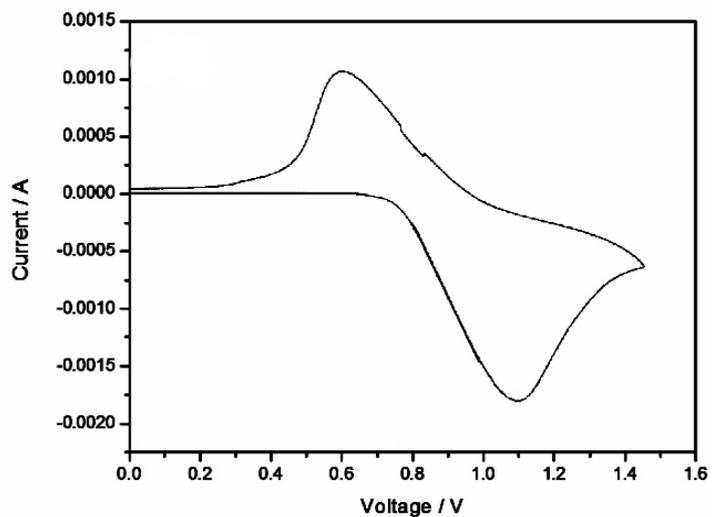


Figure S4. Cyclic voltammograms of the conjugated polymer C6 films on ITO-coated glass in acetonitrile solutions containing 0.1 M TBAP under argon atmosphere; the scan rate was 100 mV/s. $E_{\text{onset}}^{\text{ox}}$ of C6 were 0.76V, by calculation the HOMO for C6 were ~5.16 eV. The HOMO of C6 is calculated by the empirical formula $\text{HOMO} = -(E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{Fc}}) - 4.8$.

The absorbance, PL and EL spectra of the polymers

The absorbance, PL and EL spectra of C1, C2, C3, C6 and PFO are shown in Fig. S5.

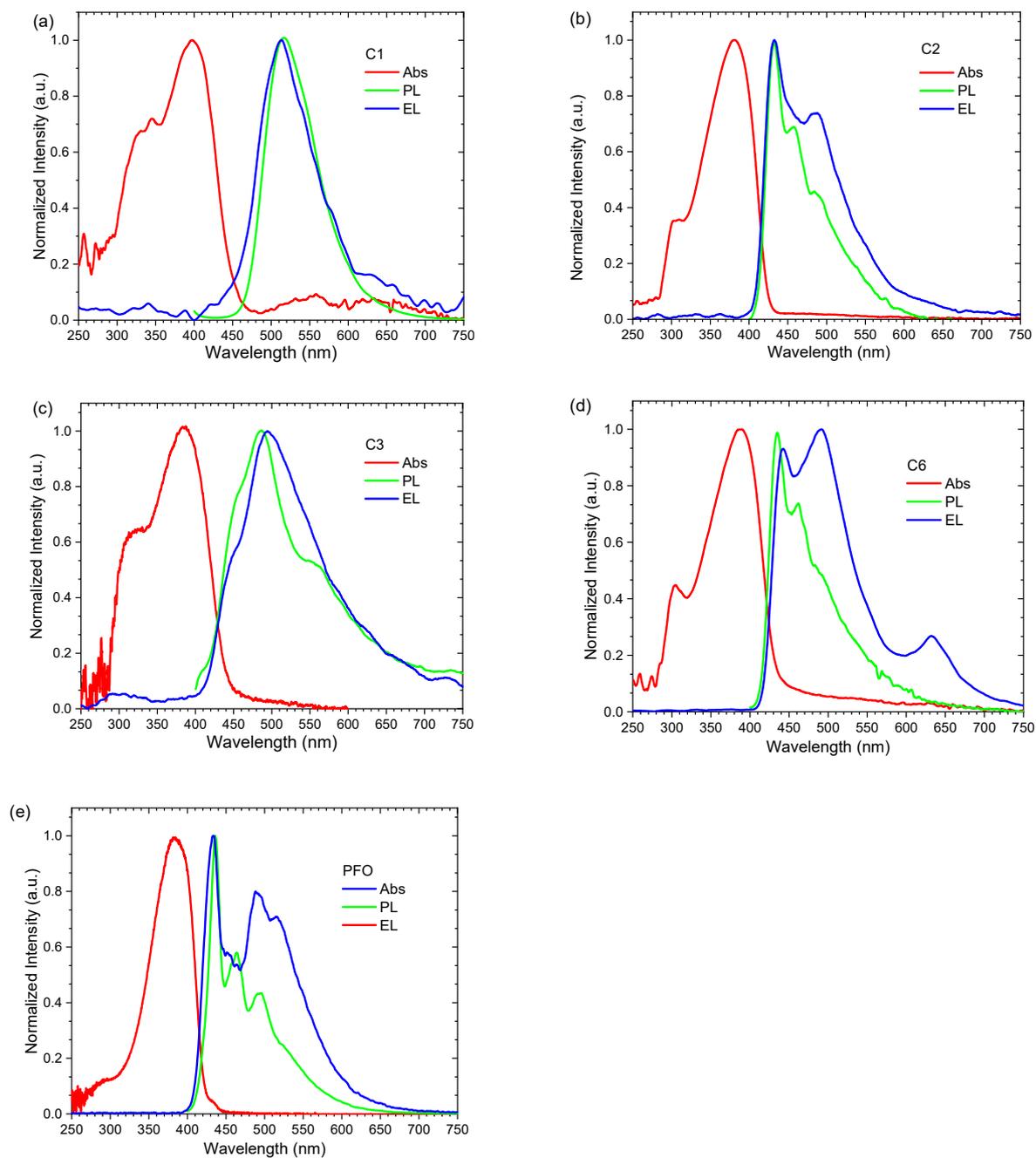


Figure S5. Absorbance, PL and EL spectra of (a) C1, (b) C2, (c) C3, (d) C6 and (e) PFO.

Reference

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