Electronic Supplementary Information

Phenyl-Substituted Fluorene-Dimer Cored Anthracene Derivatives: Highly Fluorescent and Stable Materials for High Performance Organic Blue- and White-Light-Emitting Diodes

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Synthesis section

All the experiments were conduted at inert nitrogen atmosphere except annoucement.

Synthesis of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

To a solution n-Butyllithium (1.2 equiv.) was added dropwise into a flask containing 9-bromoanthracene (1.0 equiv.) in THF at −78 ℃. The mixture was stirred further for one hour, then 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1.2 equiv.) was added at −78 ℃ in one portion and stirred for another 12 h at room temperature. The mixture was quenched with water and extracted twice with ether. The combined organic layer were dried over $MgSO_4$ and concentrated by rotary evaporation, which was further subjected to column chromatography on silica gel (petroleum ether and dichloromethane as eluant) to provide the pure product. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.500−8.481 (d, *J* = 7.6 Hz, 3H), 8.023−8.002 (d, *J* = 8.2 Hz, 2H), 7.538−7.451 (m, 4H), 1.600 (s, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 136.1, 131.3, 129.7, 129.0, 128.5, 126.0, 125.1, 84.5, 25.2. MS (EI): m/z (100%) calcd. for $C_{20}H_{21}BO_2$ 304.2; found 304 (100).

Synthesis of 9-Bromo-10-phenylanthracene

A mixture of 9,10-dibromoanthracene (0.336 g, 1.0 mmol), phenylboronic acid (1.0 mmol) and tetrakis(triphenylphosphine) palladium (69.4 mg, 3 mol %) was added to an air-free two-phase mixture of THF and (50 mL) and aqueous 2 M K_2CO_3 (15 mL). The resulting mixture was vigorously stirred under nitrogen atmosphere at 80 ℃ for 8 h. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 50 mL), the combined organic layer was washed with brine (2 × 50 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to give an light-yellow solid, which was further purified with column chromatography using petroleum ether/dichloromethane as eluant to afford the target product. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.631−8.609 (d, *J* = 8.8 Hz, 2H), 7.666−7.644 (d, *J* = 8.4 Hz, 2H), 7.616−7.536 (m, 5H), 7.420−7.362 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 138.4, 137.8, 131.1, 131.0, 130.2, 128.4, 127.8, 127.7, 127.4, 126.9, 125.5, 122.7. MS (EI): m/z (100%) calcd. for $C_{20}H_{13}Br$, 332.2; found, 332 (100).

4,4,5,5-tetramethyl-2-(10-phenylanthracen-9-yl)-1,3,2-dioxaborolane

Following the procedure of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in which 9-Bromo-10-phenylanthracene replaced 9-bromoanthracene. ^{1}H NMR (400 MHz, $CDCl_3$, δ):

8.462−8.440 (d, *J* = 8.4 Hz, 2H), 7.652−7.630 (d, *J* = 8.4 Hz, 2H), 7.596−7.536 (m, 3H), 7.500−7.462 (t, *J* = 7.6 Hz, 2H), 7.409−7.392 (d, *J* = 7.8 Hz, 2H), 7.344−7.306 (t, *J* = 7.2 Hz, 2H), 1.614 (s, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 139.6, 139.1, 135.3, 131.0, 129.7, 128.4, 128.3, 127.4, 125.4, 124.8, 84.5, 25.2. MS (EI): m/z (100%) calcd. for $C_{26}H_{25}BO_2$ 380.3; found 380 (100).

9-Bromo-10-(naphthalen-1-yl)anthracene

Following the procedure of 9-Bromo-10-phenylanthracene in which naphthalene-1-ylboronic acid was used instead of phenylboronic acid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.665−8.643 (d, *J* = 8.8 Hz, 2H), 8.077−8.057 (d, *J* = 8.0 Hz 1H), 8.016−7.995 (d, *J* = 8.2 Hz 1H), 7.704−7.667 (t, *J* = 7.2 Hz, 1H), 7.599−7.561 (t, *J* = 7.2 Hz, 2H), 7.514−7.460 (m, 2H), 7.418−7.396 (d, *J* = 8.8 Hz, 2H), 7.287−7.259 (d, *J* = 7.6 Hz, 2H), 7.215−7.177 (t, *J* = 8.0 Hz, 1H), 7.045−7.024 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 136.0, 135.8, 133.7, 133.4, 131.7, 130.3, 129.1, 128.4, 128.3, 127.9, 127.4, 127.0, 126.4, 126.1, 125.8, 125.5, 123.2. MS (EI): m/z (100%) calcd. for $C_{24}H_{15}Br$ 383.3; found 382 (100).

4,4,5,5-tetramethyl-2-(10-(naphthalen-1-yl)anthracen-9-yl)-1,3,2-dioxaborolane

Following the procedure of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in which 9-Bromo-10-(naphthalen-1-yl)anthracene replaced 9-bromoanthracene. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.482−8.460 (d, *J* = 8.8 Hz, 2H), 8.047−8.026 (d, *J* = 8.2 Hz, 1H), 7.992−7.972 (d, *J* = 8.0 Hz, 1H), 7.690−7.653 (t, *J* = 7.2 Hz, 1H), 7.495−7.434 (m, 4H), 7.391−7.369 (d, *J* = 8.2 Hz, 2H), 7.224−7.172 (m, 2H), 7.153−7.134 (d, *J* = 7.6 Hz, 1H), 7.016−6.995 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 137.5, 136.8, 135.4, 133.6, 133.4, 130.5, 128.9, 128.4, 128.1, 128.0, 127.4, 126.6, 126.2, 125.9, 125.5, 125.0, 84.6, 25.3. MS (EI): m/z (100%) calcd. for $C_{30}H_{27}BO_2$ 430.3; found, 430 (100).

1,3-Bis(4-bromobenzoyl)benzene

(Modified Procedure).[1] 20.7 g (0.155 mol) anhydrous powdered aluminum chloride was added to a stirred solution of 15 g (0.074 mol) isophthaloyl dichloride and 100 mL bromobenzene. After an exothermic reaction, the solution was stirred at room temperature for 9 h and then heated at 90 ℃ for 2 h. After cooling, the solution was poured into cold methanol to precipitate a white solid which was isolated by filtration. The crude product was recrystallized from toluene to yield white crystals. Yield: 31.4g, 95.3%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.13 (s, 1H), 8.01−7.99 (d, *J* = 8 Hz, 2H), 7.70−7.64 (m, 9H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 195.9, 194.8, 138.1, 137.7, 137.5, 137.0, 135.7, 133.9, 133.7, 133.5, 133.1, 132.0, 131.7, 131.2, 131.0, 130.0, 128.9, 128.8, 128.7, 128.3. MS (EI): m/z (100%) calcd. for $C_{20}H_{12}Br_2O_2$, 444.1; found, 446 (100).

1,3-bis(9-(4-bromophenyl)-9H-fluoren-9-yl)benzene (DBPFB)

To a three-neck flask bottle 2-bromobiphenyl (3.495 g, 15 mmol) and THF (50 ml) were mixed and cooled to −78 ℃ and then n-BuLi (2.5 M in hexane, 6 ml, 15 mmol) was added dropwise. The whole solution was stirred at this temperature for 45 minutes followed by drop-adding a solution of 1,3-Bis(4-bromobenzoyl)benzene (4.441 g, 10 mmol) in THF (100 mL). The resulting mixture was gradually warmed to ambient temperature and kept stirring for 12 h, after that 50 mL saturated aqueous $NaHCO_3$ was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (3 × 60 mL) and the combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was dissolved in acetic acid (100 mL) and catalytic amount of aqueous HCl (12 N) was added, and then the whole mixture was warmed to reflux for 10 h. After cooled to room temperature, the mixture was condensed under reduced pressure. The crude residue was purified by re-crystallization from toluene to afford 6.874 g pure DBPFB, white solid (yield: 96%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.75−7.73 (d, *J* = 8.0 Hz, 4H), 7.39 (s, 1H), 7.37−7.34 (t, *J* = 7.2 Hz, 4H), 7.31−7.29 (d, *J* = 8.0 Hz, 4H), 7.24−7.22 (d, *J* = 7.2 Hz, 3H), 7.20−7.18 (d, *J* = 8.0 Hz, 4H), 6.96−6.94 (d, *J* = 8.0 Hz, 5H), 6.94 (s, 1H), 6.84−6.82 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 150.7, 145.5, 145.2, 140.2, 131.4, 130.4, 130.1, 128.1, 127.9, 126.1, 125.9, 120.9, 120.5, 65.1. MS (EI): m/z (100%) calcd. for $C_{44}H_{28}Br_2$, 716.5; found, 716 (100).

DAPFB, DPAPFB, and DNAPFB

DAPFB, DPAPFB, and DNAPFB were synthesized using this general procedure: a mixture of 1,3-bis(9-(4-bromophenyl)-9H-fluoren-9-yl)benzene (0.716 g, 1.0 mmol), corresponding 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.0 mmol) and tetrakis(triphenylphosphine) palladium (69.4 mg, 3 mol %) was added to an air-free two-phase mixture of toluene and (50 mL) and aqueous 2 M K2CO3 (15 mL). The resulting mixture was vigorously stirred under nitrogen atmosphere at 110 ℃ for 24 h. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 50 mL), the combined organic layer was washed with brine (2 × 50 mL) and dried over anhydrous MgSO4. The solvent was evaporated under reduced pressure to give an off-white solid, which was further purified with column chromatography using petroleum ether/dichloromethane as eluant (1:8 v/v, Rf =

0.25) to afford the target product.

DAPFB: Yielding 0.78 g (86%). 1H NMR (400 MHz, CDCl3, δ): 8.467 (s, 2H), 8.017−7.996 (d, J = 8.5 Hz, 4H), 7.834−7.816 (d, J = 7.2 Hz 4H), 7.748 (s, 1H), 7.666−7.644 (d, J = 8.8 Hz 4H), 7.536−7.515 (d, J = 8.4 Hz 4H), 7.485−7.416 (m, 12H), 7.391−7.339 (m, 8H), 7.319 (s, 1H), 7.299−7.280 (d, J = 7.6 Hz 2H), 7.247−7.227 (d, J = 8 Hz, 1H), 7.048−7.011 (t, J = 7.0 Hz 1H), 6.975−6.956 (d, J = 7.4 Hz 2H). 13C NMR (400 MHz, CDCl3, δ): 150.8, 146.4, 145.4, 140.3, 137.1, 136.7, 131.3, 130.9, 130.2, 128.3, 128.2, 127.7, 127.6, 126.7, 126.5, 126.3, 125.4, 125.3, 125.1, 120.2, 65.4. MS (MADLI-TOF): m/z (100%) calcd. for C72H46, 910.36; found, 910.6. Anal. Calcd. for C72H46：C 94.91, H 5.09; found: C 94.74, H 5.10.

DPAPFB: Yielding 0.95 g (89%). 1H NMR (400 MHz, CDCl3, δ): 7.848−7.830 (d, J = 7.2 Hz 4H), 7.788 (s, 1H), 7.703−7.646 (m, 8H), 7.584−7.548 (m, 10H), 7.461 (s, 8H), 7.423−7.401 (d, J = 8.4 Hz 8H), 7.339−7.284 (m, 7H), 7.233−7.217 (m, 2H), 7.128−7.108 (d, J = 8.0 Hz 2H), 7.064−7.028 (t, J = 7.2 Hz 2H), 6.992−6.973 (d, J = 7.2 Hz). 13C NMR (400 MHz, CDCl3, δ): 150.7, 145.9, 140.2, 140.1, 132.9, 131.3, 129.9, 128.4, 128.3, 128.1, 127.8, 127.7, 127.6, 127.5, 127.2, 126.9, 126.2, 125.7, 125.0, 123.4, 120.2. 65.3. MS (MADLI-TOF): m/z (100%) calcd. for C84H54, 1062.42; found, 1062.7. Anal. Calcd. for C84H54：C 94.88, H 5.12; found: C 94.81, H 5.10.

DNAPFB: Yielding 0.91 g (78%). 1H NMR (400 MHz, CDCl3, δ): 8.057-8.036 (d, J = 8.2 Hz, 2 H), 8.006−7.985 (d, J = 8.2 Hz, 2H), 7.864−7.846 (d, J = 7.2 Hz, 4H), 7.819 (s, 1H), 7.749−7.728 (d, J = 8.2 Hz, 4H), 7.698−7.660 (t, J = 7.6 Hz, 2H), 7.601−7.582 (d, J = 7.6 Hz, 4H), 7.546−7.461 (m, 10H), 7.442−7.384 (m, 10H), 7.371−7.333 (t, J = 7.2 Hz, 4H), 7.234−7.196 (t, J = 7.8 Hz, 5H), 7.174−7.137 (m, 6H), 7.049−7.031 (d, J = 7.2 Hz, 1H), 6.992−6.973 (d, J = 7.6 Hz, 2H). 13C NMR (400 MHz, CDCl3, δ): 151.1, 146.7, 145.6, 140.5, 137.5, 137.3, 136.9, 135.1, 133.8, 133.7, 131.3, 130.8, 130.1, 129.4, 128.7, 128.5, 128.3, 128.2, 128.0, 127.8, 127.1, 126.8, 126.6, 126.4, 126.1, 125.7, 125.6, 125.3, 125.2, 120.5, 65.6. MS (MADLI-TOF): m/z (100%) calcd. for C92H58, 1162.45; found, 1162.8. Anal. Calcd. for C92H58: C 94.98, H 5.09; found: C 94.74, H 5.10.

Fig. S1. Optimized geometries, calculated HOMO, and LUMO density maps (from left to right) of the three anthracene derivaties at the B3LYP/6-31G* level (the top is DPAPFB, the middle: DAPFB, and the bottom: DNAPFB).

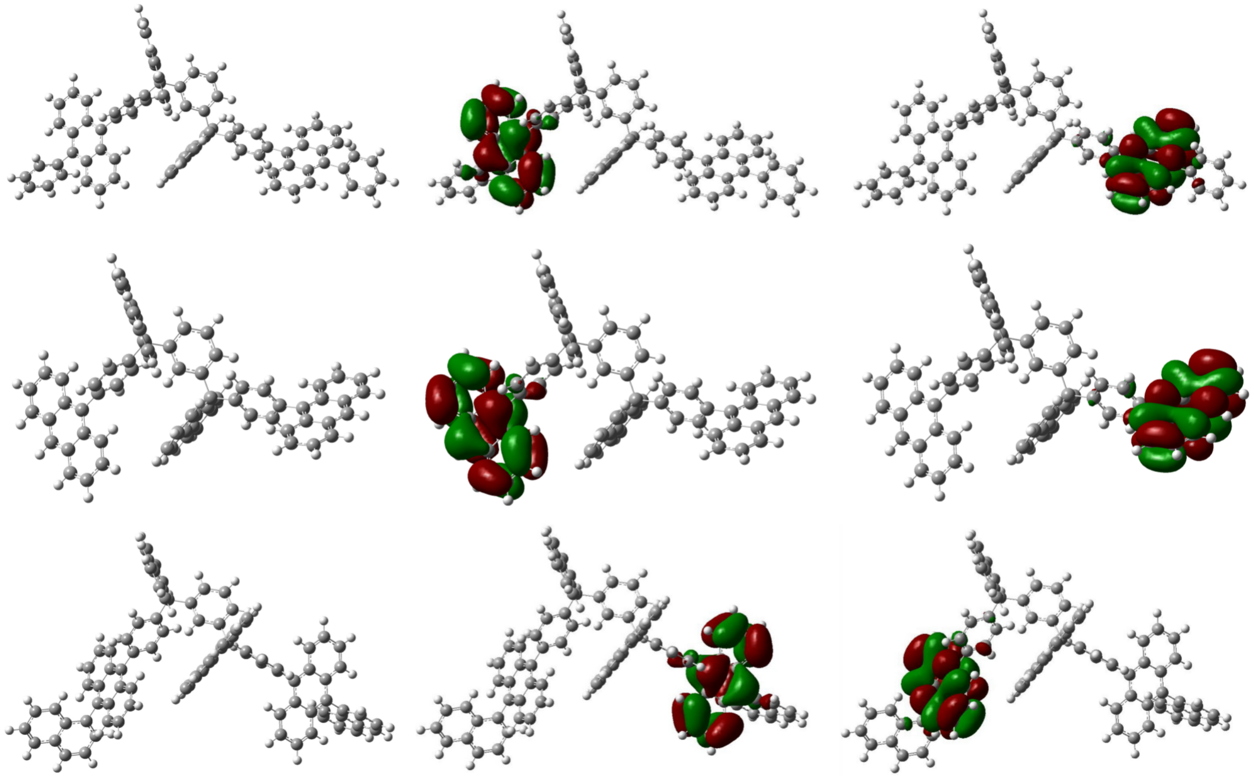
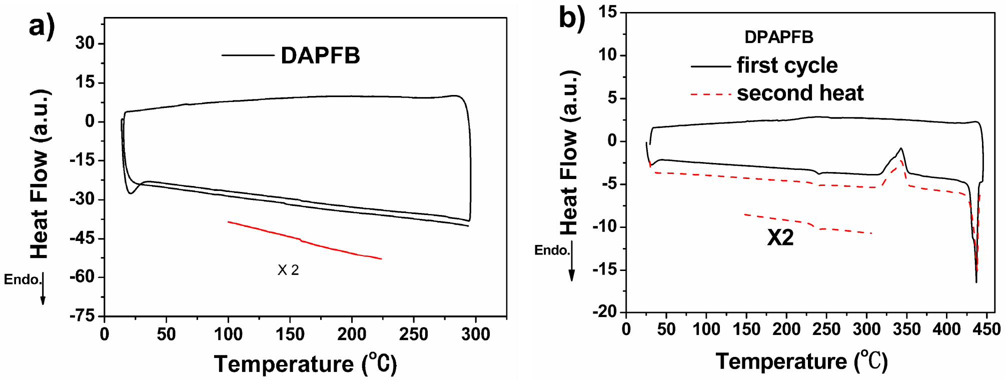


Fig. S2. DSC curves of DAPFB, DPAPFB, and DNAPFB at a scan rate of 10 ℃ min^{-1}.



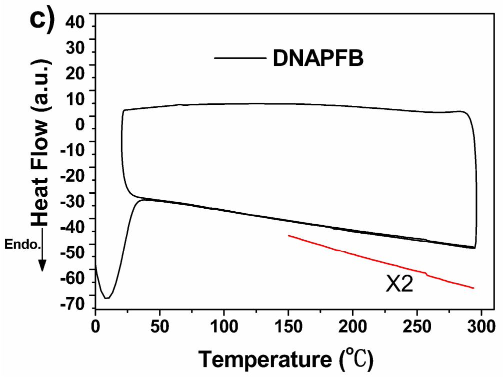


Fig. S3 UV–vis absorption spectra of DAPFB, DPAPFB, and DNAPFB in dilute dichloromethane solution (a) and in thin films on quartz slice (b).

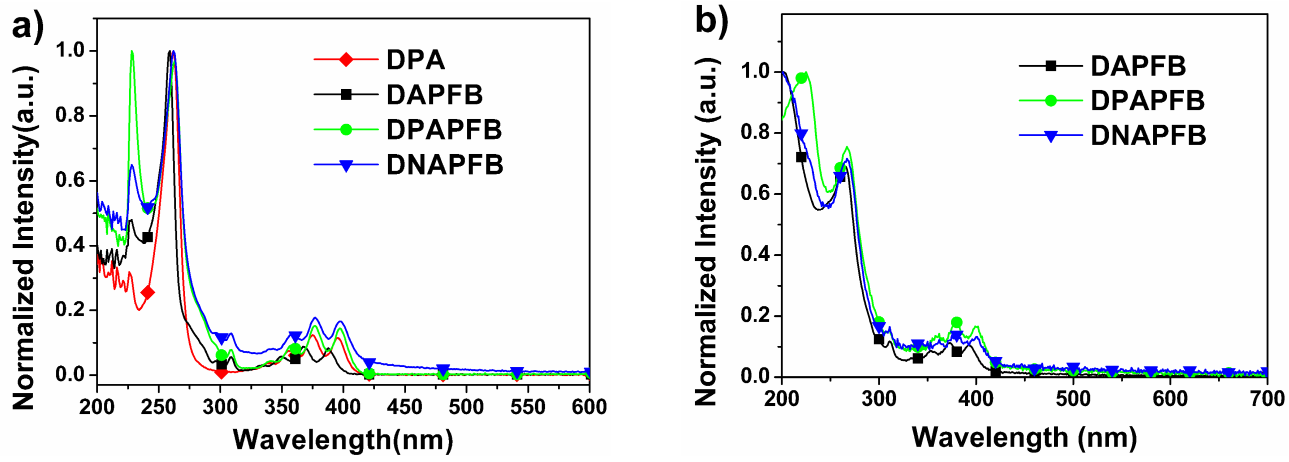
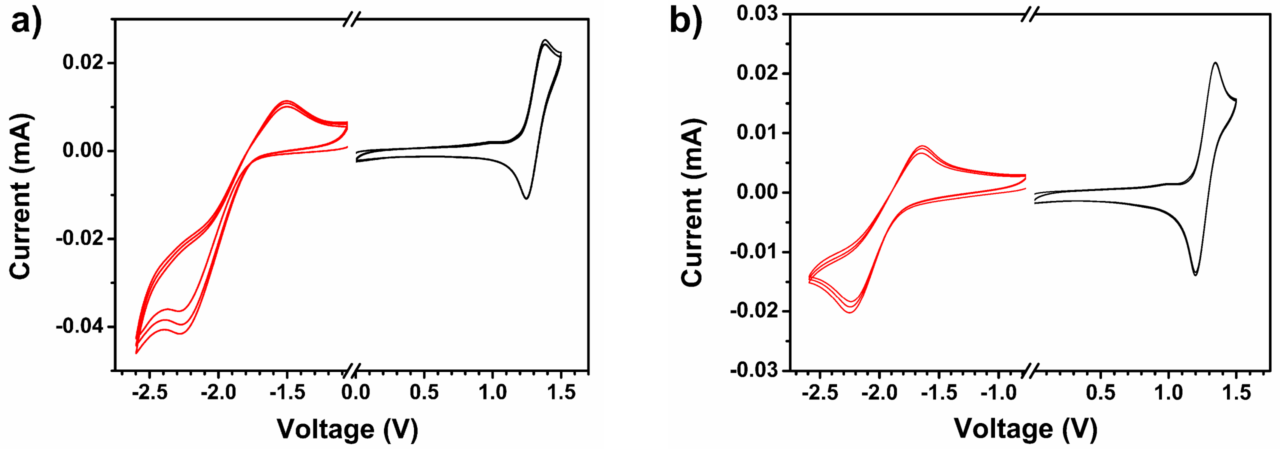


Fig. S4. Cyclic voltammograms of DAPFB (a) and DPAFB (b) in three cycles.



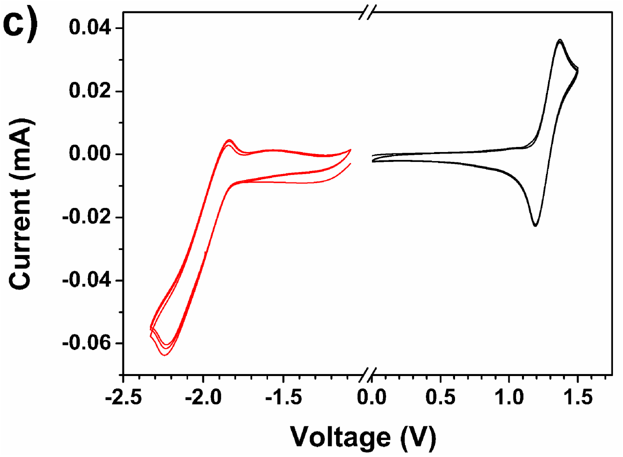
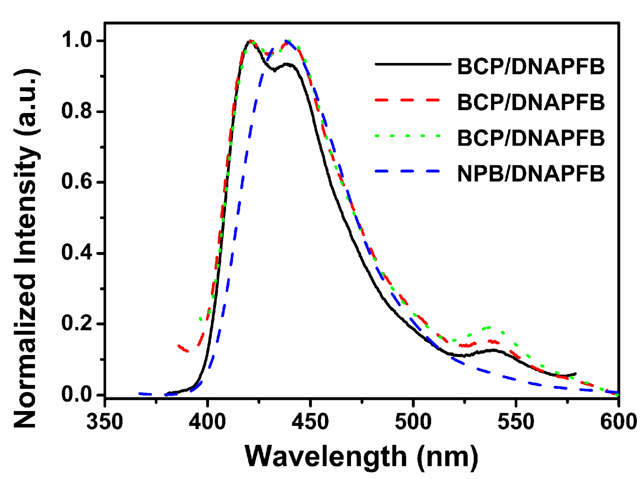


Fig. S5. PL spectra of DNAPFB and NPB or BCP blend films; blue line, excited at 350 nm; red line, excited at 360 nm; green line, excited at 380 nm; black line, excited at 300 nm.



1. Percec, V.; Clough, R. S.; Rinaldi, P. L.; Litman, V. E., *Macromolecules* **1994,** *27* (6), 1535.