

Polyfluorene copolymers containing 2,5-difluoro-1,4-phenylene chains and carbazole conjugates with 1,8-naphthalimides for stable blue OLEDs

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Photoluminescence spectra of solutions and films were recorded on a LS-100 luminescence spectrophotometer (PTI®, Canada) at the excitation wavelength 365 nm. Molecular weights and molecular weight distributions were determined by size-exclusion chromatography in THF solutions using a Shimadzu Prominence setup equipped with a HR 4E styragel column (5 µm, 7.8x300 mm (WATERS)) and photo-diode matrix spectrophotometric detector. Molecular weight characteristics were calculated using polystyrene standards. Spectral characteristics, current-voltage and brightness-voltage characteristics of organic light emitting diodes (OLED) with the emissive layer cast from the synthesized polyfluorene copolymers were measured by means of a Keithley 237 voltage/current source unit combined with an Avantes 2048 fiber optic spectrometer calibrated for absolute radiometric measurements. Photoluminescence absolute quantum yields of copolymers in films were determined by DeMello method [1-3] under excitation of laser diodes ($\lambda=378$ and 405 nm).

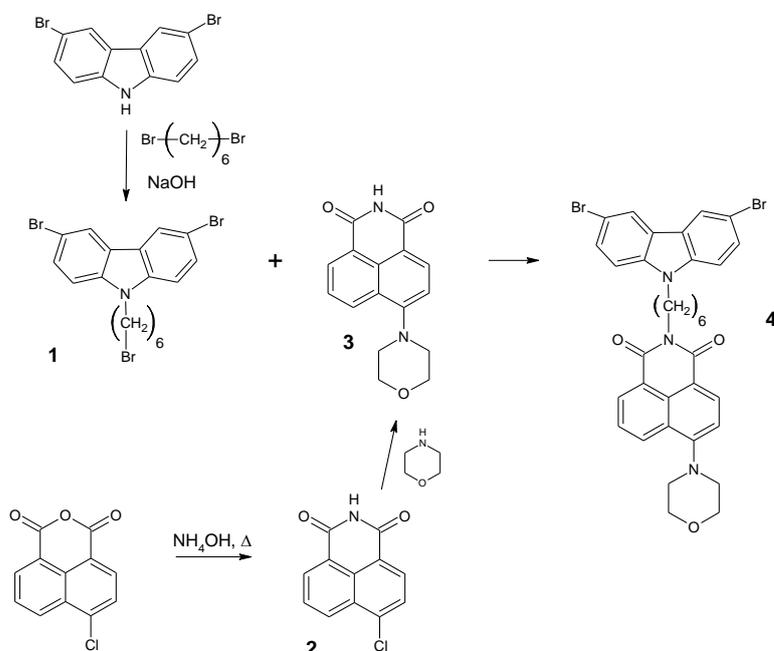
The light-emitting diodes had the architecture ITO/PEDOT:PSS(50 nm)/PFC(50-60 nm)/Ca(50 nm)/Al(100 nm). A hole-injection layer (water-soluble complex between poly(3,4-ethylenedioxythiophene) and sodium polystyrenesulfonate (PEDOT:PSS)) was spin-cast from aqueous solution onto purified glass plate treated with O₂ plasma and coated with an ITO layer (SnO₂:In₂O₃) with the resistance of 10 Ohm and dried at 120°C. Then, PFC layer was cast from solution in toluene (7 mg ml⁻¹) and dried at 80°C. Layers of Ca (60 nm) and Al (120 nm) metals were applied by thermal vacuum deposition (10⁻⁶ Torr).

Tetrahydrofuran was distilled twice under argon from sodium. The polymer-immobilized Pd(PPh₃)₄ catalyst, 1-bromo-4-*tert*-butylbenzene, monomers (2,7-dibromo-9,9-dioctylfluorene, 2,7-di(1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene, 1,4-dibromo-2,5-difluorobenzene, 4,4'-bis[(4-bromophenyl)phenylamino]biphenyl), 3,6-dibromocarbazole, 1,6-dibromohexane, morpholine, piperidine, 4-chloro-1,8-naphthalic anhydride were purchased from Sigma-Aldrich and used without additional purification.

9,9-Bis(4-diphenylaminophenyl)-2,7-dibromofluorene was synthesized according to the published procedure [4].

2,7-Dibromo-9,9-bis{4-[6-(9*H*-carbazol-9-yl)hexyloxy]phenyl}fluorene was synthesized from 9-(6-bromohexyl)-9*H*-carbazole and 2,7-dibromo-9,9-bis(4-hydroxyphenyl)fluorene as reported [5]. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.1–8.15 (4H, d), 7.6 (2H, d), 7.4–7.5 (12H, m), 7.25 (4H, t), 7.05(4H, d), 6.75 (4H, d), 4.30–4.35 (4H, t), 3.85–3.90 (4H, t), 1.90–1.95 (4H, q), 1.70–1.75 (4H, q), 1.4–1.55 (8H, m)

9-(6-Bromohexyl)-9*H*-carbazole, *N*-[6-(3,6-Dibromocarbazol-9-yl)hexyl]-4-morpholino-1,8-naphthalimide (Scheme S1), and *N*-[6-(3,6-dibromocarbazol-9-yl)hexyl]-4-piperidino-1,8-naphthalimide were synthesized as described by us earlier [6]. 2,7-Dibromo-9,9-bis(4-hydroxyphenyl)fluorene was obtained according to the literature [7].



Scheme S1 Synthesis of *N*-[6-(3,6-Dibromocarbazol-9-yl)hexyl]-4-morpholino-1,8-naphthalimide.

4-Morpholino-1,8-naphthalimide 3. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 11.6 (1H, s), 8.3–8.5 (3H, m), 7.8 (1H, m), 7.3 (1H, m), 3.9 (4H, m), 3.2 (4H, m).

N-[6-(3,6-Dibromocarbazol-9-yl)hexyl]-4-morpholino-1,8-naphthalimide 4. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.4–8.6 (3H, m), 8.1 (2H, s), 7.7 (1H, t), 7.5 (2H, d), 7.2 (2H, d), 4.1–4.3 (4H, m), 4.0 (4H, m), 3.3 (4H, m), 1.6–1.9 (4H, m), 1.4–1.5 (4H, m).

Polymer synthesis

Monomers: 2,7-dibromo-9,9-dioctylfluorene (0.0466 g, 0.085 mmol), 2,7-di(1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene (0.1426 g, 0.256 mmol), 1,4-dibromo-2,5-difluorobenzene (0.0449 g, 0.1651 mmol) were added to a 35 ml glass ampoule equipped with magnetic stirring bar. Catalyst, polymer-supported Pd(PPh₃)₄, (10 mg) was added to the ampoule under inert atmosphere in the glove box (Labconco). The ampoule was sealed with silicon cap with PTFE gasket. Then degassed THF and 2 M K₂CO₃ were syringed. Polycondensation was conducted under microwave heating in CEM Discover SP apparatus at 130 °C, 140 W (SPS mode, $\Delta T=10$ °C) for 40 min. After that to close polymer end groups, 2,7-di(1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene (15 mg in 1 ml of degassed THF) and 1-bromo-4-*tert*-butylbenzene (1 ml in 0.5 ml of degassed THF) were sequentially syringed followed by microwaving for 30 min after each addition. The reaction mixture was diluted with THF, decanted from water solution and passed through silica gel (70–230 mesh, Aldrich). The solution was concentrated by rotary evaporation and the polymer was precipitated into methanol. The precipitant was washed with methanol, water and acetone and extracted with acetone from impurities in Soxhlet apparatus for 3 days. After that polymer was reprecipitated from THF to methanol two times and dried in vacuum at 50 °C for two days.

Investigation of stability of PFCs

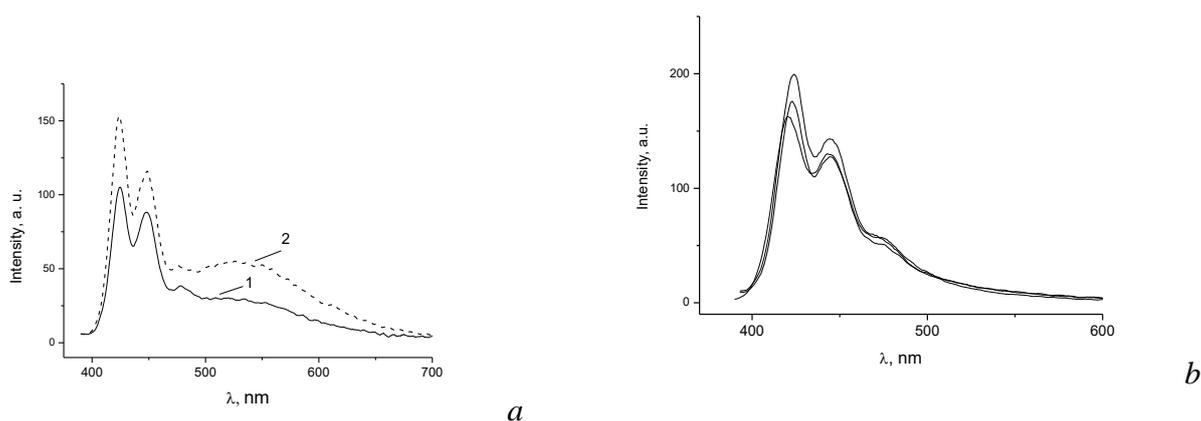


Figure S1 Photoluminescence spectra of (a) poly(9,9-dioctylfluorene) heat treated at (1) 150 and (2) 180 °C, and (b) the synthesized PFC with 33 mol % of 2,5-difluoro-1,4-phenylene units (Fig. 1, $y=0$, $z=0$) heat treatment at 60, 150, and 180 °C.

Electroluminescence spectra

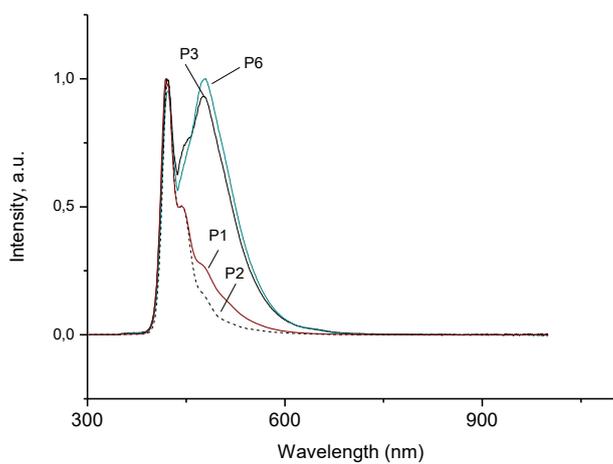


Figure S2 Electroluminescence of PFCs: P1, P2, P3, P6.

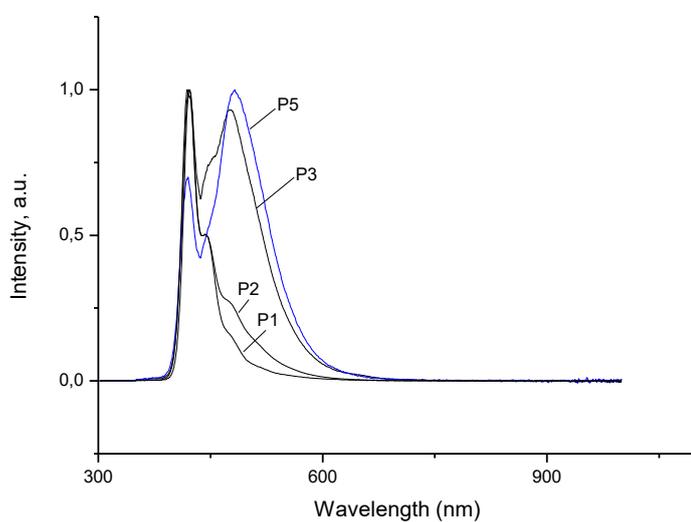


Figure S3 Electroluminescence of PFCs: P1, P2, P3, P5.

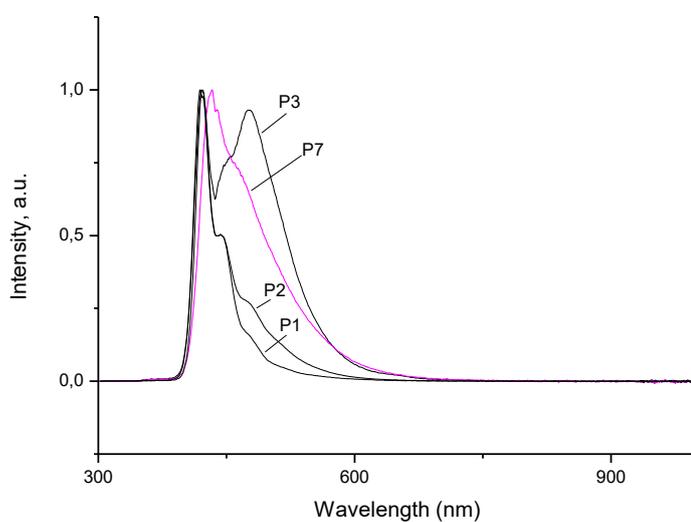


Figure S4 Electroluminescence of PFCs: P1, P2, P3, P7.

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