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White electroluminescence from polyfluorenes copolymerized with carbazole derivatives of Nile Red and 1,8-naphthalimide

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Experimental

^{1}H NMR spectra were recorded using a Bruker AC-400 spectrometer (400 MHz); samples were dissolved in DMSO-d_6 or $CDCl_3$. The elemental composition was performed using an Elementar vario EL cube device. Photoluminescence spectra of solutions and films were taken using the LS-100 luminescence spectrophotometer (PTI®, Canada). The excitation wavelength was 365 nm. Molecular weights and molecular weight distributions were determined by size-exclusion chromatography in THF solutions using a Shimadzu Prominence setup equipped with the 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 relationships and current-luminance relationships of organic light emitting diodes (OLED) were registered using a Keithley 237 voltage/current source unit combined with an Avantes 2048 fiber optic spectrometer calibrated for absolute radiometric measurements.

The light-emitting diodes with the architecture ITO/PEDOT:PSS(50 nm)/PF(50-60 nm)/Ca(50 nm)/Al(100 nm) were prepared using synthesized PFs. The hole-injection layer (complex between poly(3,4-ethylenedioxythiophene) and sodium polystyrenesulfonate (PEDOT:PSS)) was applied by centrifugation from water solution onto purified glass plate treated with O_2 plasma and coated with an ITO layer (SnO_2:In_2O_3) with a resistance of 10 Ohm and dried at 120°C. Then, CPF solution in toluene (7 mg mL^{-1}) was applied and dried at 80°C. Layers of Ca (60 nm) and Al (120 nm) metals were applied by thermal vacuum deposition (10^{-6} Torr).

Toluene and THF were distilled under argon from sodium. Dimethylformamide (DMF) was distilled in vacuum from CaH_2. The catalysts $Pd(PPh_3)_4$, bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$)), 2,2′-bipyridyl, 1,5-cyclooctadiene, trioctylmethylammonium chloride, 4-*tert*-butylbromobenzene, 9,9-dioctyl-2-bromofluorene, monomers (2,7-dibromo-9,9-dioctylfluorene and 2,7-di(1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene), and phase transfer catalyst (trioctylmethylammonium chloride, Aliquat® 336) were purchased from Sigma-Aldrich and used without further purification.

The Suzuki cross-coupling polymerization. A 100 mL flask equipped with a reflux condenser connected with an adapter with two valves (for work in argon/vacuum system) and a tap for introducing solvents (Aldrich Z530255) was loaded with 2,7-di(1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene (0.2852 g, 0.501 mmol) and 9,9-dioctyl-2,7-dibromofluorene (0.2742 g, 0.5 mmol), NilRm (0.0011 g, 0.0015 mmol) and NBi (0.0017 g, 0.005 mmol). In order to remove oxygen, the flask was subjected to three cycles of evacuation and filling with argon. Then, it was placed into an argon-filled glove box, and the catalyst $Pd(PPh_3)_4$ (17 mg, 0.014 mmol) was charged into the flask. The reaction mixture was again exposed to three cycles of evacuation and filling with argon. Toluene (6 ml), 2 *M* aqueous solution of K_2CO_3 (2.5 mL) and solution of trioctylmethylammonium chloride (Aliquat® 336, 50 mg in 0.5 mL toluene) were syringed into the flask through the adapter (oxygen was preliminarily removed from these liquids). The reaction mixture was stirred at 110°C for 25 h. Then, 2,7-di(1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene (25 mg in 1 mL of toluene), and in more 8 h, 4-*tert*-butylbromobenzene (0.4 mL in 1 mL of toluene) were introduced as end-capping reagents. Stirring and heating were continued for more 8 h. Then the formed polymer was precipitated into methanol, filtered off, dissolved in chloroform and reprecipitated into methanol. Low molecular weight fractions were removed by extraction with acetone in a Soxhlet apparatus for 2 days. Then the product was dissolved in THF and precipitated into methanol. The precipitate was dried under vacuum at 50°C for 2 days. After purification, the modified polyfluorene yield was 85%. If necessary, it was purified by fractional precipitation.

The Yamamoto homocoupling polymerization. A 100 mL flask equipped with a reflux condenser connected with an adapter with two valves (for work in argon/vacuum system) and a tap for introducing solvents was subjected to three cycles of evacuation and filling with argon. Then, it was placed into an argon-filled glove box, $Ni(COD)_2$ (1 g, 3.63 mmol), 2,2′-bipyridyl (0.565 g, 3.62 mmol), and 1,5-cyclooctadiene (0.400 g, 3.62 mmol) were loaded into the flask. The flask was again exposed to three cycles of evacuation and filling with argon. Then, dry DMF (8 ml) previously purged with argon for 1 h was introduced. The reaction mixture was heated at 80°C for 20 min. After activation of the catalyst, solution of 2,7-dibromo-9,9-dioctylfluorene

(0.881 g, 1.608 mmol) and NilRp (0.0018 g, 0.0024 mmol) in toluene (7 mL), purged with argon for 1 h, was syringed. Polymerization was carried out in argon atmosphere at 80°C under intense stirring for 4 days. Afterwards, 4-*tert*-butylbromobenzene (0.4 mL in 2 mL of toluene) was introduced as an end-capping reagent. The obtained reaction mixture was poured into the solvent mixture consisting of concentrated HCl, methanol and acetone (100 mL each). After nickel compounds were dissolved, the precipitated yellow-rose polymer was filtered off and washed with water, methanol and acetone. Then the product was extracted with acetone in the Soxhlet apparatus for 2 days, dissolved in THF and precipitated into methanol. The precipitate was dried under vacuum at 50°C for 2 days. The polymer yield was 87%.

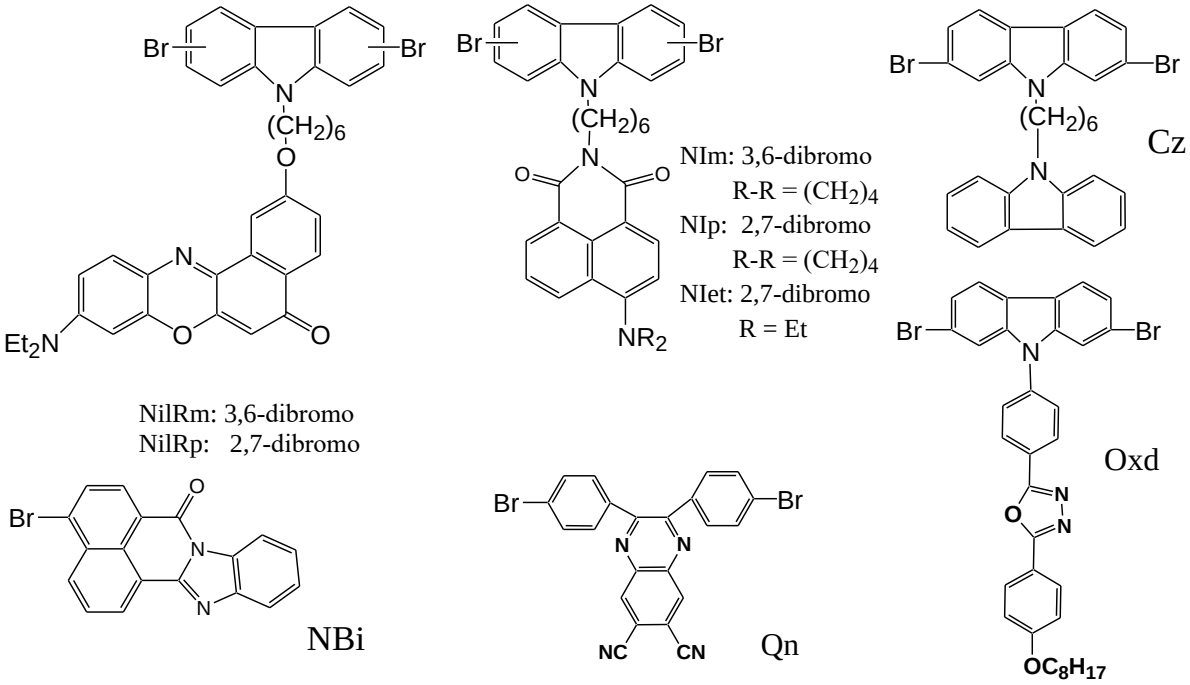

Figure S1 Luminophores, charge-transporting components and terminal group introduced into CPFs. †

† The syntheses of monomers: 2-[6-(2,7-dibromocarbazol-9-yl)hexyloxy]-9-diethylamino-5*H*-benzo[*a*]phenoxazine-5-one (NilRp), 2-[6-(3,6-dibromocarbazol-9-yl)hexyloxy]-9-diethylamino-5*H*-benzo[*a*]phenoxazine-5-one (NilRm), 2,7-dibromo-9-[6-(carbazol-9-yl)hexyl]-9*H*-carbazole (Cz), 2,7-dibromo-9-{4-[2-(4-octyloxyphenyl)-1,3,4-oxadiazol-5-yl]-phenyl}-9*H*-carbazole (Oxd), *N*-[6-(3,6-dibromocarbazol-9-yl)hexyl]-4-pyrrolidino-1,8-naphthalimide (NIm), *N*-[6-(2,7-dibromocarbazol-9-yl)hexyl]-4-pyrrolidino-1,8-naphthalimide (Nip), *N*-[6-(2,7-dibromocarbazol-9-yl)hexyl]-4-diethylamino-1,8-naphthalimide (NIet) were described in [S1]. 4-Bromonaphthalbenzimidazole was synthesized as described in [S2].

Table S1 Composition and molecular mass characteristics of modified polyfluorenes.

Sample	Molar amount of Nile Red, %	Molar amount of naphthalimide, %	Molar amount of charge-transporting groups, %	End groups[a]	$M_w \times 10^{-3}$	M_w/M_n
P-1	NilRm 0.15	0	0	NBi 1	51	1.8
P-2		NIm 0.5	0	NBi 0.3	137.8	3.50
P-3		NIm 1	Cz 0.5	NBi 0.5	33.2	1.95
P-4	NilRp 0.15	NIp 0.5	Cz 0.25, Qn 0.5	4-^{t}BuC$_6$H$_4$	26	1.9
P-5		NIet 0.5	Cz 0.5, Oxd 0.25	Fl[c]	58.6	3.18
P-6	NilRp 1.2	0	0	Fl[c]	20.4	1.95
P-7[b]	NilRp 0.15	0	0	4-^{t}BuC$_6$H$_4$	144.8	3.06

[a] Molar ratio between end groups and monomers is given. [b] The polymer was synthesized by the Yamamoto method. [c] Fl - 9,9-dioctylfluoren-2-yl.

Elemental analysis data.

P1: Calcd (%): $[(C_{29}H_{40})_{98.75}(C_{38}H_{35}N_3O_3)_{0.15}(C_{18}H_9N_2O)_1]_n$: C 89.602; H 10.249; N 0.089; O 0.06. Found: C 89.62; H 10.28; N 0.08.

P2: Calcd (%): $[(C_{29}H_{40})_{99.05}(C_{38}H_{35}N_3O_3)_{0.15}(C_{34}H_{31}N_3O_2)_{0.5}(C_{18}H_9N_2O)_{0.3}]_n$: : C 89.579; H 10.257; N 0.092; O 0.072. Found: C 89.60; H 10.3; N 0.1.

P3: Calcd (%): $[(C_{29}H_{40})_{97.85}(C_{38}H_{35}N_3O_3)_{0.15}(C_{34}H_{31}N_3O_2)_1(C_{30}H_{26}N_2)_{0.5}\ (C_{18}H_9N_2O)_{0.5}]_n$: C 89.485; H 10.198; N 0.196; O 0.121. Found: C 89.51; H 10.22; N 0.18.

P4: Calcd (%): $[(C_{29}H_{40})_{98.6}(C_{38}H_{35}N_3O_3)_{0.15}(C_{34}H_{31}N_3O_2)_{0.5}(C_{30}H_{26}N_2)_{0.25}(C_{22}H_{10}N_4)_{0.5}]_n$: C 89.550; H 10.230; N 0.160; O 0.060. Found: C 89.58; H 10.26; N 0.15.

P5: Calcd (%): $[(C_{29}H_{40})_{98.6}(C_{38}H_{35}N_3O_3)_{0.15}(C_{34}H_{33}N_3O_2)_{0.5}(C_{30}H_{26}N_2)_{0.5}(C_{34}H_{31}N_3O_2)_{0.25}]_n$: C 89.549; H 10.238; N 0.133; O 0.080. Found: C 89.58; H 10.25; N 0.13.

P6: Calcd (%): $[(C_{29}H_{40})_{98.8}(C_{38}H_{35}N_3O_3)_{1.2}]_n$: C 89.49; H 10.233; N 0.129; O 0.148. Found: C 89.52; H 10.25; N 0.12.

P6: Calcd (%): $[(C_{29}H_{40})_{99.85}(C_{38}H_{35}N_3O_3)_{0.15}]_n$: C 89.666; H 10.300; N 0.016; O 0.018. Found: C 89.68; H 10.31; N 0.02.

SPECTRA

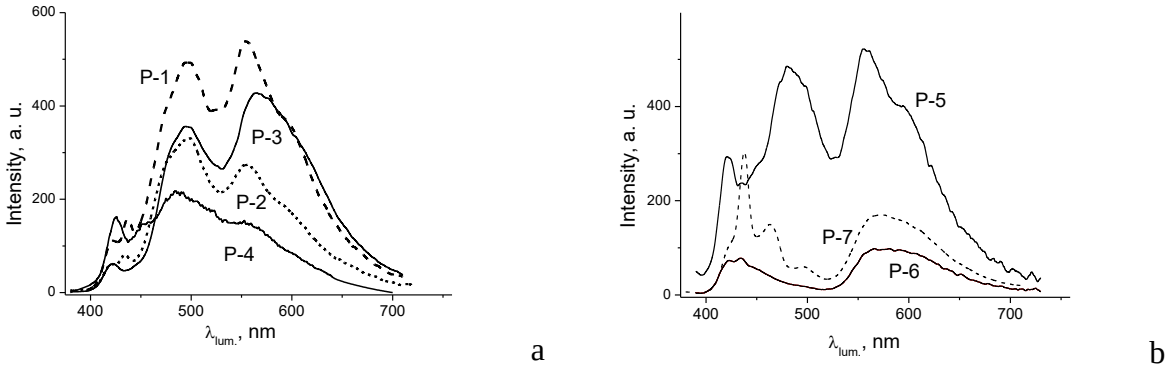

Figure S2 Photoluminescence spectra of modified polyfluorenes in films. The excitation wavelength is 365 nm.

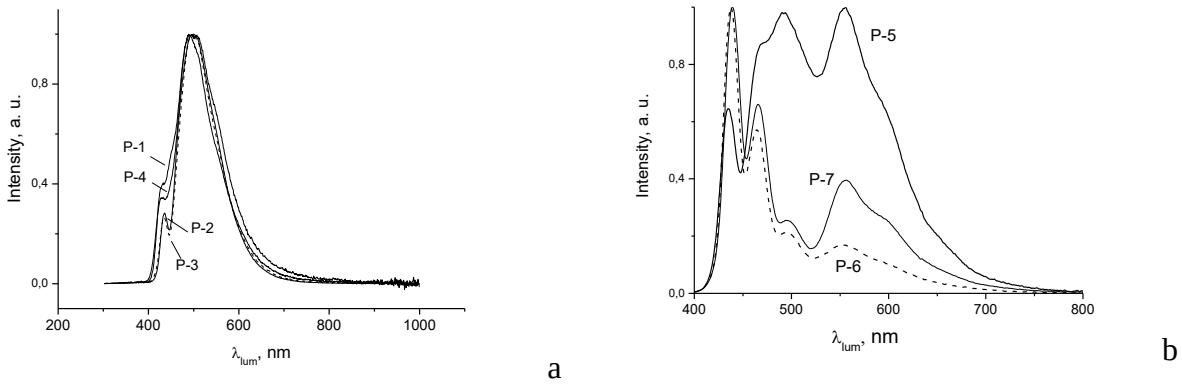

Figure S3 Electroluminescence spectra of modified polyfluorenes.

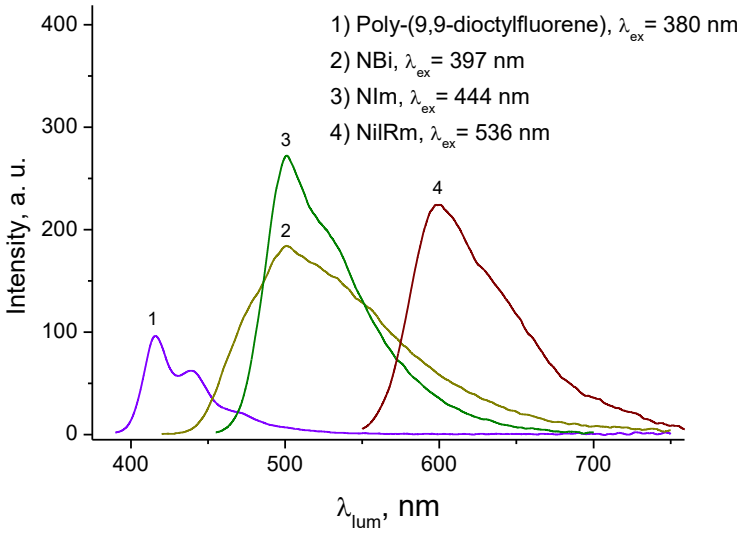

Figure S4 Photoluminescence spectra of chloroform solutions of monomers and poly-(9,9-dioctylfluorene) (c=0.01 mg/ml).

References

S1. G. I. Nosova, D. A. Lypenko, R. Yu. Smyslov, I. A. Berezin, E. V. Zhukova, E. I. Mal'tsev, A. V. Dmitriev, L. S. Litvinova, N. A. Solovskaya, O. V. Dobrokhotov, I. G. Abramov and A. V. Yakimanskii, *Polym. Sci. Ser. B.*, 2014, **56**, 59.

S2. H. D. Burrows, J. S. de Melo, M. Forster, R. Günter, U. Scherf, A. P. Monkman and S. Navaratnam, *Chem. Phys. Lett.*, 2004, **385**, 105.