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

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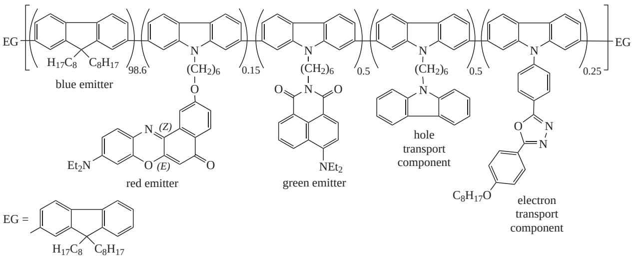
Seven polyfluorenes containing new carbazole derivatives of Nile Red dye and 1,8-naphthalimide in the chain (obtained by the Suzuki and Yamamoto coupling) are characterized by the Nile Red emission band being less intense in their electroluminescence spectra than in photoluminescence spectra. In the optimal composition, 0.15 mol% fraction of Nile Red and 0.5 mol% fraction of *N*-[6-(2,7-dibromocarbazol-9-yl)hexyl]-4-diethylamino-1,8-naphthalimide provide a nearly white light electroluminescence (CIE coordinates *x* = 0.28; *y* = 0.36) with the brightness of 3278 cd m^{-2} and the current efficiency of 1.86 cd A^{-1}.



Conjugated polymers are widely studied in order to develop various electronic devices, such as light-emitting diodes, transistors, photovoltaic cells and sensors.[1–8] Polyfluorenes (PFs) are especially advantageous due to their high thermal and chemical stability and high luminescence quantum yields. Their good film-forming properties and possibilities of modification of the polymer structure at the fluorene 9-position without change in the main chain comprise a challenge for searching the novel polymers that exhibit intense photo- and electroluminescence (PL and EL) over a wide spectral range.

To enhance the efficiency of optoelectronic devices based on these polymers, the balance between mobility of charge carriers (holes and electrons) within the light-emitting layer should be optimized. Therefore, various groups which improve charge carrier characteristics (*e.g.*, electron-donating carbazole and triphenylamine, and electron-withdrawing quinoxaline and aryloxadiazole) are introduced into PFs.[1] The methods of introducing these moieties into PF chains require further improvement.

An important task in the synthesis of white light emitting PFs is the search for new effective red and green luminophores. Nile Red dye, well-known as a luminophore with high quantum yield of red luminescence,[9] can potentially be introduced into PF chains for polymer OLEDs. To the best of our knowledge, literature data on such a topic are scarce. Therefore, it is important to analyze energy transfer from fluorene to Nile Red derivative and to obtain EL data for thus modified PFs. Naphthalimide derivatives possess high luminescence efficiency in the green spectral range and electron-transporting properties.[10–14]

In this work, for modification of PF, 2,7- and 3,6-dibromo carbazole derivatives of Nile Red and naphthalimide with an efficient white light EL were used as synthetic building blocks (Figure 1). Derivatives of Nile Red dye (NilRm and NilRp) were used as red-emitting luminophore components, naphthalimide derivatives (NIm and NIp; NIet)[13] and 7*H*-benzimidazo[2,1-*a*]benzo[*de*]isoquinolin-7-one (naphthoyl benzimidazole derivative, NBi)[15] were used as green-emitting luminophore components.

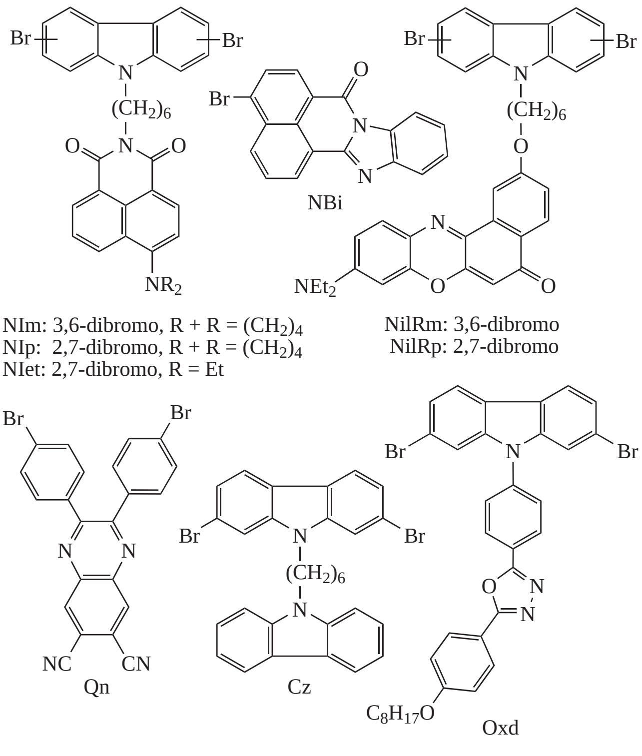


Figure 1 Building blocks of luminophores, charge-transporting components and terminal groups used for modification of PFs.

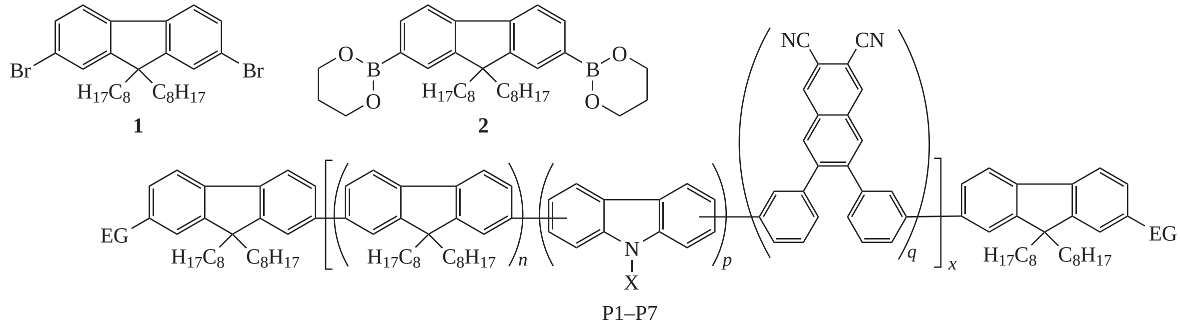


Figure 2 General structure of polymers P1–P7; $n/(p+q) > 98:2$. For substituents X, end-capping groups (EG), substitution pattern, monomer ratio in the chain, see Figure 1 and experimental details in Online Supplementary Materials.

In order to reach a proper balance between hole and electron mobilities, specially functionalized monomers with hole-transporting donor groups (carbazole, Cz) and electron-transporting acceptor groups (oxadiazole, Oxd and quinoxaline, Qn) were also used.

Polymers P1–P6 (Figure 2, Table 1) were synthesized by the Suzuki cross-coupling polymerization of dibromide **1** and bisboronate **2** [conditions: $Pd(PPh_3)_4$, K_2CO_3, toluene, Aliquat 336, 110 °C, 25 h], with the use of less than 2% dibromide additives (see Figure 1) to be incorporated into the polymer chain. For comparison, sample P7 was obtained by the standard Yamamoto homocoupling polymerization of only dibromide monomers **1** and NilRp [conditions: $Ni(COD)_2$, 2,2′-bipyridyl, DMF, 80 °C, 4 days]. Compositions and molecular weight characteristics of the synthesized PFs are given in Online Supplementary Materials.

The quantities of naphthalimide fragments, charge-transporting and end groups were varied at a constant concentration of red luminophore (Nile Red). In a number of cases, a fixed amount of NBi end units was introduced into the reaction at an early stage along with monomers. The chemical composition of PFs was varied to obtain white luminescence. In the PL spectra of samples P1–P5, containing either naphthalimide comonomer units (P2–P5) or NBi end groups (P1), the bands attributed to blue, green and red-emitting components are present [P5, Figure 3(*a*); for PL spectra of P1–P4, see Figure S2(*a*), Online Supplementary Materials].

In the PL spectra of samples P6 and P7 containing neither naphthalimide units nor NBi end groups, green-emission band is not observed and red-emission band is rather weak [Figure 3(*a*)]. These results make it possible to conclude that naphthalimide or NBi groups serve as molecular antennas transferring the excitation energy from blue emitters (fluorene fragments of the PF backbone) to red luminophores (Nile Red groups in side chains of PFs). A nearly white PL emission is observed for sample P5 [Figure 3(*a*), Table 1].

The EL spectra of polymers are shown in Figure 3(*b*); properties of OLEDs with configuration ITO/PEDOT: PSS (50 nm)/PF (50–60 nm)/Ca (50 nm)/Al (100 nm) are given in Table 1. The PL and EL spectra of polymers P1–P4 differ considerably [Figures S2(*a*) and S3(*a*)]. In contrast to PL, in all EL spectra the vibrational structure of fluorene is manifested more clearly (the 420–500 nm range). In the EL spectra of these samples, no red emission attributed to Nile Red luminophore groups was detected. These results agree with the EL data obtained earlier.[13]

Table 1 Photo- and electroluminescence characteristics of modified PFs.

Sample	CIE coordinates x; y		$U_n{}^a$/V	I^b/ mA cm^{-2}	$I_{lum}{}^b$/ cd m^{-2}	LE^c/ cd A^{-1}
	PL	EL				
P1	0.333; 0.426	0.230; 0.360	6.3	644	1700	0.27
P2	0.309; 0.413	0.237; 0.412	6.3	420	4136	1.09
P3	0.379; 0.443	0.230; 0.410	3.0	561	7450	2.00
P4	0.244; 0.320	0.220; 0.350	5.2	767	2940	0.60
P5	0.329; 0.370	0.280; 0.360	7.0	176	3278	1.86
P6	0.398; 0.336	0.209; 0.163	4.1	478	1320	0.27
P7^d	0.341; 0.293	0.252; 0.226	5.8	268	1350	0.60

$^a U_n$ is the U value corresponding to a luminance of 1 cd m^{-2}. $^b I$ and I_{lum} are current density and luminescence intensity at 10 V, respectively. ^{c}LE is luminescence current efficiency. ^{d}The polymer was synthesized according to the Yamamoto method.

The results (Table 1) demonstrate that EL properties of the synthesized PFs depend on the nature and molar ratio between luminophores, charge-transporting groups and end groups. It can be seen that the presence of naphthalimide fragments or NBi end groups in the polymer structure leads to a growth of their luminescence intensity (compare samples P1–P5 and P6, P7). A nearly white EL is observed only for sample P5 [Figure 3(*b*)] containing both electron-donor carbazole and electron-acceptor oxadiazole moieties in the side chains and NIet green-luminophore groups.

When the molar fraction of Nile Red is raised from 0.15% (P7) to 1.2% (P6), no sharp increase in the intensity of the Nile Red luminescence band is observed [Figure 3(*b*)], and colour coordinates of the emission of this sample correspond to blue light (see Table 1). This result evidences for a low efficiency of the direct excitation energy transfer from fluorene to Nile Red groups.

Note that the red emission band of Nile Red is considerably more intense in the EL spectrum of P7 than that in the spectrum of P6

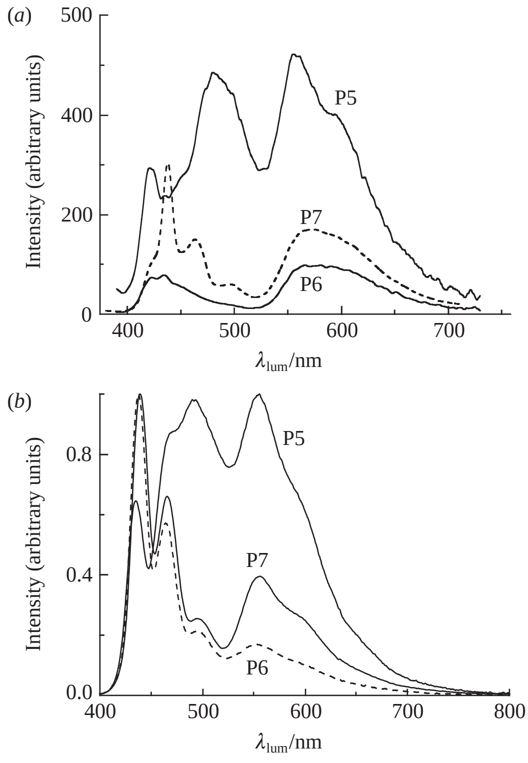


Figure 3 (*a*) PL and (*b*) EL spectra of PFs in films.

[Figure 3(*b*)]. The colour of EL emission of sample P7 is close to yellow. The observed distinctions are probably due to different distributions of luminophore groups along the PF chain in sample P6 synthesized by the Suzuki method and sample P7 obtained by the Yamamoto one. Thus, carbazole-containing monomer groups in PFs synthesized by the Suzuki method are always surrounded by fluorene groups since all dibromide comonomers react with the only organoboron monomer, whereas in PFs synthesized by the Yamamoto method a direct interaction between two dibromo carbazole monomers cannot be excluded.[16]

In conclusion, the properties of PFs copolymerized with carbazole derivatives of Nile Red (red luminophores), 4-pyrrolidino-1,8-naphthalimides and 4-diethylamino-1,8-naphthalimide (green luminophores) were studied. Introducing 1,8-naphthalimide fragments *via* the correspondingly functionalized dibromo carbazole monomer derivatives and NBi end groups into PFs leads to a considerable increase in the brightness of EL (up to 3300 cd m^{-2}) and current efficiency (up to 2 cd A^{-1}). In addition, these groups play the role of green luminophores, facilitating energy transfer from blue-emitting fluorene to red-emitting Nile Red groups, which is crucial for obtaining white photo- and electroluminescence. This energy transfer is virtually absent in polymers that do not contain green luminophore groups (sample P6). 4-Diethylamino-1,8-naphthalimide component is the best one to obtain close to white EL (CIE coordinates $x = 0.28$; $y = 0.36$, sample P5). An enhanced red emission of Nile Red groups in P7 compared to that in P6 is obviously due to the structural distinctions in these polymers caused by different synthetic procedures (Suzuki *vs*. Yamamoto coupling polymerization).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2017.05.016.

References

1 *Polyfluorenes*, eds. U. Scherf and D. Neher, Springer, Berlin, 2008.
2 S. Güne, Y. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324.
3 I. V. Kurdyukova and A. A. Ishchenko, *Russ. Chem. Rev.*, 2012, **81**, 258.
4 B. Bao, L. Yuwen, X. Zheng, L. Weng, X. Zhu, X. Zhan and L. Wang, *J. Mater. Chem.*, 2010, **20**, 9628.
5 S. Dong, D. Ou, J. Qin and Z. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 3314.
6 I. E. Kuznetsov, D. K. Susarova, L. N. Inasaridze, M.V. Klyuev and P. A. Troshin, *Mendeleev Commun.*, 2015, **25**, 277.
7 A. V. Dmitriev, A. R. Yusupov, R. A. Irgashev, N. A. Kazin, E. I. Mal'tsev, D. A. Lypenko, G. L. Rusinov, A. V. Vannikov and V. N. Charushin, *Mendeleev Commun.*, 2016, **26**, 516.
8 A. V. Akkuratov, D. K. Susarova, O. A. Mukhacheva and P. A. Troshin, *Mendeleev Commun.*, 2016, **26**, 248.
9 J. Jose and K. Burgess, *J. Org. Chem.*, 2006, **71**, 7835.
10 G. L. Tu, C. Y. Mei, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing and F. S. Wang, *Adv. Funct. Mater.*, 2006, **16**, 101.
11 J. Liu, S. Y. Shao, L. Chen, Z. Y. Xie, Y. X. Cheng, Y. H. Geng, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Mater.*, 2007, **19**, 1859.
12 P. Sreearunothai, A. Estrada, S. Asaoka, M. Kowalczyk, S. Jang, A. R. Cook, J. M. Preses and J. R. Miller, *J. Phys. Chem. C*, 2011, **115**, 19569.
13 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 (*Vysokomol. Soedin.*, *Ser. B*, 2014, **56**, 64).
14 A. N. Arkhipova, P. A. Panchenko, Yu. V. Fedorov and O. A. Fedorova, *Mendeleev Commun.*, 2017, **27**, 53.
15 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.
16 N. P. Yevlampieva, A. P. Khurchak, G. I. Nosova, R. Yu. Smyslov, I. A. Berezin, D. M. Ilgach, T. N. Kopylova, R. M. Gadirov and A. V. Yakimansky, *Chem. Phys. Lett.*, 2016, **645**, 100.

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