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ScienceDirect
Mendeleev Commun., 2020, **30**, 165–167

Mendeleev Communications

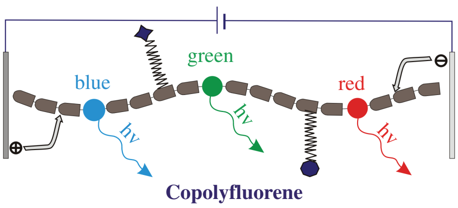
Role of benzothiadiazole substituents in white electroluminescent single macromolecules of fluorene-based copolymers

Dmitry A. Lypenko,*[a,b] Galina I. Nosova,[c] Ivan A. Berezin,[c] Alexey R. Tameev[a] and Eugene I. Mal'tsev[a]

[a] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation. E-mail: dalypenko@gmail.com*
[b] *National Research Nuclear University MEPhI, 115409 Moscow, Russian Federation*
[c] *Institute of Macromolecular Compounds, Russian Academy of Sciences, 199004 St. Petersburg, Russian Federation*

DOI: 10.1016/j.mencom.2020.03.011

Estimation of the influence of molecular substituents on electroluminescence and electron–hole mobility in copolyfluorenes with the use of a CELIV technique has revealed that minor changes in the number of benzothiadiazole fragments in copolyfluorenes has a dramatic effect on the optoelectronic properties of these polymers to improve the electroluminescence and electron mobility by factors of 20 and 10, respectively.



Keywords: random copolymers, fluorescence, PLEDs, CELIV, electron–hole mobility.

Polymer white light-emitting diodes (PWLEDs) attract much attention because of their potential applications in flat-panel color displays and backlighting and solid-state ambient lighting sources. In contrast to organic light-emitting diodes (OLEDs) based on small molecules, PWLEDs combine the advantages of simple device structures and cost-effective solution-processing technologies. Currently, several strategies for producing polymers with a white spectrum of electroluminescence (EL) have been developed.[1–10] Among them are white single macromolecules based on fluorine copolymers (FCPs) containing chromophore groups in the backbone and/or covalently attached to it.[7–12] These materials are promising candidates for PWLEDs due to their high fluorescence quantum yield, good film-forming and charge-transporting properties, and lack of intrinsic phase separation. Moreover, they are of interest because of their ability to produce color-tunable EL. Incorporated luminophore substituents can also act as electron–hole transport centers in the mechanism of EL.

The synthesis of FCPs was described previously.[9] The emission layers were fabricated by casting the solutions of FCPs in toluene. The resulting layers were dried at 80 °C in argon for 4 h under careful temperature and optical absorption control. Under these conditions, we observed the appearance of an absorption band and a shoulder at about 430 nm for FCP-I and FCP-II, respectively. They presumably belong to a β-phase and correspond to the $0 \to 0$ vibronic transition.[13]

Standard techniques were applied to manufacture PWLEDs. A series of ten FCP samples had the structure ITO/PEDOT:PSS(35 nm)/FCP(80 nm)/PF-EP(20 nm)/LiF(1 nm)/Al(80 nm). The ethanol-soluble PF-EP[14] served as an electron-transporting layer spin-coated onto the FCP.

Electron and hole mobilities in the layers of FCPs were measured using the charge extraction by linearly increasing voltage (CELIV) method.[15,16] The measurements were performed on ITO/SiO_2(70 nm)/FCP(100 nm)/Al structure devices described elsewhere.[17–19] Since the concentration of intrinsic charge carriers in the FCPs was very low, the photo-CELIV technique was chosen.[16] A pumping light pulse (wavelength, 460 nm) was used to photogenerate charge carriers prior to start their extraction by voltage. For all the studied devices, the displacement current $j(0)$ was observed to exceed the maximum drift current Δj, *i.e.* $\Delta j << j(0)$ (Figure S1, see Online Supplementary Materials). The charge carrier mobility was estimated from the formula:

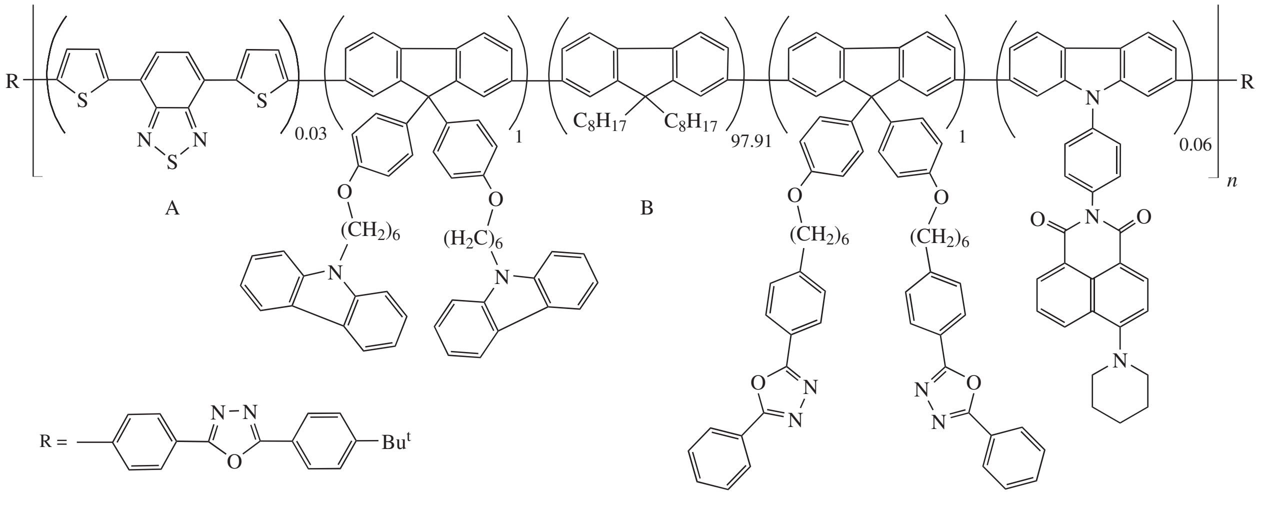
$$\mu = 2d^2/3A\,t^2_{\max},$$

where d is the thickness of a FCP layer, A is the applied voltage ramp rate, and $t_{\max}$ is the time when the drift current exhibits its maximum Δj.

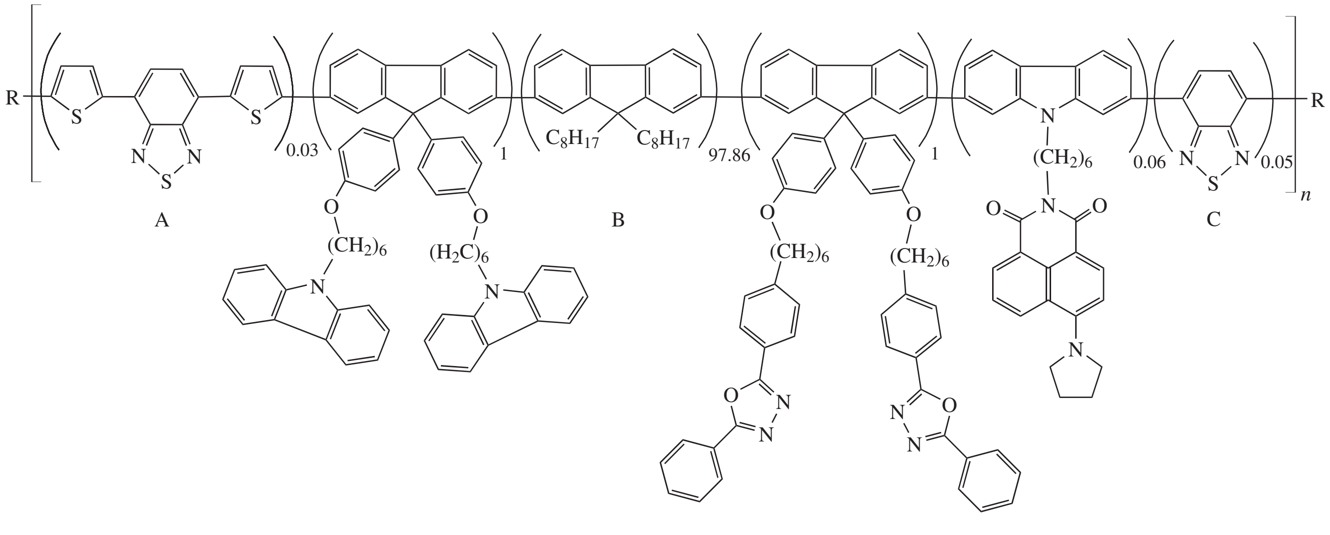
FCP-I (Figure 1) was the first synthesized random copolymer with suitable substituents that provided ideally white FL and EL spectra (the CIE chromaticity coordinates $x = 0.326$ and $y = 0.345$) (Table 1).

However, the EL characteristics of the PWLED structures based on FCP-I were low: a brightness of 2650 cd m^{-2} and a luminous efficiency of 1.98 cd A^{-1}. Since highly efficient luminophores have been incorporated into the copolymer, it was reasonable to associate the obtained values with the imbalance in charge carrier injection and electron–hole mobility in the light-emitting layers. The electron mobility measured for FCP-I was almost five times lower than the hole mobility (see Table 1).

To improve the operation of PWLEDs, we introduced one more molecular fragment of benzothiadiazole (BT) in a concentration of 0.05 mol% into the FCP-I chain. This compound is an example of the most efficient electron-transporting building blocks for organic optoelectronics.[5,20–23] The extra BT is depicted as fragment C (see Figure 1, FCP-II). While the numbers of functional fragments in both copolymers remained nearly constant, the brightness dramatically increased and reached 40900 cd m^{-2} at 6.04 cd A^{-1} in the case of FCP-II. PLED characteristics for FCP-I and FCP-



FCP-I



FCP-II

Figure 1 Chemical structures of FCP-I and FCP-II.

II are shown in Figure 2(*b*). Despite the fact that the BT content of FCP-II increased insignificantly, its contribution to radiation sharply increased [Figure 2(*a*)], and the CIE coordinates changed only slightly (see Table 1).

The observed twentyfold increase of the FCP-II emission should be related to the enhancement of electron–hole injection into the light-emitting layer and electron–hole mobility balance in the system. It is reasonable to assume that the morphology of FCP-II plays a key role here since the β-phase is an energetically favorable environment for charge carriers and excitons. After heating (Figure 3), a characteristic peak at about 430 nm presumably belonging to the FCP-I β-phase was observed, while a shoulder was detected in the FCP-II layer. On the face of it, one may infer that the β-phase content of FCP-I was higher. Meanwhile, note that the absorption peak of the β-phase at 430 nm is not so characteristic: a similar absorption maximum in the same wavelength range was identified for a crystalline polyfluorene phase (α). The latter greatly degrades the optoelectronic properties.[24] It is likely that the β-phase concentration in the FCP-II is much higher than that in FCP-I. Therefore, such a great increase of emission was observed in the case of FCP-II PWLED. However, this conclusion requires further confirmation.

Table 1 Charge carrier characteristics and CIE chromaticity coordinates determined for FCP-I and FCP-II by the CELIV method.

Polymer	Electron mobility/ $cm^2\ V^{-1}\ s^{-1}$	Hole mobility/ $cm^2\ V^{-1}\ s^{-1}$	CIE chromaticity coordinates (*x*, *y*)
FCP-I	1.8×10^{-5}	7.9×10^{-5}	0.326, 0.345
FCP-II	1.8×10^{-4}	2.3×10^{-4}	0.343, 0.460

On the other hand, it is obvious that a balance of electron–hole mobility can also contribute to the revealed effect. The electron mobility of FCP-II (see Table 1) increased by a factor of ten in the presence of the second BT and nearly reached the hole mobility. In addition to morphology, this increase could also be enhanced by a significant difference between electron-transporting properties

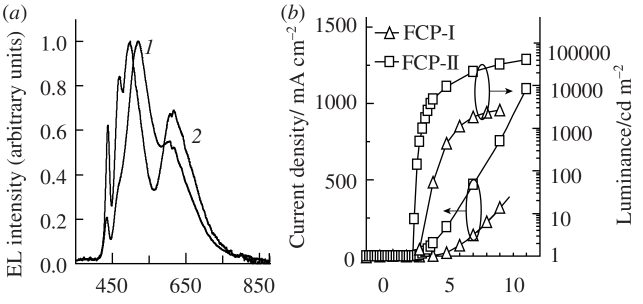


Figure 2 (*a*) EL spectra of (*1*) FCP-I and (*2*) FCP-II and (*b*) their current–voltage and luminance–voltage characteristics.

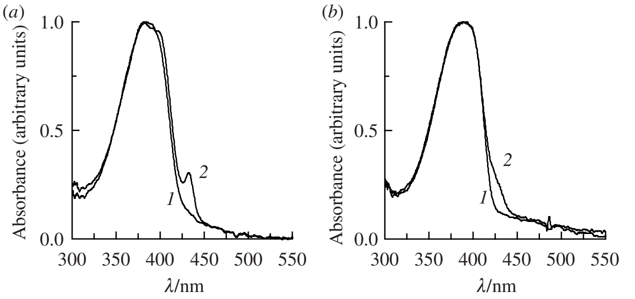


Figure 3 Absorption spectra of (*a*) FCP-I and (*b*) FCP-II layers (*1*) without heating and (*2*) after heating at 80 °C for 4 h.

of two BT fragments A and C in the FCP-II (see Figure 1). In the FCP-II backbone, one of the two BTs is chemically bonded to two thiophene moieties (fragment A). The same molecular group is present in FCP-I. Thiophene molecules are highly effective electron donors.[25] Consequently, the two neighboring thiophene moieties increase the electron richness of the BT due to the delocalization of contributing molecular orbitals. This causes a decrease in the efficiency of BT as an electron transporting center and leads to the lower brightness in the case of FCP-I. In contrast, the second BT (fragment C) in FCP-II is localized between other adjacent molecular fragments of much weaker electron-donating nature.[5,26]

Thus, we have examined two specially synthesized copolyfluorene structures containing a low concentration of electron-transporting benzothiadiazoles in the main chains. An extremely small change in the chemical composition of these polymers brought increased the brightness of PLEDs by a factor of about 20. A certain choice of molecular fragments allowed us to optimize the electron–hole mobility balance and to reach a tenfold increase in electron mobility.

The work was supported by the Russian Science Foundation: OLED manufacture and study were carried out within the project no. 18-19-00588, and charge carrier mobility was studied within the project no. 18-13-00409. Analysis of the macromolecule morphology was carried out at the expense of the grant no. 17-03-01179 A from the Russian Foundation for Basic Research.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.03.011.

References

1 X. Gong, S. Wang, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2005, **17**, 2053.
2 Y. Sun, N.C. Giebink, H. Kanno, B. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, **440**, 908.
3 S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem and K. Leo, *Nature*, 2009, **459**, 234.
4 K. T. Kamtekar, A. P. Monkman and M. R. Bryce, *Adv. Mater.*, 2010, **22**, 572.
5 P. Herguth, X. Jiang, M. S. Liu and A. K.-Y. Jen, *Macromolecules*, 2002, **35**, 6094.
6 J. Wang, Y. Zhao, K. Wei, G. Wen, X. Li, Z. Lin and Q. Ling, *Synth. Met.*, 2017, **230**, 18.
7 V. A. Kostyanovsky, D. K. Susarova, G. Adam, R. N. Lyubovskaya and P. A. Troshin, *Mendeleev Commun.*, 2013, **23**, 26.
8 B. Zhang, C. Qin, J. Ding, L. Chen, Z. Xie, Y. Chen and L. Wang, *Adv. Funct. Mater.*, 2010, **20**, 295.
9 D. M. Ilgach, G. I. Nosoba, T. N. Kopylova, E. N. Nikonova, R. M. Gadirov, R. Yu. Smyslov, L. S. Litvinova and A. V. Yakimansky, *Mendeleev Commun.*, 2017, **27**, 357.
10 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).
11 A. V. Akkuratov, D. K. Susarova, O. A. Mukhacheva and P. A. Troshin, *Mendeleev Commun.*, 2016, **26**, 248.
12 G. I. Nosova, D. M. Ilgach, I. A. Berezin, E. V. Zhukova, T. N. Kopylova, E. N. Nikonova, R. M. Gadirov, R. Yu. Smyslov and A. V. Yakimansky, *Mendeleev Commun.*, 2017, **27**, 265.
13 F. Montilla, A. Ruseckas and I. D. W. Samuel, *Chem. Phys. Lett.*, 2013, **585**, 133.
14 C. V. Hoven, A. Garcia, G. C. Bazan and T. Q. Nguyen, *Adv. Mater.*, 2008, **20**, 3793.
15 G. Jušūka, K. Arlauskas, M. Viliunas and J. Kočka, *Phys. Rev. Lett.*, 2000, **84**, 4946.
16 A. Pivrikas, N. S. Sariciftci, G. Juška and R. Österbacka, *Prog. Photovolt. Res. Appl.*, 2007, **15**, 677.
17 S. V. Kostromin, V. V. Malov, A. R. Tameev, S. V. Bronnikov and A. Farcas, *Tech. Phys. Lett.*, 2017, **43**, 173.
18 V. V. Malov, T. Ghosh, V. C. Nair, M. M. Maslov, K. P. Katin, K. N. N. Unni and A. R. Tameev, *Mendeleev Commun.*, 2019, **29**, 218.
19 M. I. Kozlov, A. N. Aslandukov, A. A. Vashchenko, A.V. Medvedko, A. E. Aleksandrov, R. Grzibovskis, A. S. Goloveshkin, L. S. Lepnev, A. R. Tameev, A. Vembris and V. V. Utochnikova, *Dalton Trans.*, 2019, **48**, 17298.
20 J. Lee, M. Jang, S. M. Lee, D. Yoo, T. J. Shin, J. H. Oh and C. Yang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 20390.
21 B. A. D. Neto, A. A. M. Lapis, E. N. da Silva, Jr. and J. Dupont, *Eur. J. Org. Chem.*, 2013, 228.
22 A. Pathak, K. R. J. Thomas, M. Singh and J.-H. Jou, *J. Org. Chem.*, 2017, **82**, 11512.
23 E. Angioni, M. Chapran, K. Ivaniuk, N. Kostiv, V. Cherpak, P. Stakhira, A. Lazauskas, S. Tamulevičius, D. Volyniuk, N. J. Findlay, T. Tuttle, J. V. Grazulevicius and P. J. Skabara, *J. Mater. Chem. C*, 2016, **4**, 3851.
24 S. H. Chen, A. C. Su and S. A. Chen, *J. Phys. Chem. B*, 2005, **109**, 10067.
25 P. Zhou, Z.-G. Zhang, Y. Li, X. Chen and J. Qin, *Chem. Mater.*, 2014, **26**, 3495.
26 A. Venkateswararao, K. R. J. Thomas, C.-P. Lee, C.-T. Li and K.-C. Ho, *ACS Appl. Mater. Interfaces*, 2014, **6**, 2528.

Received: 10th October 2019; Com. 19/6040