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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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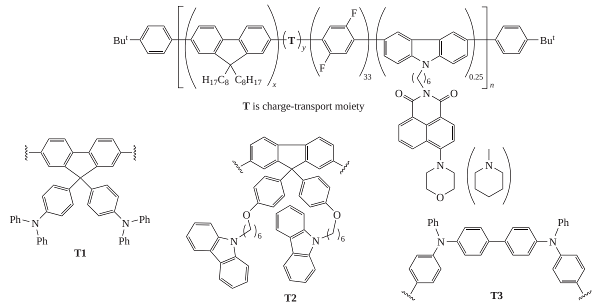
Polyfluorene copolymers containing 33 mol% of 2,5-difluoro-1,4-phenylene units and other comonomers comprising charge-transporting triphenylamine, carbazole, and 1,8-naphthalimide groups were synthesized by the Suzuki polycondensation under microwave irradiation. On heating the obtained copolymers to 180 °C, their photoluminescence spectra remain stable. The best sample herein obtained provided the OLED brightness of 2830 cd m^{-2}, current efficiency of 0.5 cd A^{-1} and CIE coordinates of x = 0.168 and y = 0.228.



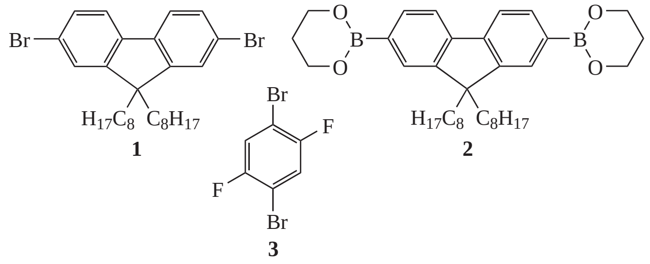
T is charge-transport moiety

Conjugated polymers are promising light-emitting materials for optoelectronic devices such as OLEDs.[1,2] They are superior to inorganic luminophores in the production cost, processibility, and structural tuning ability. In this respect, polyfluorenes are at the focus of current investigations due to their outstanding thermal and chemical stability, high luminescence quantum yields, good film-forming properties, and possibilities of rather simple modifications of the polymer structure at the 9-position of fluorene moiety.[3] However, the use of blue-emitting poly(9,9-dioctylfluorene) in OLEDs is restricted by its relatively low emission efficiency and low spectral stability caused by a partial oxidation of fluorene groups to fluorenone ones, occurring upon heating of the polymer and shifting its emission band to green spectral range.[4] Spectral stability of polyfluorenes can be improved by the use of fluorenes with bulky, *e.g.*, 4-alkoxyphenyl, substituents at the 9-position,[4,5] or spirofluorenes,[6] or 9-silafluorene[7,8] as monomer units. It was also reported that the introduction of 15 mol% of anthracene[9] or 33 mol% of 1,4-dibromo-2,5-difluorobenzene[10] comonomers provided a stable blue luminescence.

To improve brightness characteristics of OLEDs based on polyfluorene copolymers (PFC), it is necessary to balance the mobility of holes and electrons in the emissive layer for the recombination zone to lie in the bulk of the film. To increase the hole mobility, electron-donor groups such as triphenylamine[11–13] or carbazole[14–17] ones are introduced into the main or side chains. To improve the injection and mobility of electrons in the emissive layer, such electron-acceptor groups as oxadiazoles,[12,18] CN-containing,[19–21] or fluorinated[10,22] fragments are incorporated into PFCs. Luminophores based on 1,8-naphthalimides are also used to increase the brightness of OLEDs with PFCs in the emissive layer.[23]

In the present work, in order to increase the spectral stability, 33 mol% of 2,5-difluoro-1,4-phenylene units were introduced into the copolyfluorene chain (*cf.* ref. 10). New carbazole derivatives of 1,8-naphthalimide were synthesized and introduced as charge-transporting units into the polyfluorene copolymer chains in order to increase brightness characteristics of PFC-based OLEDs.

PFCs were obtained by the Suzuki cross-coupling polycondensation under microwave irradiation,[24] with the principal reactants being components **1**, **2** and **3**. The structure of minor modificators (the corresponding dibromo derivatives) is outlined in Figure 1. The reaction was conducted in 35 ml sealed tubes in THF under pressure at 120–130 °C (Discover SP microwave reactor in SPS regime, *i.e.* cycles of heating up to 130 °C at 140 W and cooling down to 120 °C). To simplify the polymer purification procedure, Pd(PPh$_3$)$_4$ catalyst immobilized on a cross-linked polystyrene was used. As was shown by our investigations, this method makes it possible to obtain PFCs as quickly as within 1.5 h, while the synthesis upon ordinary heating takes 72 h.



1 **2** **3**

A number of PFC structures were obtained (Figure 1). Photoluminescence (PL) spectra of copolymer with x = 67 mol%, y = 0, z = 0 were stable upon heating at 180 °C in air for 30 min [see Figure S1(*b*), Online Supplementary Materials], *i.e.*, a stable blue luminescence was observed, in contrast to the case of

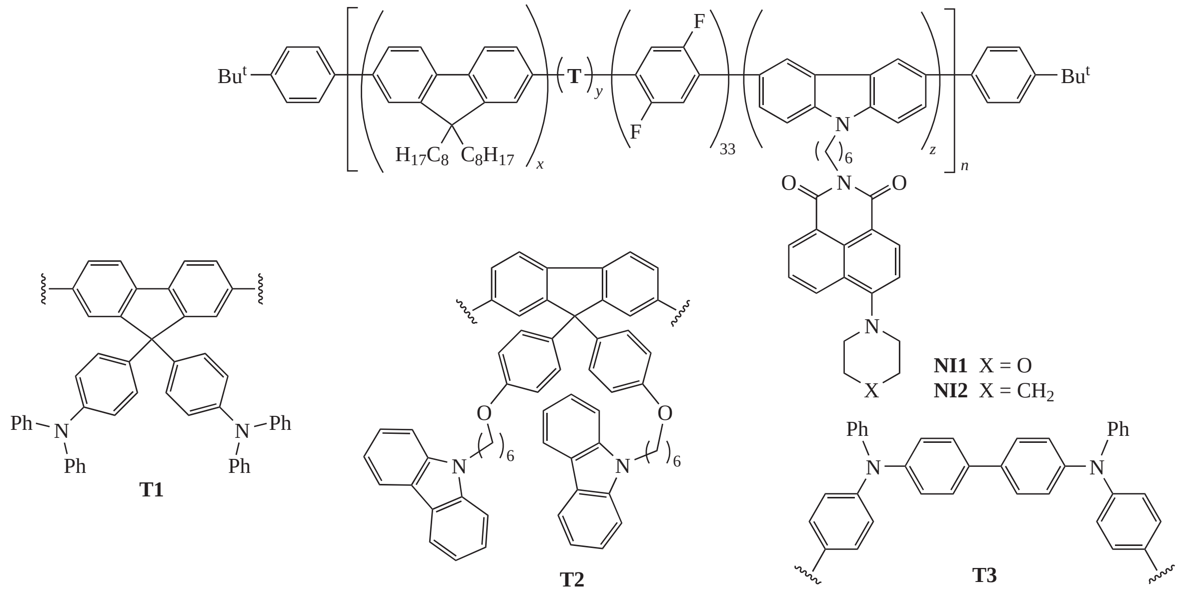


Figure 1 Chemical structures of PFCs.

poly(9,9-dioctylfluorene) [see Figure S1(*a*), Online Supplementary Materials].

Various charge-transporting comonomers were introduced into PFC chains to balance the mobility of holes and electrons injected into PFC-based emissive layers of OLEDs. Triphenylamine- and carbazole-containing structures (Table 1) were used as hole-transporting groups, decreasing the polymer HOMO level and approaching it to the level of PEDOT/PSS. For this, 9,9-bis(4-diphenylaminophenyl)-2,7-dibromofluorene (precursor **T1**), 2,7-dibromo-9,9-bis-{4-[6-(9*H*-carbazol-9-yl)hexyloxy]phenyl}fluorene (precursor **T2**), and 4,4′-bis[*N*-(4-bromophenyl)-*N*-phenylamino]-biphenyl (precursor **T3**) were used as comonomers.

Previously,[25] we reported that carbazole derivatives of 1,8-naphthalimide **NI1** and **NI2** (see Figure 1) could be used as efficient blue-green luminophores for the creation of white light-emitting OLEDs. Owing to their electron-acceptor properties, they also facilitate injection of electron into the emissive layer of PFCs, thus enhancing the brightness of electroluminescence (EL).

The study of PL and EL of the synthesized PFCs has shown that the introduction of 1,8-naphthalimide-containing fragments into the polymer chain shifts the polymer emission spectrum to blue-green spectral range (samples P1 and P2, Table 2, see also Figures S2–S4, Online Supplementary Materials). Note that a more pronounced excitation energy transfer from fluorene to 1,8-naphthalimide units is observed in PL spectra as compared to that in EL spectra. To avoid such a green shift from a purely blue luminescence, a very low amount of 1,8-naphthalimide-containing units (0.25 mol%) was introduced. This slight modification of the PFC structure led to an increase in the quantum yield and brightness of EL (samples P1 and P2, P8 and P6). Comparing two different 1,8-naphthalimide structures (**NI1** and **NI2**), one can see that **NI2** causes stronger negative effects of the excitation energy transfer from fluorene to 1,8-naphthalimide units and the shift of luminescence spectrum to the blue-green spectral range (color coordinates 0.175; 0.289, Table 2). However, the PL quantum yield and EL brightness are higher for **NI2**-containing PFCs than those for **NI1**-containing ones (samples P3 and P4).

Table 1 Chemical composition of the synthesized PFCs (see Figure 1).

Sample	Naphthal-imide	z	Charge-transport moiety	y	M_w	M_w/M_n
P1		0.00		0.00	81000	2.7
P2	**NI1**	0.25		0.00	70000	2.3
P3	**NI1**	0.25	**T1**	10.00	17000	2.3
P4	**NI2**	0.25	**T1**	10.00	13000	2.9
P5	**NI1**	0.25	**T2**	10.00	15000	2.4
P6	**NI1**	0.25	**T1**	16.75	23000	3.1
P7	**NI1**	0.25	**T3**	10.00	30000	3.7
P8		0.00	**T1**	17.00	46000	2.4

Table 2 Photo- and electroluminescent properties of the synthesized PFCs.

Sample	φ^a	L^b/cd m^{-2} (U/V)	Efficiency/ cd A^{-1} (U/V)	EL^c (x; y)	PL^c (x; y)
P1	0.52	194 (6)	0.024 (6)	0.164; 0.060	0.1647; 0.0823
P2	0.64	359 (7)	0.015 (7)	0.164; 0.106	0.1684; 0.2621
P3	0.60	570 (8) 1125 (10)	0.190 (10)	0.169; 0.218	0.1707; 0.2599
P4	0.83	1767 (8)	0.350 (7)	0.175; 0.289	0.1859; 0.3623
P5	0.77	281 (8)	0.100 (6)	0.172; 0.274	0.1732; 0.2967
P6	0.57	2830 (8)	0.500 (8)	0.168; 0.228	0.1692; 0.2422
P7	0.39	264 (8)	0.056 (7)	0.178; 0.175	0.1830; 0.2008
P8	0.31	1271 (9.4)	0.280 (5)	0.163; 0.097	0.1647; 0.0823

[a] PL quantum yield in film, λ = 378 nm. [b] L is a brightness of EL. [c] Color coordinates according to CIE 1931 model.

The introduction of charge-transporting groups essentially affects the luminescence of PFCs. Additives of **T1** (see Figure 1) caused a slight decrease in the PL quantum yield due to lower quantum yields of luminescence of **T1** monomer units as compared to 9,9-dioctylfluorene ones (*cf.* samples P2 *vs.* P3, P6, Table 2). Meanwhile, the brightness of EL for sample P8 is higher than that for P1 and for P3 and P6 is higher than that for P2. Obviously, this is due to more balanced flows of holes and electrons in the emissive layer of P8 *vs.* P1 and of P3, P6 *vs.* P2. Note that hole-trapping triphenylamine fragments shift the recombination zone from the surface of the emissive layer into its bulk. It is also seen that the introduction of a higher amount of **T1** in P2 (16.75 mol%) than in P3 (10 mol%) results in a twofold increase in the EL brightness (see Table 2).

The triphenylamine-containing monomer **T3** caused no increase in either brightness or efficiency of EL (*cf.* sample P2 *vs.* P7, Table 2). Comparison of the effects of triphenylamine-containing (**T1**) and carbazole-containing (**T2**) comonomers (see Table 2) demonstrates that PFC containing **T1** units (sample

P3) reveals considerably higher EL brightness and efficiency than PFC containing **T2** groups (sample P5).

In conclusion, a series of PFCs possessing a stable blue luminescence due to 2,5-difluoro-1,4-phenylene units introduced into their chains has been synthesized. The effect of introduction of 1,8-naphthalimide, triphenylamine-, and carbazole-containing comonomers on the luminescent properties of PFCs has been examined. It has been shown that even low amount of 1,8-naphthalimide derivatives **NI1** and **NI2** (0.25 mol%) gives rise to an essential increase in the electroluminescence intensity. The use of only **NI1** allows luminescence to remain blue, while the use of **NI2** shifts the luminescence spectrum to blue-green spectral range. The best balance of electron and hole mobilities and, hence, the best EL characteristics are provided by the introduction of triphenylamine groups *via* comonomer **T1**. Polyfluorene copolymer containing 16.75 mol% of **T1** and 0.25 mol% of **NI1** (see Figure 1) incorporated into the emissive layer of OLED structure emits an intense (brightness 2830 cd m^{-2}, current efficiency 0.5 cd A^{-1}) nearly blue light (CIE coordinates $x = 0.168$, $y = 0.228$).

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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.2017.07.012.

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