doi:10.1246/cl.2010.522

Synthesis and Characterization of 1,8-Carbazole-based π-Conjugated Copolymer with Zigzagged Conformation for Stable Deep-blue Emission

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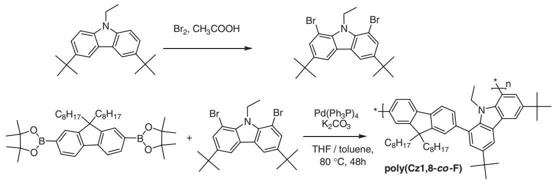
1,8-Dibromocarbazole was employed to construct zigzagged conformation via the Suzuki-type cross-coupling polycondensation. Model copolymer, poly(Cz1,8-*co*-F), showed deep-blue 420 nm emission in thin film. Air-annealing experiments for 18 h at 200 °C with a low green index ($I_{\mathrm{Green}}/I_{\mathrm{Blue}}$) of 0.38 indicated the introduction of nonlinear zigzag-shaped 1,8-dibromocarbazole building blocks into polyfluorene (PF) clearly improved spectral stabilities.

It is of particular importance to explore high performance, color stable, and deep-blue polymeric light-emitting diodes (PLEDs) for the commercialization of full-color flat panel displays and solid-state white-lighting sources.[1–3] Major disadvantages of PLEDs using conjugated poly(9,9-dioctylfluorene) (PFO) and its derivatives with high quantum efficiency of photoluminescence are high turn-on voltage as well as poor spectral stabilities with an undesired low-energy green emission band (LEEB) centered at 520–530 nm during high-voltage operation.[4,5] To resolve these issues, efforts were made to introduce electron-donating or electron-withdrawing groups into polyfluorenes to not only reduce the barrier of HOMO and LUMO energy level with respect to work function of ITO and cathode but also balance carrier (electron and hole) injection and transport.[6,7] After this, the introduction of bulky spirocyclic aromatic hydrocarbons,[8,9] congested diarylfluorene and shielding dendron groups into the 9-position of fluorene were developed to enhance the spectral stability of polyfluorenes resulting from steric hindrance suppressing interchain aggregations. More recently, various conformations and topologies, including ladder, hairy-rod, helical, multiarmed, hyperbranched, and 3D dendrimers,[10,11] offer an alternative strategy to resolve the above issues, also facilitating further construction of multifunctional organic semiconductors.

One typical example is carbazole-based blue light-emitting copolyfluorenes.[12,13] 3,6-Carbazole or 2,7-carbazole were initially exploited to improve the hole-injecting ability,[14–18] followed by carbazole as dendron to suppress the aggregations.[19] Recently, there have been reports on hyperbranched conjugated polycarbazoles.[20–22] However, to our best knowledge, little attention has been paid to 1,8-carbazole building blocks in conjugated polymers with fascinating zigzagged conformation.[23] In this communication, a novel soluble poly(1,8-carbazole-*alt*-2,7-fluorene) [poly(Cz1,8-*co*-F)] with deep-blue emission was synthesized by the Suzuki-type polycondensation. Its high thermal and spectral stabilities were unambiguously confirmed by air-annealing experiments in extreme conditions.



Scheme 1. Synthetic routes of poly(Cz1,8-*co*-F).

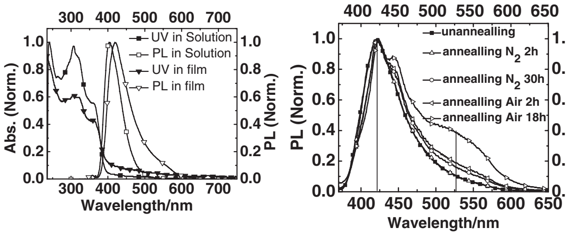


Figure 1. The absorption and PL spectra of poly(Cz1,8-*co*-F) in chloroform solution (1×10^{-6} M) and in thin film as well as annealed in nitrogen (2 and 30 h) and air (2 and 18 h).

The synthetic route of poly(Cz1,8-*co*-F) is outlined in Scheme 1. The starting 3,6-disubstituted carbazole was treated with 2 equivalents of bromine, affording the 1,8-dibromocarbazole in a 90% yield. The resulting copolymer was soluble in common organic solvents such as tetrahydrofuran, toluene, and chloroform. Its chemical structures and optoelectronic properties were systematically characterized by gel permeation chromatography (GPC), NMR, UV–vis absorption and photoluminescence (PL) spectra, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and cyclic voltametry (CV).

The number-average molecular weight (M_{n}) of poly(Cz1,8-*co*-F) is 3400 with a polydispersity index (PDI, $M_{\mathrm{w}}/M_{\mathrm{n}}$) of 1.1. It is deduced that there was an average of 5-repeat units with a molecular weight of 694 per poly(Cz1,8-*co*-F). The decomposition temperature (T_{d}) of poly(Cz1,8-*co*-F) with a 5% weight loss is approximately 391 °C. No crystallizing and melting points were observed with a glass transition temperature (T_{g}) of up to 164 °C. These results indicated that poly(Cz1,8-*co*-F) is amorphous with high morphological stability.

The UV–vis absorption and PL spectra of the poly(Cz1,8-*co*-F) were measured both in dilute chloroform solution and in thin film, as shown in Figure 1. In dilute chloroform solution, the maximum absorption peak of poly(Cz1,8-*co*-F) is 306 nm with a shoulder peak of 362 nm, indicating the short conjugation length of zigzagged poly(Cz1,8-*co*-F).[17] And its maximum emission peak of 404 nm with the FWHM of 61 nm, similar to the counterpart poly(3,6-carbazole-*alt*-2,7-fluorene) with an emission of 404 nm,[19] clearly blue-shifted with respect to poly(2,7-carbazole-*alt*-2,7-fluorene) centered at 417 nm.[15] The thin film on quartz slides as substrate was prepared by spin coating a 10 mg mL^{-1} poly(Cz1,8-*co*-F) solution in chloroform.

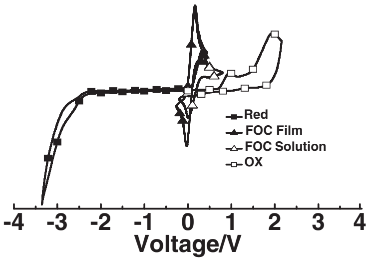


Figure 2. CV curves of poly(Cz1,8-*co*-F) and ferrocene reference (Fc/Fc$^+$).

Its maximum PL emission peak is red-shifted to 420 nm compared with dilute solution. This is very similar to 3,6- and 2,7-carbazole co-polyfluorenes with the peaks of 424 and 426 nm, respectively.[15,17] However, a shoulder at about 450 nm in two counterparts is not observed in poly(Cz1,8-*co*-F). Its fluorescence quantum yield in cyclohexanone solution with respect to 9,10-diphenylanthracene as a standard is 0.58. The annealing experiments in nitrogen atmosphere at 200 °C for 30 h exhibited the green index (I_{Green}/I_{Blue}, defined as a ratio of the green emission at ca. 530 nm to the strongest peak of the blue emission) changing from 0.08 to 0.1. The small alteration of LEEBs in PL spectra with respect to PFO indicates that PFO suffers from aggregates under the same N_2 conditions because of their similar propensity toward oxidation. In a follow-up experiment, annealed for 2 h in air atmosphere at 200 °C, the green index is 0.18, which was much lower than that of PFO (up to 3.7) under the same conditions.[5] After annealing for 18 h in air at 200 °C, the green index was only 0.38, clearly lower than PFO and other polyfluorene derivatives. The annealing experiments revealed that the introduction of nonlinear zigzag-shaped 1,8-dibromocarbazole building blocks into polyfluorene weakened interchain aggregation and the origin of LEEB in air is probably attributed to keto defect.

In order to investigate the electrochemical behavior of poly(Cz1,8-*co*-F), cyclic voltammetry (CV) measurements were performed in a three-electrode cell with n-Bu$_4$NPF$_6$ as a supporting electrolyte. The oxidation and reduction processes were obtained from CH_2Cl_2 solution and film in CH_3CN, respectively. CV curves are shown in Figure 2. The highest-occupied molecular orbital (HOMO) energy level was estimated to be about −5.44 eV from the first-oxidation onset potential of 0.72 V with regard to an external ferrocene reference (Fc/Fc$^+$, 0.08 eV in CH_2Cl_2). This indicates improved hole-injecting ability resulting from electron-rich carbazole, although 1,8-linkage is not strongly favorable for electron delocalization. The lowest-unoccupied molecular orbital (LUMO) energy level was −2.38 eV from the onset potential reduction of −2.4 V (Fc/Fc$^+$, 0.02 eV in film). The band gap of poly(Cz1,8-*co*-F) is 3.06 eV, well matching its optical band gap (3.00 eV).

In conclusion, we introduced 1,8-carbazole into π-conjugated polymers to synthesize poly(Cz1,8-*co*-F) with nonplanar zigzagged conformations. PL spectra in spin-coating film exhibit a deep-blue emission at 420 nm. The annealing experiments in nitrogen and air atmosphere exhibited low green index of 0.13 and 0.38, respectively. Poly(Cz1,8-*co*-F) is a promising host and deep-blue light-emitting material with stable morphological and optoelectrical properties.[24]

For the financial support for this work, we thank the "973" project (No. 2009CB930600), NNSFC (Grants Nos. 20704023, 60876010, 60706017, and 20774043), the Key Project of Chinese Ministry of Education (Nos. 104246, 208050, and 707032), and the NSF of the Education Committee of Jiangsu Province (Grants Nos. 08KJB510013, BK2008053, SJ209003, TJ209035, and TJ207035).

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