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Electrochemical and spectroelectrochemical comparison of alternated monomers and their copolymers based on carbazole and thiophene derivatives

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ABSTRACT

Here we report the preparation of 3,6- bis(bithenyl)-N-decylcarbazole with low oxidation potential due to extended conjugation that underwent facile electrochemical polymerization to form stable electroactive polymer. We extended the conjugation of the monomers in comparison to the carbazole and large decrease were observed in the oxidation potential at which polymerization occurs. To lower the oxidation potential of the monomer and control the optical and electronic properties of the polycarbazole, we attached the thiophene, bithiophene and 3,4-ethylenedioxythiophene (EDOT) at both the 3 and 6 positions of N-substituted carbazole. The monomers and their polymers were compared through electron paramagnetic resonance (EPR) and UV-Vis-NIR spectroelectrochemistry resulting in interesting properties. As optically active materials the CIE L*a*b chromaticity and other optical properties were observed.

1. Introduction

Electronic conducting polymers as functional materials are now considered a very important class of electroactive and photoactive materials because of their novel electrochemical and chemical properties; these properties lead to extensive applications, such as supercapacitors [1,2], organic field effect transistors (OFET) [3,4], organic light emitting diodes (OLEDs)[5,6], polymer solar cells (PSCs)[7,8], electrochromic devices [9,10], and charge storage devices [11,12]. The properties of conducting polymers strongly depend on their structural characteristics, based on which it is possible to develop novel materials with properties for practical applications like solution processed OLEDs [13–20]. Conjugated polymers (CPs) that can be developed by electropolymerization of a heterocyclic monomer depends on the oxidation potential of the monomer. The disadvantages of direct electropolymerization of thiophene, bithiophene and carbazole is their high oxidation potential compared to the polymers, the high-applied potential causes some degradation of the polymer (overoxidation) rendering the polymerization process slow. This problem can be overcome by extending the conjugation of the monomer by combining different kind of monomers, like in this case thiophene, bithiophene and 3,4-ethylenedioxythiophene (EDOT) with carbazole resulting in a significant reduction in the oxidation potential. Among typical polymers like polypyrrole, polythiophene, polyphenylene vinylene (PPV) and polyfluorene, polycarbazoles have been known for their good electroactivity, thermal, electrical, photo-physical, and electrochromic properties [21–29].

In the case of processability, the issues of solubility of CP are forbidding for thin film production, from this point of view, electropolymerizable carbazole monomers overcome this limitation and form soluble polymers. It is known that during poly-*N*-carbazole growth, *N*-alkylated monomers electropolymerized at the 3 and 6 heterocyclic positions, forms mainly soluble oligomers in the electrochemical medium [30–32]. From the electronic point of view, polycarbazoles are known as not only an efficient short wavelength emitter but also as a strong electro-donating (*p*-type) chromophores [33–37]. Another advantage of carbazoles is that they are very promising for tailoring functional groups and can be easily functionalized at their (3,6-), (2,7-) or *N*-positions [37–50]. The investigated compounds (Fig. 1) were examined for the effect of the different thiophene derivatives on the polymer obtained

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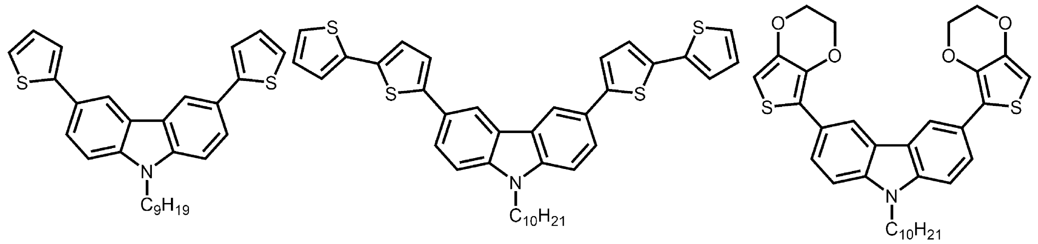
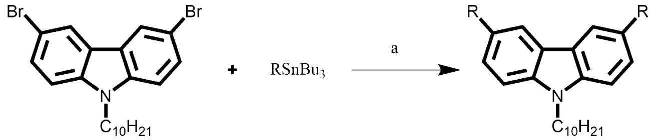


p(BTC-C9) **p(BBTC-C10)** **p(BEdC-C10**

Fig. 1. Investigated compounds.



Scheme 1. Synthesis of 3,6-bis(3,4-Ethylenedioxythiophene)-*N*-decylcarbazole (3) and 3,6-bis(2,2′-bithiophene-5-ylo)-*N*-decylcarbazole (2) *via* Stille's coupling.

during electrochemical polymerization. Due to the fact that no prior studies have compared the effect of 3,6-connected thiophene, bithiophene and EDOT substituents on monomer and resulting polymer, we decided to provide such investigations.

2. Experimental Section

Materials. All solvents for synthesis were dried and then distilled before use. Other commercially-available substances and reagents were used without purification. Electrochemical measurements were performed in 1.0 mM concentrations of all monomers for all cyclic voltammetry measurements. Electrochemical studies were conducted in 0.1 M solutions of Bu_4NBF_4, 99% (Sigma Aldrich) in dichloromethane (DCM) solvent, CHROMASOLV®, 99.9% (Sigma Aldrich) at room temperature. UV-Vis spectroelectrochemical measurements were performed on an Indium Tin Oxide (ITO) quartz glass working electrode coated with polymers. Polymeric layers were synthesized in an ITO electrode in conditions similar to that of cyclic voltammetry measurements.

9-nonyl-3,6-di(thiophen-2-yl)-9*H*-carbazole (BTC-C9) - monomer were synthesized according to our previously published procedures [42].

Synthesis of 3,6-bis(2,2′-bithiophene-5-ylo)-*N*-decylcarbazole (BBTC-C10) and 3,6-bis(3,4-Ethylenedioxythiophene)-*N*-decylcarbazole (BEdC-C10)

BEdC-C10 and **BBTC-C10** compounds have been synthesized *via* Stille's coupling of 3,6-dibromo-*N*-decylcarbazole with an appropriate stannate derivative of thiophene mediated by $[Pd(PPh_3)_4]$ or Pd-complexes generated *in situ* from $[Pd(acac)_2]$ and PPh_3 as a catalysts–Scheme 1.a = $[Pd(PPh_3)_4]$ for **BEdC-C10** or $[Pd(acac)_2]$ and PPh_3 for **BBTC-C10**

R = 3,4-ethylenedioxythiophene-2-yl **(BEdC-C10)** or 2,2′-bithiophene-5-yl **(BBTC-C10)**

Both of the above-mentioned reactions were carried out according to the same procedure described in the literature for **BEdC-C10**. The substrates for the coupling reactions, i.e. 3,6-dibromo-*N*-decylcarbazole [42,51], 3,4-ethylenedioxy-2-tributylstannylthiophene [52], and 5-tributylstannyl-2,2′-bithiophene [52] were prepared by the methods described in previously published literature. However, the procedures of removing pure products **BEdC-C10** and **BBTC-C10** from the post-reaction mixtures have been developed in our laboratory for both synthesized compounds.

2.1. *3,6-bis(2,2′-bithiophene-5-ylo)-N-decylcarbazole (BBTC-C10)*

The synthesis was carried out *via* a typical Schlenk's technique. The mixture containing 3,6-dibromo-*N*-decylocarbazole (1.8 mmol), $[Pd(acac)_2]$ (0.05 mmol), PPh_3 (0.25 mmol) and 1.7 ml of 0.28 M solution of 5-tributylstannyl-2,2′-bithiophene in mesitylene was heated at 160 °C for 2 h. After cooling to room temperature, the mixture was filtered and the volatile components (mainly mesitylene) were evaporated. Pure product was separated from the obtained mixture by column chromatography (first purification: hexane/CH_2Cl_2 1/0.45, second purification: hexane/CH_2Cl_2 1/0.25). Finally, after two chromatography procedures, 529 mg (38%) of pure product was obtained. ^1H NMR: ($CDCl_3$, 400 MHz) $\delta = 0.79$ (t, $J = 6.8$ Hz, 3H), 1.11-1.35 (m, 14H), 1.79 (m, 2H), 4.18 (t, $J = 7.1$ Hz, 2H), 6.97 (dd, $J = 4.9$, $J = 3.8$ Hz, 2H), 7.11 (d, $J = 3.7$ Hz, 2H), 7.14 (d, $J = 4.9$ Hz, 2H), 7.14 (dd, $J = 3.7$ Hz, $J = 1.2$ Hz, 2H), 7.18 (dd, $J = 3.7$ Hz, $J = 1.8$ Hz, 2H), 7.29 (d, $J = 8.5$, 2H), 7.64 (dd, $J = 8.5$ Hz, $J = 1.7$ Hz, 2H), 8.24 (d, $J = 1.5$ Hz, 2H) ppm; ^{13}C NMR: ($CDCl_3$, 100 MHz) $\delta = 14.26$, 22.80, 27.39, 29.12, 29.41, 29.51, 29.64, 29.68, 31.99, 43.38, 109.37, 117.71, 122.71, 123.30, 123.35, 124.09, 124.30, 124.78, 125.66, 127.96, 135.60, 137.92, 140.55, 144.57 ppm; M.p. = 124.2 °C (±0.2 °C); HRMS: calc. for $C_{38}H_{37}NS_4$ $[M]^+$ 635.1809; found 635.1818.

2.2. *3,6-bis(3,4-Ethylenedioxythiophene-2-yl)-N-decylcarbazole (BEdC-C10)*

The synthesis was carried out *via* a typical Schlenk's technique. The mixture containing 3,6-dibromo-*N*-decylcarbazole (0.64 mmol), 3,4-ethylenedioxy-2-tributylstannylthiophene (1.42 mmol), 10 ml of anhydrous toluene and 15 mg tetrakis(triphenylphosphine)palladium(0) was stirred overnight at 110 °C. Then, the mixture was filtered and toluene was evaporated by vacuum rotatory evaporator. The remaining mixture was dissolved in dichloromethane and separated by column chromatography (SiO_2, hexane/toluene 20/1 to 10/1 gradient v/v). The crude product was crystallized (from dichloromethane/n-pentane) and 144.0 mg (38%) of pure product was obtained. The properties of the obtained product agreed with the ones described earlier in the literature [42].

Measurements. Melting points were determined on automatic melting point SMP40 (Stuart) apparatus. NMR spectra were taken in $CDCl_3$ by Avance 400 (Bruker) at 300 MHz for ^1H and at 75.5 MHz for ^{13}C. HRMS spectra were recorded in methanol by Mariner ESI-TOF mass spectrometer (Applied Biosystems) using polyethylene glycol 400 (PEG 400) sodiated ions as internal standard. The electrochemical investigation was carried out using an potentiostats Autolab PGSTAT20 and PGSTAT100 (Metrohm Autolab). The electrochemical cell comprised of platinum disk with 1 mm diameter of working area as working electrode and ITO glass as a working electrode, Ag/AgCl electrode as reference electrode and