



# Electrochemical synthesis of new conjugated polymers based on carbazole and furan units



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## ABSTRACT

In this study, synthesis of four new monomers; 3,6-di(2-furyl)-9H-carbazole (**M1**), 3,6-di(2-furyl)-9-ethyl-carbazole (**M2**), 2,7-di(2-furyl)-9H-carbazole (**M3**), 2,7-di(2-furyl)-9-(tridecan-7-yl)-9H-carbazole (**M4**), was achieved via Stille cross-coupling reaction. The monomers were electrochemically polymerized, via repetitive cycling in acetonitrile–tetrabutylammonium hexafluorophosphate electrolytic medium. Optical and electrochemical properties of the monomers and their corresponding polymers were investigated and it was found that optical properties show slight variations depending on the connectivity between the carbazole and furan moieties. However, all the monomers synthesized in this work exhibited an irreversible oxidation peak at around 1.0 V. Electrochemically obtained polymer films, on the other hand, exhibited quasi-reversible redox behavior due to doping/dedoping of the polymers which was accompanied by a reversible electrochromic behavior. Their band gap values ( $E_g$ ) were elucidated utilizing spectroelectrochemical data and it was found that polymers obtained from 2,7-substituted carbazole derivatives have slightly lower band gap values. Furthermore, scanning electron micrographs were used for morphological examinations.

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## 1. Introduction

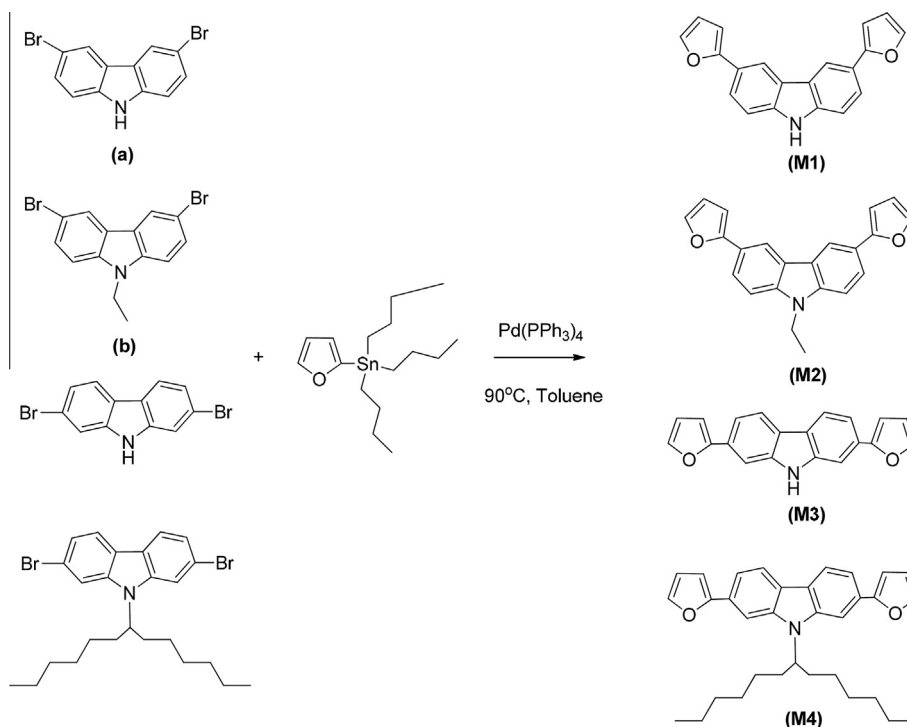
Conjugated polymers still are of great interest due to their advantages in various applications including solar cells [1,2] and light emitting diodes (LEDs) [3–5]. Furthermore, their electrical and optical properties might be easily tailored via functionalization of the monomer structure prior to polymerization. Among various conjugated polymers, polycarbazoles are of great importance due to their good electroactive and photochemical properties [6] which make polycarbazoles and their derivatives potential candidates for various applications including light emitting diodes [7,8], electroluminescent [9,10] and electrochromic displays [11]. Moreover, carbazole derivatives are widely used as charge-transporting materials. Although 3,6- or 2,7-linked polycarbazoles with different optoelectronic properties are known, due to higher reactivity of 3 and 6 positions, polymerization of carbazoles generally results in 3,6-linked polycarbazoles [12,13]. Furthermore, direct electrochemical polymerization of carbazoles in aprotic solvents leads to oligomeric chains [14]. One of the most promising ways to obtain long polycarbazole chains via electrochemical

polymerization is to introduce heteroaromatic substituents at 2,7- or 3,6-positions of the carbazoles as electron donor groups. These types of monomers, with proper donor side groups, are expected not only to have lower oxidation potentials but also may have lower band gap values. Thiophene and 3,4-ethylenedioxythiophene (EDOT) are the examples of heteroaromatics which were commonly used as donor group [15–17]. Reynolds and coworkers utilized pyrrole and EDOT as heteroaromatic side groups in 3,6-substituted carbazoles. They reported that hybrid monomers exhibit lower oxidation potentials and their polymers can be readily obtained via repetitive cycling [15]. Heinze et al. reported that electrochemical polymerization of 3,6-bis(2-thienyl)-*N*-ethylcarbazole in dichloromethane (DCM) [16] yields polymers exhibiting high conductivity and electrochromism.

Furan on the other hand, is another five-membered heterocyclic unit which can be easily obtained from natural products [18]. However, its use as building block for the design and synthesis of new  $\pi$ -conjugated polymers has remained limited due to its lower stability especially in the oxidized state [19,20]. Woo et al. demonstrated that furan can be incorporated into conjugated polymer backbones and resulting polymers exhibited similar electrical and optical properties as thiophene counterparts [21]. A new donor–acceptor (D–A) type copolymer based on furan containing benzothiadiazole and benzodithiophene with good solubility and

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**Scheme 1.** Synthetic route for monomer synthesis.

thermal stability was reported by Wang and coworkers [22]. More recently, we investigated electrochemical polymerization of a series of furan–fluorene and furan–benzochalcogeno-diazole-based hybrid monomers [23,24]. However, to the best of our knowledge, the only report utilizing furan as side group of carbazoles, is about the synthesis and polymerization of *N*-alkylated-2,7-di(2-furyl)-carbazoles [25]. Keeping all this in mind, we have synthesized four new conjugated monomers to clarify the effect of linkage site of carbazole, with and without *N*-alkyl substitution, utilizing furan as the side group of hybrid monomers. The monomers, 3,6-di(2-furyl)-9-*H*-carbazole (**M1**), 3,6-di(2-furyl)-9-ethyl-carbazole (**M2**), 2,7-di(2-furyl)-9-*H*-carbazole (**M3**), 2,7-di(2-furyl)-9-(tridecan-7-yl)-9-*H*-carbazole (**M4**) were polymerized via potential cycling. Electrochemical and optical properties of the polymers (poly(3,6-di(2-furyl)-9-*H*-carbazole) (**P1**), poly(3,6-di(2-furyl)-9-ethyl-carbazole) (**P2**), poly(2,7-di(2-furyl)-9-*H*-carbazole) (**P3**), and poly(2,7-di(2-furyl)-9-(tridecan-7-yl)-9-*H*-carbazole) (**P4**) were investigated using cyclic voltammetry and in situ spectroelectrochemical technique, respectively. Photophysical and optical properties of the monomers were also investigated in terms of the connectivity between the carbazole and furan moieties.

## 2. Experimental

### 2.1. General information

*N*-Bromosuccinimide (Fluka),  $\text{CaH}_2$  (Acros, 99%), Tetrakis(triphenylphosphine)palladium(0) (Aldrich, 99%), 2-(Tributylstannyl)furan (Aldrich, 97%), 2,7-dibromo-9-*H*-carbazole (Lumtec, >98%), 2,7-dibromo-9-(tridecan-7-yl)-9-*H*-carbazole (Lumtec, >98%) were used as received. For electrochemical studies, tetrabutylammonium hexafluorophosphate (TBAH) (Fluka, >98%), was used as a supporting electrolyte without further purification. Acetonitrile (ACN) (Merck) and dichloromethane (DCM) (Merck) were refluxed on  $\text{CaH}_2$  (Acros, >99%) and then distilled. Platinum disc (0.02 cm<sup>2</sup>) and platinum wire electrodes were used

as working electrode and counter electrode respectively. A Ag/AgCl electrode in 3 M NaCl (aq) solution was used as a reference electrode. Polymer films were synthesized by both repetitive cycling and constant potential electrolysis. Repetitive cycling was used to obtain the polymer films for the investigation of optoelectronic properties of the polymers. On the other hand, to obtain polymer films in significant quantities for FTIR and SEM measurements, constant potential electrolysis was used. For the analysis of polymers, monomer-free electrolytic solution including ACN and 0.1 M TBAH was used and measurements were conducted at room temperature.

In situ optical properties were investigated using an indium-tin oxide (ITO, Delta. Tech. 8–12 Ω, 0.7 cm × 5 cm) electrode in a UV cuvette. A platinum wire and silver wire were used as counter electrode and pseudo-reference electrode, respectively. The polymer films coated on ITO had been switched between the neutral and oxidized states several times in order to equilibrate its redox behavior in electrolytic solution prior to electrochemical and optical analyses. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat-galvanostat and the electronic absorption spectra were monitored on a Hewlett–Packard 8453A diode array spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer and chemical shifts were given relative to tetramethylsilane as the internal standard. FT-IR spectra were recorded ex situ on a Bruker Vertex 70 Spectrophotometer with attenuated total reflectance (ATR).

### 2.2. Monomer synthesis

All monomers; 3,6-di(2-furyl)-9-*H*-carbazole (**M1**); 3,6-di(2-furyl)-9-ethyl-carbazole (**M2**); 2,7-di(2-furyl)-9-*H*-carbazole (**M3**) and 2,7-di(2-furyl)-9-(tridecan-7-yl)-9-*H*-carbazole (**M4**) were synthesized via Stille cross-coupling reaction of 2-(tributylstannyl)furan with corresponding 2,7- and 3,6-dibrominated carbazole derivatives in the presence of Pd as the catalyst. 2,7-

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