



Effect of furan, thiophene and selenophene donor groups on benzoselenadiazole based donor-acceptor-donor systems



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ABSTRACT

A series of the monomers called 4,7-di(furan-2-yl)benzo[c][1,2,5]selenadiazole (**OSeO**), 4,7-di(thiophen-2-yl)benzo[c][1,2,5]selenadiazole (**SSeS**) and 4,7-di(selenophen-2-yl)benzo[c][1,2,5]selenadiazole (**SeSeSe**) was synthesized via a donor-acceptor-donor (D-A-D) approach. Benzoselenadiazole was used as an acceptor unit and furan, thiophene and selenophene were used as donor units. The effects of chalcogen atoms (O, S, and Se) in furan, thiophene and selenophene were investigated systematically on the properties of the monomers and their corresponding polymers (**POSeO**, **PSSeS** and **PSeSeSe**, respectively), which were polymerized electrochemically via potentiodynamic or potentiostatic methods. The monomers **OSeO**, **SSeS** and **SeSeSe** exhibited low oxidation potentials of 1.15, 1.25 and 1.19 V vs. Ag/AgCl, respectively. Intramolecular charge transfer interaction between donor and acceptor units was demonstrated from the emission spectra of the monomers. Also, the optical studies showed that the ambipolar and electrochromic polymers **POSeO**, **PSSeS** and **PSeSeSe** have low band gaps of 1.57, 1.47 and 1.45 eV, respectively.

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1. Introduction

After the pioneering work of Shirakawa and his colleagues, a new area called “conducting polymers” had been opened in material sciences [1,2]. This new topic also leads to other sub-applications such as photovoltaics [3–5], organic light emitting diodes [6,7], sensors [8], field-effect transistors [9,10] and electrochromic devices [11,12] due to their tunable electrical and optical properties. For example, by the help of structural modifications the related conjugated polymers can have multiple colors, low band gap, high optical transparency, high coloration efficiency, fast switching time and so forth [12–19] when compared to their inorganic analogues like tungsten oxide, titanium oxide, etc. [20].

Recently, the electro-optical properties of conjugated polymers started to tune via a donor-acceptor-donor (D-A-D) approach. In this approach, by using the intramolecular charge transfer between the donor and acceptor units combined under the same roof, it will be possible to get lower band gap, lower oxidation potential and higher coloration efficiency when compared to their parent homopolymers.

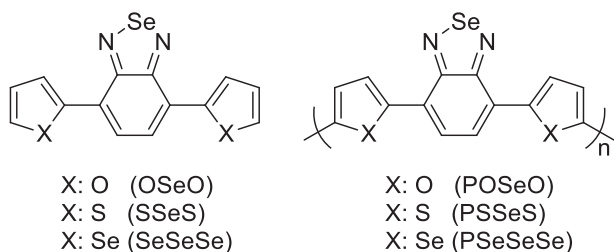
In literature, after the pioneering work of Havinga et al. [21], a myriad of donor-acceptor based conjugated polymers containing furan [22], thiophene [23,24], selenophene [25] and their derivatives as donor units and benzooxadiazoles [14], benzothiadiazoles [16,26], benzoselenadiazoles [27] and benzotriazoles [16] units as acceptor units were synthesized, characterized and used in various application areas. For instance, by

inspiration of this approach Sonmez et al. reported electro-optical properties of the first electrochemically and chemically prepared processable neutral state green conjugated polymers [28,29]. This study can be thought as a milestone in the family of electrochromic polymers since it was opened up a door to realize the application of the conjugated polymers in RGB based displays. After introducing various kinds of donor acceptor based polymers, scientists started to investigate the effect of structural modification on the electro-optical properties of the corresponding polymers by using a systematic approach [16,17,30–32]. For instance, Icli et al. reported a series of D-A-D type systems to demonstrate the effect of donor and acceptor units on the structure-property relationships of electrochromic polymers [16]. It was found that these units play key roles on the redox behavior, band gap, neutral state color, and the electrochromic performance (stability, optical contrast, coloration efficiency, and switching time) of the system. Also, Cihaner and his colleagues systematically investigated the effect of benzochalcogenadiazole type acceptor units by fixing the furan donor unit in the system [22]. It was reported that the power of the acceptor moieties, heavy atom substitution, electronegativity, acceptor aromaticity, etc. have important roles in electro-optical properties. Nonetheless, examples of systematic approaches to investigate the effect of acceptor and donor units on the properties of conjugated polymers have still been rare and newer ones are welcome.

Herein we wish to unveil our results concerning the synthesis, polymerization and characterization of a new series of conjugated monomers which were 4,7-di(furan-2-yl)benzo[c][1,2,5]selenadiazole (**OSeO**), 4,7-di(thiophen-2-yl)benzo[c][1,2,5]selenadiazole (**SSeS**)

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Scheme 1. Chemical structures of the monomers and their corresponding polymers.

and 4,7-di(selenophen-2-yl)benzo[*c*][1,2,5]selenadiazole (**SeSeSe**), firstly synthesized in this study (Scheme 1). Also, in terms of electrochemical and optical properties, the monomers containing benzo[*c*][1,2,5]selenadiazole acceptor unit and their corresponding polymers will be discussed in comparison with their donor (furan, thiophene, selenophene) and acceptor (benzooxadiazole and benzothiadiazole) analogues.

2. Experimental

All chemicals were purchased from Sigma-Aldrich Chemical and used as received unless otherwise noted. For electrochemical and optical studies, dichloromethane was freshly distilled over CaH₂ under nitrogen atmosphere. ¹H and ¹³C NMR spectra of obtained monomers were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with CDCl₃ and chemical shifts were given relative to tetramethylsilane as the internal standard. Chemical shifts are reported in terms of ppm and that of CDCl₃ is 7.26 ppm. The spectrum of high resolution mass spectrometry was recorded on a Waters, Synapt HRMS. Photographs of the polymer films were taken using a Nikon (D600) digital camera. Colorimetric measurements were recorded on Specord S600 (standard illuminator D65, field of width 10° observer) and color space was given by the International Commission of Illumination with luminance (*L*), hue (*a*), and intensity (*b*). Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references for colorimetric measurements.

Cyclic voltammetry and electrolysis were performed by using a Gamry PCI4/300 and Gamry Reference 600 potentiostat-galvanostat. The electro-optical spectra were monitored on a Specord S600 spectrometer. The optoelectrochemical spectra of the films were recorded in-situ under applied different potentials. Also, a square wave potential method was used to investigate the ability of switching of the polymer films at various redox states. Tetrabutylammonium hexafluorophosphate (TBAH) was used as an electrolyte. Electrochemical and optical properties and polymerization were performed in an electrolyte solution of 0.1 M TBAH dissolved in dichloromethane. In a three-electrode system, platinum disk (0.03 cm²) and platinum wire

electrodes were used as working and counter electrodes, respectively. A Ag/AgCl electrode in 3 M NaCl(aq) solution was used as a reference electrode calibrated externally using 0.36 mM solution of ferrocenium/ferrocene (Fc⁺/Fc) redox couple in 0.1 M TBAH/CH₂Cl₂ solution. The half wave potential of Fc⁺/Fc was found as 0.43 V vs. Ag/AgCl at a scan rate of 100 mV/s. Electrochemically obtained polymer films were synthesized by both repetitive cycling and constant potential electrolysis. After electropolymerization, the polymer coated on the working electrode was washed with CH₂Cl₂ to remove the unreacted monomers and oligomeric species. Then, the polymer film was broken by switching several times between its redox states to get repeatable results for electrochemical and optical studies. Optical properties were investigated in situ by using an indium-tin oxide (ITO, Delta. Tech. 8–12 Ω, 0.7 × 5.0 cm²) electrode as a working electrode in a UV cuvette. A platinum (Pt) and a silver (Ag) wire were used as a counter and a pseudo-reference electrode, respectively.

2.1. General procedure for D-A-D based monomers

The previously synthesized 4,7-dibromobenzo[*c*]selenophene [22, 23] (**1**) (100 mg, 0.295 mmol, 1 eq.) and the related donor group (2.2 eq.) are mixed in a 20 mL of toluene. After degassing of the obtained mixture, a catalytic amount of bis(triphenylphosphine)palladium(II) dichloride (10.4 mg, 14.8 μmol, 0.05 eq.) was added and refluxed overnight under argon pressure. After being stopped by thin layer chromatography monitoring, the reaction flask was poured onto distilled water and extracted with ethyl acetate (2 × 25 mL). Then, the mixture was dried over MgSO₄ and filtrated. The obtained viscous crude product was purified by using of silica gel column chromatography by a mixture of hexane:ethyl acetate (8:1).

2-(4-(Furan-2-yl)benzo[*c*]selenophen-7-yl)furan (**OSeO**) [16,22]: 57 mg (61.6%) was obtained as reddish-orange solid.

2-(4-(Thiophen-2-yl)benzo[*c*]selenophen-7-yl)thiophene (**SSeS**) [16]: 73.5 mg (72.1%) was obtained as red solid.

4,7-Di(selenophen-2-yl)benzo[*c*]selenophene (**SeSeSe**): 73 mg (56.3%) was obtained as red solid. ¹H NMR: (400 MHz, CDCl₃) δ 8.24 (dd, *J* = 5.7, 1.0 Hz, 2H), 8.10 (dt, *J* = 3.0, 1.5 Hz, 2H), 7.88 (s, 2 h), 7.49–7.42 (m, 2H). ¹³C NMR: (100 MHz, CDCl₃) δ 158.05, 144.16, 134.33, 129.82, 129.07, 127.80, 125.03. HRMS: 443.7589 g/mol (calculated: 443.8183 g/mol) in – 133.9 ppm.

3. Results and discussion

Three different monomers (**OSeO**, **SSeS** and **SeSeSe**) bearing the same benzoselenadiazole acceptor units with different donor units like furan, thiophene and selenophene were synthesized via Stille coupling reaction (Scheme 1). Their characterizations were done by ¹H, ¹³C NMR, HRMS, UV-Vis and fluorescence spectroscopic techniques.

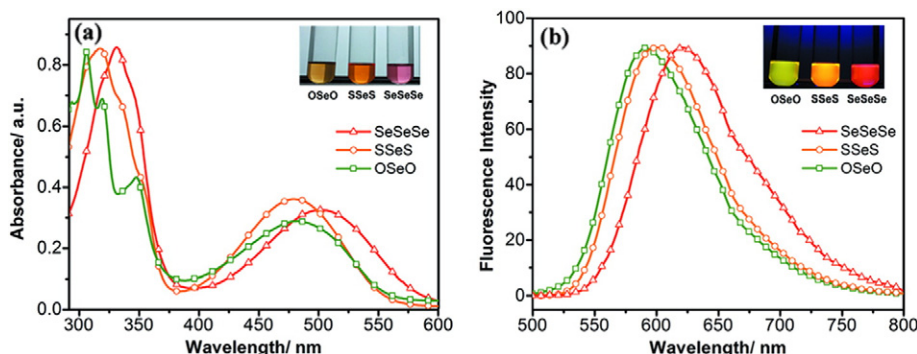


Fig. 1. (a) Absorption and (b) emission spectra of **OSeO**, **SSeS** and **SeSeSe** in toluene. Inset: The colors of the monomer in toluene under (a) day light and (b) a handheld UV lamp.

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