



Synthesis by Stille cross-coupling procedure and electrochemical properties of C3-symmetric oligoarylobenzenes

Krzysztof R. Idzik^{a,b,*}, Rainer Beckett^{a,*}, Sylwia Golba^c, Przemyslaw Ledwon^c, Mieczyslaw Lapkowski^c

^a Institute of Organic and Macromolecular Chemistry, Friedrich Schiller Universität Jena, Humboldtstraße 10, D-07743 Jena, Germany

^b Department of Chemistry, Faculty of Medicinal Chemistry and Microbiology, Wrocław University of Technology, Wybrzeże Wyspińskiego 27, 50-370 Wrocław, Poland

^c Silesian University of Technology, Department of Chemistry, Strzody 9, 44-100 Gliwice, Poland

ARTICLE INFO

Article history:

Received 7 January 2010

Revised 4 February 2010

Accepted 8 February 2010

Available online 12 February 2010

Keywords:

C3-Symmetric oligomers

Stille coupling reaction

Electroconductivity

Electrochemical polymerization

Poly(arylbenzene)s

ABSTRACT

A series of various C3-symmetric molecules were synthesized by Stille cross-coupling procedure. Monomers have been characterized by ¹H NMR, ¹³C NMR. Received oligomers in the process of electropolymerization, containing thienyl, furyl, and EDOT groups provide good conductivity and show stability in common organic solvents such as CHCl₃, toluene, and CH₂Cl₂ and exhibit thermal stability. Electrochemical results suggest that obtained materials can be successfully used in wide scale of organic–electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells.

© 2010 Elsevier Ltd. All rights reserved.

Symmetrical substrates are very useful building units in the design of target molecules, and the symmetry of the target molecule can then be used to decrease the number of steps involved in its synthesis. Symmetrical molecules can be also used as central cores for various oligomers. Tour et al. have synthesized symmetrical conjugated oligo(phenylene ethynylene)s.¹ Kinoshita and Shirota obtained C3-symmetric compounds based on a di- and tri-thienylbenzene core, which is useful in the design of organic electroluminescent devices.²

Branched oligothiophenes based on central phenyl rings have come to the fore, both as monomers in cross-linked semiconducting polymers,³ and as the components of conjugated dendrimers.^{4,5}

We describe here a simple and convenient method to obtain conjugated poly(arylbenzene) polymers based on thiophene,⁶ furan, and EDOT-linkages. Conjugated polymers in general, and polythiophenes in particular, have found widespread use in organic–electronic devices, such as organic light-emitting diodes (OLEDs),⁷ organic field-effect transistors (OFETs),⁸ and organic solar cells and photovoltaics.^{5,9}

In this work, we present series of various C3-symmetric molecules which were synthesized by Stille cross-coupling. The resulting compounds (**2a–e**) are characterized by their high yield (84–92%). Oxidative polymerization of the monomers **2a**, **2c**, and

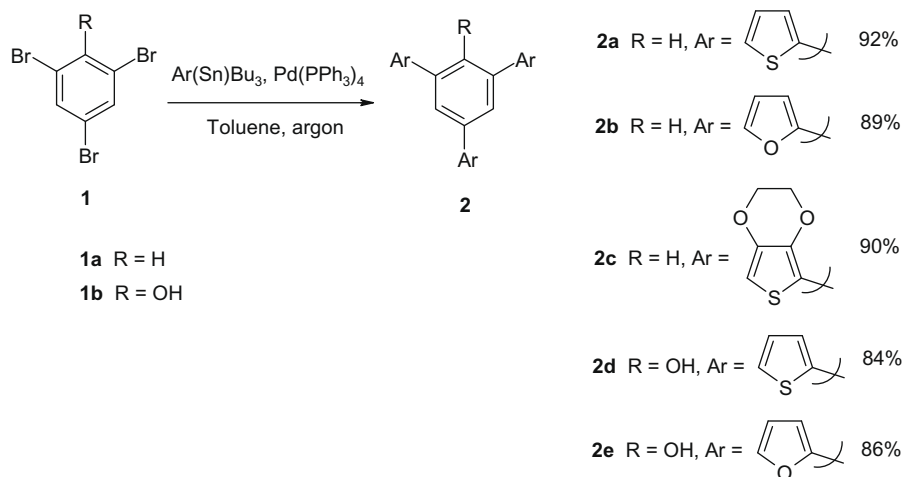
2d are expected to yield C–C coupling of the thiophene moieties in the 5-position, forming bithiophene-linkers.

We present one-step reaction routes for the synthesis of 1,3,5-tri(aryl)benzene (**2a–c**) and 2,4,6-tri(aryl)-1-phenol (**2d** and **2e**) (Scheme 1). Stille cross-coupling reaction of compound **1a–b** with 2-(tributylstannyl)arylenes followed by palladium-catalyzed gave the desired products **2a–e** with a yield of 84–92%. All the monomers obtained were characterized by spectroscopic methods and elemental analysis.¹⁰

All monomers (**2a–e**) are electroactive and undergo at least two-step oxidation; these relative oxidation potentials have been examined in some detail. Cyclic voltammetry of the **2a–e** compounds, as measured in acetonitrile (CH₃CN) containing tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) as supporting electrolyte, different processes during oxidation at a scan rate of 50 mV/s were recorded in their dependence on the terminal arm moieties. It is expected that there is coupling between thiophene or furan moieties in the 5-position. In all cases, formation of polymer films on the surface of the electrode is observed. The compound **2c** polymerizes near the potential connected with the first oxidation peak as evidenced by the current growth in the potential range between 0.2 and 0.7 V (Fig. 1). The surface of the working electrode is covered with a deep-red electroactive film. Oxidation of the polymer chain simultaneous with doping process results in oxidation peak formation at 0.51 V (oxidation onset at 0.33 V) and reduction peak at 0.41 V (Fig. 2). A sharp drop in the current value after changing polarization direction indicates the formation of the conducting layer. In addition, the obtained polymer is a middle stable one,

* Corresponding authors. Tel.: +49 15779202076; fax: +49 3641948212 (K.R.I.); tel.: +49 3641948230; fax: +49 3641948212 (R.B.).

E-mail addresses: krzysztof.idzik@pwr.wroc.pl (K.R. Idzik), rainer.beckett@uni-jena.de (R. Beckett).



Scheme 1. Synthesis of 1,3,5-tri(aryl)benzene (**2a–c**) and 2,4,6-tri(aryl)-1-phenol (**2d–e**).

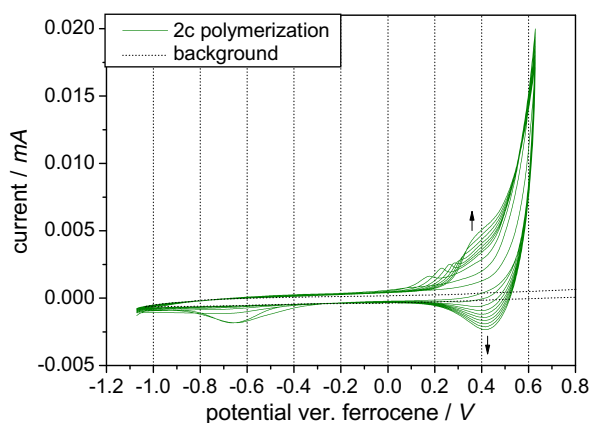


Figure 1. Cyclic voltammery of 1,3,5-tri[2-(3,4-ethylenedioxythienyl)]-benzene (**2c**) in 1 mM solution of 0.1 M Bu_4NBF_4 in CH_3CN , potential sweep rate $v = 50 \text{ mV/s}$.

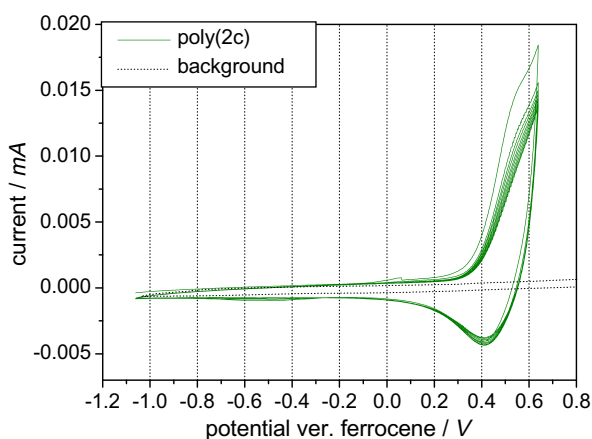


Figure 2. Cyclic voltammery of poly-[1,3,5-tri[2-(3,4-ethylenedioxythienyl)]-benzene] (poly(**2c**)) film in 0.1 M solution of Bu_4NBF_4 in CH_3CN , potential sweep rate $v = 50 \text{ mV/s}$.

and after 50 CV cycles, we observed a disappearance of the clear redox system with a concurrent shifting of the peak position to the higher potential.

The oxidation potential of monomer **2d** is approximately 0.55 V versus Ag and upon redox cycling a fast adsorption on the working electrode takes place resulting in a smooth film for-

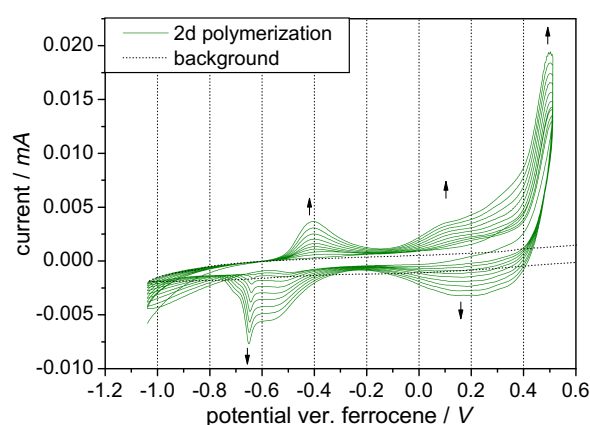


Figure 3. Cyclic voltammery of 2,4,6-tri(2-thienyl)-1-phenol (**2d**) in 1 mM solution of 0.1 M Bu_4NBF_4 in CH_3CN . Potential sweep rate $v = 50 \text{ mV/s}$.

Generally very complex redox behavior was observed during polymerization as well as for the prepared polymer film on the electrode (Fig. 4), indicating a variety of oxidation products. In the first anodic cycle there are two oxidation peaks located at the potential -0.37 and 0.40 V which represents two oxidation states. In the first one a polaron is generated and in the second, further oxidation proceeds, and a bipolaron is formed.

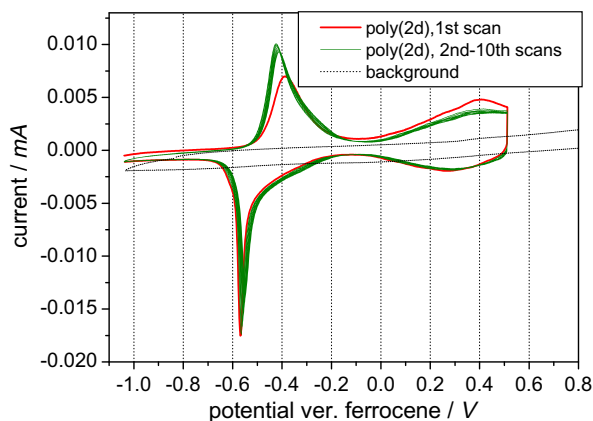


Figure 4. Cyclic voltammery of poly-[2,4,6-tri(2-thienyl)-1-phenol] (poly(**2d**)) in solution of 0.1 M Bu_4NBF_4 in CH_3CN . Potential sweep rate $v = 50 \text{ mV/s}$.

As the direction of the polarization potential is changed, a reduction process take place, as shown by two peaks located at 0.28 and -0.57 V. The sharp and reversible spike in the cyclic voltammogram could indicate a phase transformation,¹¹ or a transition between hydroquinone and quinone-like states.¹² The second broad polymer oxidation peak indicates a variety of chain lengths. The first cyclic wave differs significantly from the subsequent ones. It is observed as shift of the first and second oxidation peak potential and their peak current ratio, however total charge consumed during oxidation process remains the same. During subsequent cycles the first peak current increases and the second peak decreases. The electrochromical behavior of the polymeric film was observed during doping process. As the potential reached the first oxidation stage, a rapid change from black to colorless occurred. Future studies are required to clarify nature of this unusual oxidation behavior.

Poly(**2d**) is stable, as indicated by the lack of a significant change in its anode current during multiple doping and dedoping processes within the range between -1.1 and 0.8 V. Poly(**2d**) is only p-doped. Different conditions were employed, like different scan rates, solvents and electrolytes, in order to record an n-doping process, however it was not successful.

In the case of **2d** oxidation, changes in color from a colorless monomer solution, through to a greenish, then brown solution, was observed. The solution of **2e** was yellow. These phenomena occurred both in acetonitrile as well as dichloromethane. UV-vis spectra, before and after electrooxidation, confirmed that much of the initial products diffused from the electrode surface to the solution. This indicates the formation of soluble oligomers in the initial phase of electropolymerization.

Polymer films of compounds **2a**, **2b**, **2c**, and **2e** demonstrate strong adhesion to the electrode surface, even in solvents, in contrast to poly(**2d**), which under the influence of CH_3CN , easily diffused away from the surface.

The basic electrical and optical properties of the formed films are collected in Table 1. As expected, the electron-donating effect of the hydroxyl groups attached to benzene ring results in a decreasing oxidation potential. In the case of the furan arms, the hydroxyl substituent lowers the oxidation potential about 0.88 V. An even greater decrease is observed for polymers with thiophene moieties.

The UV-vis absorption spectrum of the neutral form of the polymer films confirms the high impact of the hydroxyl substituent. The energy band gaps (E_g), as determined from the onset of the absorption bands of the π - π^* transition, range between 2.64 eV and 3.34 eV for polymeric films without hydroxyl group, and 2.00 eV to 2.73 eV for the hydroxyl derivatives. As expected, the hydroxyl substituent has decreased E_g , but it seems surprising that the size of the reduction band gap is 0.61 eV and 0.8 eV for polymers with furan and thiophene arms, respectively. Especially noteworthy is poly(**2d**), whose spectrum is significantly red shifted.

The monomer structures suggest there should be the formation of cross-linked or branched polymers. In some cases the lack of coupling through the phenyl ring between the aryl arms in the

Table 1
Electrochemical and optical results

Compound	E_m^{ox}	$E_p^{\text{onset ox}}$ (V)	E_p^{ox} (V)	λ_{max}	E_g (eV)
2a	1.02	0,61	0,69	307	2.80
2b	1.13	0,87	*	291	3.34
2c	0.81	0,33	0,51	318	2.64
2d	0.55	$-0,53$	$-0,37$	484	2.00
2e	0.57	$-0,005$	0,16	363	2.73

Where E_m^{ox} is the monomer oxidation, $E_p^{\text{onset ox}}$ is the polymer oxidation onset, E_p^{ox} is the oxidation, λ_{max} is the polymer absorption maximum, and E_g is the HOMO-LUMO gap. *Ill-defined peak.

meta position¹³ enable the creation of polymers with a definite conjugated length. The incorporation of groups that enable coupling between arms may lead to low bandgap CPs.

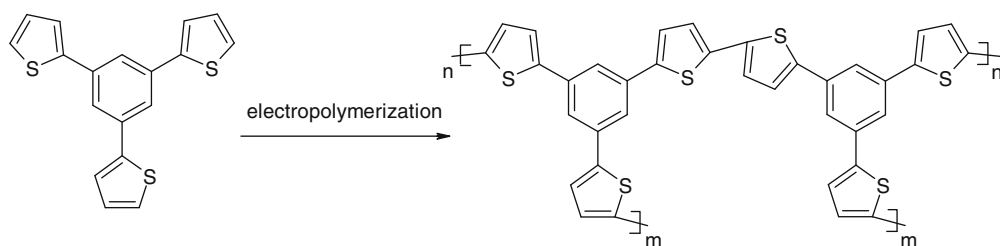
Based on an effective, iterative, palladium-catalyzed cross-coupling protocol, a homologous series of triarylbenzene and triarylphenol derivatives have been synthesized with good yields. All monomers undergo electropolymerization, which resulted in thin film formation directly on the electrode. In all cases the cyclic voltammograms of compounds, as well as UV-vis spectra, and visual observations of forming colored films confirm deposition of the polymers on electrode surface. In addition, based on the data set obtained from the optical and electrochemical measurements, the structure-property relationships were established, which give further information about the nature of the parent oligoarylenes. Polymers produced in the process of electropolymerization containing thienyl and EDOT groups demonstrated good conductivity. The attachment of a hydroxyl group dramatically changed the properties of both monomers and polymers by decreasing their oxidation potentials and E_g values, as well as improving the stability of films. Taken together, these data lay the foundation for further research into the possible use of these materials in organic-electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells.

Acknowledgements

This work was supported by grant of Ministry of Science and Higher Education NN205106935. This work was supported by the European Community from the European Social Fund within the RFS2 2 project. This work was also realized within the European Union Project (SNIB, MTKD-CT-2005-029554).

References and notes

- Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; Campbell, I. *Chem. Eur. J.* **2001**, *7*, 5118.
- Kinoshita, M.; Shirota, Y. *Chem. Lett.* **2001**, *7*, 614.
- Belot, C.; Filiatre, C.; Guyard, L.; Foissy, A.; Knorr, M. *Electrochem. Commun.* **2005**, *7*, 1439.
- Köse, M. E.; Mitchell, W. J.; Kopidakis, N.; Chang, C. H.; Shaheen, S. E.; Kim, K.; Rumbles, G. *J. Am. Chem. Soc.* **2007**, *129*, 14257.
- Mitchell, W. J.; Kopidakis, N.; Rumbles, G.; Ginley, D. S.; Shaheen, S. E. *J. Mater. Chem.* **2005**, *15*, 4518.
- Electropolymerization of 1,3,5-tri(2-thienyl)-benzene (**2a**).



7. Justin Thomas, K. R.; Lin, J. T.; Tao, Y.-T.; Ko, C.-W. *Chem. Mater.* **2002**, *14*, 1354.
8. Ponomarenko, S. A.; Kirchmeyer, S.; Elschner, A.; Huisman, B.-H.; Karbach, A.; Drechsler, D. *Adv. Funct. Mater.* **2003**, *13*, 591.
9. de Bettignies, R.; Nicolas, Y.; Blanchard, P.; Levillain, E.; Nunzi, J.-M.; Roncali, J. *Adv. Mater.* **2003**, *15*, 1939.
10. *Examples of procedures and spectroscopic data.* General procedure for the preparation of 1,3,5-tri(aryl)benzene (**2a–c**) and 2,4,6-tri(aryl)-1-phenol (**2d** and **2e**). To 1,3,5-tribromobenzene (**1a**) or 2,4,6-tribromo-1-phenol (**1b**) (2.0 mmol) in a 250 mL round two-bottom flask under argon into an anhydrous toluene (150 mL), was added 2-(tributylstannyl)aryl (6.6 mmol) and Pd(PPh₃)₄ (0.460 g, 0.4 mmol). The resulting mixture was stirred for 4 days at 110 °C. After this time the mixture was cooled to the room temperature. Water (100 mL) was added and the resulting solution was extracted with 3 × 50 mL portions of CHCl₃. The combined organic layers were washed with 50 mL of brine, dried over MgSO₄ and evaporated to a brown oil. The crude product was purified over a chromatographic silica gel column (hexane/AcOEt, 10:1).
 1. 1,3,5-Tri(2-thienyl)-benzene (**2a**). White solid (mp = 142–143 °C, 92%). (250 MHz, CDCl₃): ¹H NMR δ = 7.76 (s, 3H); 7.43 (d, J = 3.6 Hz, 3H); 7.35 (d, J = 5.1 Hz, 3H); 7.14 (dd, J = 5.1, 3.7 Hz, 3H). ¹³C NMR δ = 143.5; 135.7; 128.1; 125.4; 123.9; 122.8. Elemental Anal. Calcd for: C₁₈H₁₂S₃: C, 66.63; H, 3.73; N, 0.00. Found: C, 66.37; H, 3.31; N, 0.00.
 2. 1,3,5-Tri(2-furyl)-benzene (**2b**). Yellow solid (mp = 121–122 °C, 89%). (250 MHz, CDCl₃): ¹H NMR δ = 7.88 (s, 3H); 7.53 (d, J = 1.3 Hz, 3H); 6.78 (d, J = 3.4 Hz, 3H); 6.52 (dd, J = 3.4, 1.8 Hz, 3H). ¹³C NMR δ = 153.5; 142.3; 131.7; 118.1; 111.7; 105.7. Elemental Anal. Calcd for: C₁₈H₁₂O₃: C, 78.25; H, 4.38; N, 0.00. Found: C, 77.98; H, 4.61; N, 0.00.
 3. 1,3,5-Tri(2-(3,4-ethylenedioxythienyl))-benzene (**2c**). Yellow solid (mp = 76–77 °C, 90%). (250 MHz, CDCl₃): ¹H NMR δ = 7.92 (s, 3H); 6.32 (s, 3H); 4.36–4.31 (m, 6H); 4.27–4.20 (m, 6H). ¹³C NMR δ = 142.2; 138.4; 133.7; 122.2; 117.2; 97.8; 64.8; 64.5. Elemental Anal. Calcd for: C₂₄H₁₈O₆S₃: C, 57.81; H, 3.64; N, 0.00. Found: C, 57.64; H, 3.76; N, 0.00.
 4. 2,4,6-Tri(2-thienyl)-1-phenol (**2d**). Green solid (mp = 72–73 °C, 84%). (250 MHz, CDCl₃): ¹H NMR δ = 7.68 (s, 2H); 7.46–7.44 (m, 4H); 7.28–7.26 (m, 2H); 7.20–7.17 (m, 2H); 7.09 (dd, J = 5.0, 3.7 Hz, 1H); 6.13 (s, 1H). ¹³C NMR δ = 148.7; 143.4; 138.2; 128.0; 127.7; 127.5; 127.0; 126.7; 126.6; 124.4; 122.8; 122.3. Elemental Anal. Calcd for: C₁₈H₁₂OS₃: C, 63.50; H, 3.55; N, 0.00. Found: C, 63.16; H, 3.37; N, 0.00.
 5. 2,4,6-Tri(2-furyl)-1-phenol (**2e**). Brown solid (mp = 81–82 °C, 86%). (250 MHz, CDCl₃): ¹H NMR δ = 8.01 (s, 1H); 7.91 (s, 2H); 7.55 (d, J = 1.2 Hz, 2H); 7.48 (d, J = 1.2 Hz, 1H); 6.96 (d, J = 3.4 Hz, 2H); 6.65 (d, J = 3.3 Hz, 1H); 6.57 (dd, J = 3.4, 1.8 Hz, 2H); 6.49 (dd, J = 3.3, 1.8 Hz, 1H). ¹³C NMR δ = 153.5; 151.2; 148.2; 141.6; 141.5; 123.9; 121.0; 118.5; 111.9; 111.6; 108.8; 104.1. Elemental Anal. Calcd for: C₁₈H₁₂O₄: C, 73.97; H, 4.14; N, 0.00. Found: C, 73.58; H, 4.52; N, 0.00.
11. Kontrec, J.; Setlicic, V. *Electrochim. Acta* **1997**, *43*, 589.
12. Song, Ch.; Swager, T. *Macromolecules* **2005**, *38*, 4569.
13. Cornacchio, A. L. P.; Price, J. T.; Jennings, M. C.; McDonald, R.; Staroverov, V. N.; Jones, N. D. *J. Org. Chem.* **2009**, *74*, 530.