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COMMUNICATION TO THE EDITOR

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Low-Bandgap Benzodifuranone-Based Polymers

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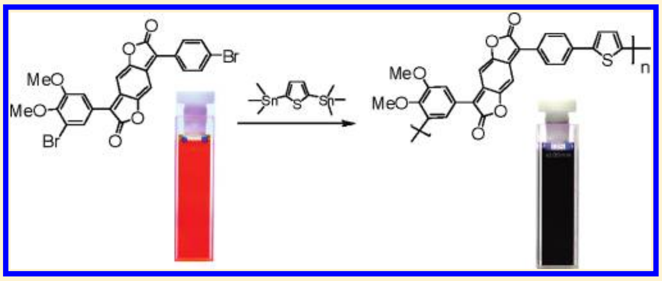
Supporting Information

ABSTRACT: π-Conjugated monomers and polymers containing benzodifuranone units in the main chain were prepared. Polymers were obtained using palladium-catalyzed Suzuki and Stille polycondensation reactions of dibromo-substituted benzodifuranone derivatives with either dihexylfluorene diboronester or bis(trimethylstannyl)thiophene. The optical and electronic properties were investigated using UV/vis absorption spectroscopy and cyclic voltammetry. It was found that the polymers show very broad absorption bands with a high extinction coefficient up to 32 500 L mol^{-1} cm^{-1}. The polymers also show reversible redox behavior, giving small HOMO—LUMO gaps up to 1.30 eV with strong donor—acceptor character.



INTRODUCTION

For the design of new polymers for electronic applications, the incorporation of chromophores highly absorbing and emitting in the visible and near-infrared region in π-conjugated polymers chains has been widely used. Potentially useful chromophores can be found among the various organic colorants, especially in the field of so-called "high-performance pigments" developed in the last three decades.[1] Among these pigments are 2,5-diketopyrrolo[3,4-*c*]pyrrole (DPP) derivatives, which were commercialized in the 1980s.[2,3] In recent years, a growing number of polymer chemists and physicists became interested in DPPs since it was shown that DPP-containing polymers exhibit light-emitting[2] and photovoltaic properties.[3] Very recently, Janssen et al. demonstrated the utility of thiophene-2-yl-DPP-containing conjugated polymers for application in photovoltaic devices exhibiting a power conversion efficiency up to 4.0%.[4] Another interesting chromophore with a related structure, benzodifuranone (Scheme 1) has attracted our interest very recently. Benzodifuranones have been developed as a class of relatively new dyes and chromophores in the last 30 years.[5] Because of their deep color, good brightness of shape and light fashion, they were commercialized as disperse dyes for textiles, especially for polyesters.[6] Depending on the substitution pattern, benzodifuranones exhibit red to blue colors,[7] and are strongly solvatochromic in organic solvents.[8] Benzodifuranones are prepared upon condensation of hydroquinone or 1,2-dihydroxybenzene with derivatives of mandelic acid.[9] The final deep color originates from the quinoid structure of the central core unit, which is obtained upon oxidation of the benzene unit with chloranil. The broad absorption in the visible combined with the high color depth render benzodifuranones interesting as building blocks for novel π-conjugated polymers with potential electronic applications.

In this Communication, we report the synthesis and characterization of a series of symmetrical and unsymmetrical benzodifuranone monomers (Scheme 1). New π-conjugated polymers containing bifunctionalized benzodifuranone units in the main chain were synthesized upon palladium-catalyzed polycondensation reactions, such as Suzuki and Stille cross-coupling (Scheme 2). The key compounds were investigated using spectroscopic methods (NMR, UV/vis) and cyclic voltammetry.

RESULTS AND DISCUSSION

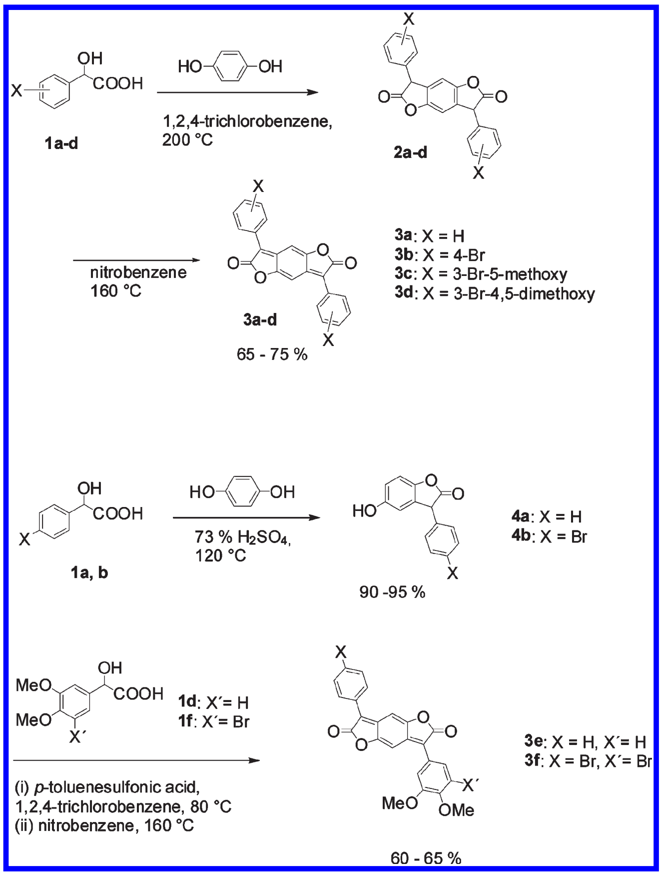
Synthesis. The synthetic route to new benzodifuranone-based monomers is described in Scheme 1. The starting compounds **1a**—**1d** were prepared according to literature procedures.[10] The key compounds **3a**—**3e** were synthesized as shown in Scheme 1. In general, the synthesis of the symmetrical monomers **3a**—**3d** required the condensation of 0.5 eq. hydroquinone and 1 eq. of a mandelic acid derivative (**1a**—**1d**), respectively, leading to a double cyclization of benzodihydrofuranone **2a**—**2d**, followed by oxidation to the conjugated benzodifuranones **3a**—**3d** in a yield of 65—75%. A Dean—Stark apparatus was used for separation of water as byproduct favoring the double cyclization of dihydrofuranone in **2a**—**2d**. Monomer **3a** is a soluble yellow solid. In comparison, the bifunctionalized monomers **3b**—**3d** were less soluble in common solvents, and were not used for further palladium-catalyzed polymerization reactions. Only UV/vis absorption spectra were recorded.

The unsymmetrical benzodifuranone monomers **3e** and **3f**, however, showed a very high solubility in common solvents such as chloroform, dichloromethane, DMF, THF and toluene, for

Received: April 15, 2011
Revised: May 27, 2011
Published: June 07, 2011

example. This could be caused by the high polarity of the molecules, which can resonance easily into a polarized form and interact with the adjacent solvent molecules (see a suggested mechanism in Supporting Information). The ^{1}H NMR spectra of **3e** and **3f** displayed all the expected resonances with no discernible peaks corresponding to impurities (see Supporting Information). Significantly, the two adjacent singulet signals with a chemical shift at about 4.00 ppm are typical for the CH_3 groups of the benzene ring on one side of the benzodifuranone core. The other signals are similar to those of the unsubstituted monomer **3a**.

Scheme 1. Synthesis of Monomers 3a−3f



3f was polymerized with comonomers **5**[11] and **6**[12] using palladium-catalyzed cross-coupling methods. The yields were 70% for **P1**, and 76% for **P2**, respectively. The synthetic route is described in Scheme 2. **P1** and **P2** are dark solids and soluble in common organic solvents. The ^{1}H NMR spectra (see Supporting Information) show broad signals for aromatic protons from 6 to 8 ppm. Typical peaks at about 4 ppm originate from the CH_3 protons of the methoxy groups. For **P1**, the NMR spectrum exhibits typical proton signals of the alkyl groups attached to the fluorene units at 0.7−1.6 ppm.

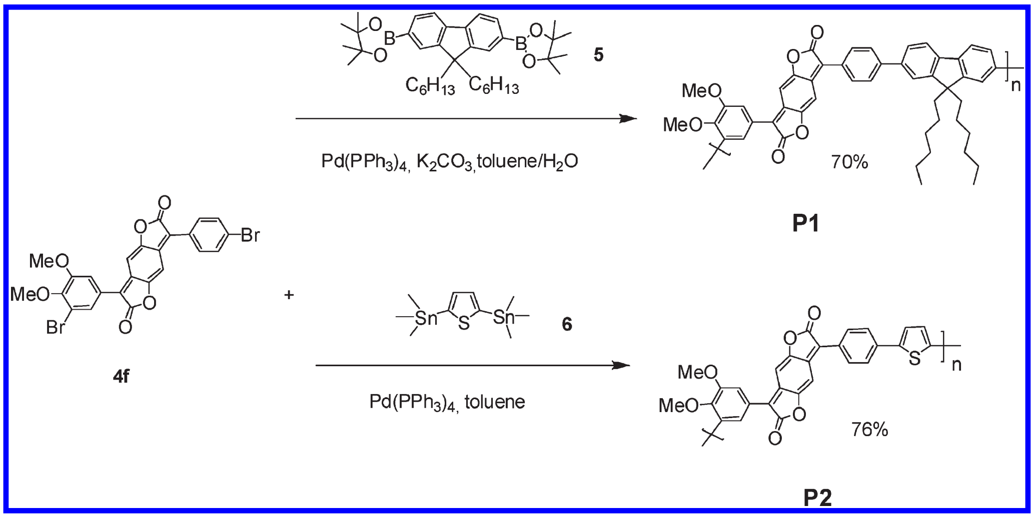
UV/Vis Spectroscopy. The monomers **3a**−**3f** show a strong absorption and weak emission in the visible with large Stokes shifts in a range from 80 to 140 nm. The optical data are listed in Table 1 and the UV/vis absorption and emission spectra are displayed in the Supporting Information. The nonsubstituted benzodifuranone derivative **3a** shows an absorption maximum at 469 nm, and the brominated monomer **3b** shows a bathochromically shifted absorption maximum at 483 nm, which can be caused by the inductive effect of the two bromine atoms of the phenyl rings attached to the benzodifuranone core. In comparison, the absorption of monomer **3c** with 3-Br-5-methoxyphenyl substituents is divided into two bands with maxima at 477 and 391 nm. The maximum at 477 nm can be ascribed to the main absorption of the benzodifuranone core, and the maximum at 391 nm should belong to the two phenyl rings attached to the benzodifuranone core. In this case, an inductive effect caused by bromine and a mesomeric effect by the methoxy group should be considered. The same effects are even stronger for the monomer **3d** with 3-Br-4,5-dimethoxyphenyl substituents, where the absorption maxima of the benzodifuranone core and the two phenyl rings are more

Table 1. Optical Data of Monomers 3a−3f[a]

	3a	3b	3c	3d	3e	3f
absorption/nm	469	483	391, 477	382, 521	525	441, 490
emission/nm	600	586	610	606	635	645

[a] Absorption spectra were taken in dichloromethane solutions.

Scheme 2. Synthesis of P1 and P2



largely divided and placed at 521 and 382 nm. For the unsymmetrical monomer **3e**, only the mesomeric effect is shown. It shows an absorption maximum at 525 nm. In comparison, the brominated unsymmetrical monomer **3f** shows an absorption maximum at 441 nm with a broad shoulder at 500 nm, where an additional inductive effect caused by bromine occurs.

The soluble monomers **3a**, **3e**, and **3f** show high extinction coefficients with 35 000, 42 000, and 32 000 L mol^{-1} cm^{-1}, respectively. The fluorescence quantum yields of the monomers are very low (from 0.3 to 2%). From the absorption edge of the monomers in a range from 540 to 600 nm, optical HOMO–LUMO gaps between 2.00 and 2.20 eV can be calculated. Compared to the corresponding monomer **3f**, the absorption spectra of **P1** and **P2** are bathochromically shifted, giving large Stokes shifts of 179 nm for **P1**, and 162 nm for **P2** (Figure 1). The polymers exhibit high extinction coefficients with 28 000 L mol^{-1} cm^{-1} for **P1**, and 32 500 L mol^{-1} cm^{-1} for **P2**. From the absorption edge at about 660 nm optical HOMO–LUMO gaps of 1.70 eV for **P1**, and 1.90 eV for **P2** (Table 2) can be calculated.

Cyclic Voltammetry. The electrochemical response of compounds **3e**, **P1**, and **P2** was studied using cyclic voltammetry (Figure 2). The measurement conditions are described in the Supporting Information. The electrochemical data of the polymers **P1** and **P2** are listed in Table 2. Both polymers show reversible oxidative and reductive waves. For **P1**, the oxidative cycle exhibits a reversible peak at +0.90 V, which is reverted at +0.71 V, and a quasi-reversible peak at +0.57 V. The reductive cycle shows two reversible waves at −0.80/−0.99 and −1.23/−1.52 V. **P2** shows a quasi-reversible peak at +0.89 V and a reversible peak at +0.50 V. Significantly, the reductive cycle shows two reversible cathodic waves at −0.78/−0.92 and −1.19/−1.33 V. For both polymers, reversible reductive waves were observed indicating a high stability of the anion radical. This could possibly be explained with a stabilizing negative charge of the oxygen atoms in the carbonyl groups of both lacton groups in the benzodifuranone units. A suggested reduction mechanism is shown in the Supporting Information. For both polymers **P1** and **P2**, the reversibility of the oxidative and reductive cycles with very small HOMO–LUMO gaps of 1.13 eV for **P1** and 1.13 eV for **P2** suggests a strong donor–acceptor character of the polymers, respectively.

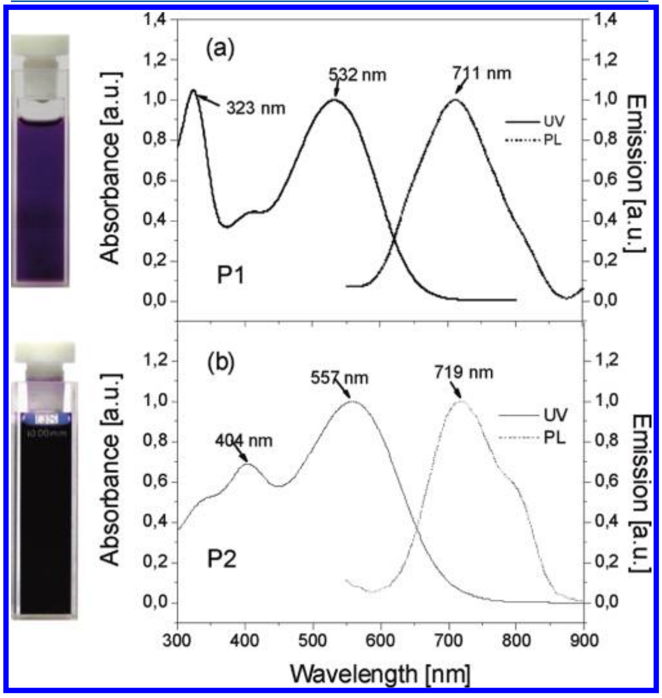


Figure 1. UV/vis absorption and fluorescence spectra of **P1** and **P2** in dichloromethane solution. Photographs of polymer solutions are also shown.

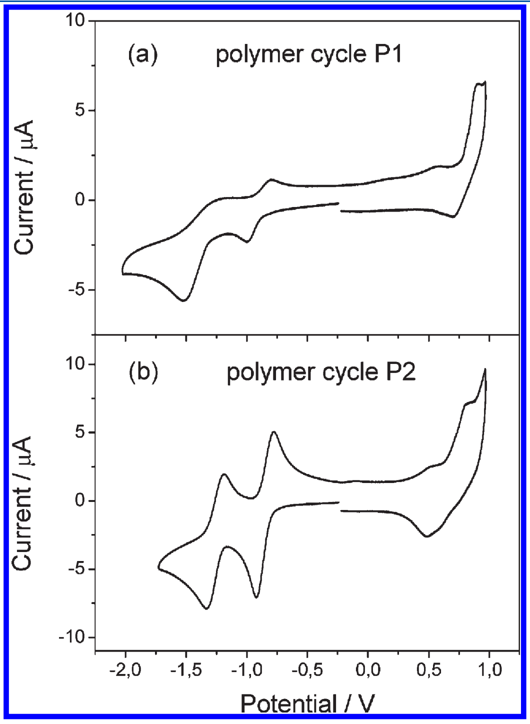


Figure 2. Cyclic voltammograms of **P1** and **P2** as thin films deposited on ITO. Solvent: 0.1 M $TBAPF_6$/acetonitrile. Potential calculated versus ferrocene. Scan rate: 100 mV s^{-1}; T = 20 °C.

Table 2. Optical and Electrochemical Data of Polymers P1 and P2[a]

	UV/nm	HOMO–LUMO gap/opt/eV	Onset of oxidation/V	HOMO/eV	Onset of reduction/V	LUMO/eV	HOMO–LUMO gap/eV
P1	323, 532	1.70	+0.26	−5.06	−0.87	−3.93	1.13
P2	404, 557	1.90	+0.29	−5.09	−0.81	−3.99	1.10

[a] Absorption spectra were taken in dichloromethane solutions. All redox potentials are referenced to the ferrocene/ferrocenium redox couple. HOMO–LUMO gap according to the following equation: $-E_{\mathrm{LUMO}} = E_{\mathrm{onset(red)}} + 4.8$ eV and $-E_{\mathrm{HOMO}} = E_{\mathrm{onset(ox)}} + 4.8$ eV, where $E_{\mathrm{onset(ox)}}$ and $E_{\mathrm{onset(red)}}$ are the onset potentials for the oxidation and reduction processes vs ferrocene.

CONCLUSIONS

In summary, we have presented the synthetic route and the key properties of a series of new conjugated monomers containing the benzodifuranone unit in the molecule. We also have synthesized the first π-conjugated polymers using palladium-catalyzed cross-coupling methods. The polymers exhibit a broad absorption, low HOMO- and high LUMO-levels and small band gaps (1.13 eV for **P1** and 1.10 eV for **P2**). They also show interesting electrochemical properties with reversible oxidation and reduction behavior, which suggests a strong donor−acceptor character. According to their broad absorption bands, small band gaps and the reversibility of oxidation and reduction processes, **P1** and **P2** might be useful for electronic applications. Further studies on the conductivity of these materials are under way.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthetic procedures of some starting compounds, the monomers **3a**−**3f**, and polymers **P1**−**P2**, UV/vis absorption spectra of **3a**−**3f**, ^{1}H NMR spectra of **3a**, **3e**, **3f**, **P1**, and **P2**, a suggested mechanism of polarization of unsymmetrical benzodifuranone, and a suggested reduction mechanism of benzodifuranone. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Financial support by BASF Schweiz AG, Basle, Switzerland, is gratefully acknowledged. Drs. M. Düggeli, R. Lenz and P. Hayoz from BASF Schweiz AG are kindly thanked for helpful discussions.

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