



1,6-Naphthodione-Based Monomers and Polymers

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Complete List of Authors:	Zhang, Haichang; Universität zu Köln, Department für Chemie Neudoerfl, Joerg; University of Cologne, Chemistry Tieke, Bernd; Universität zu Köln, Department für Chemie

1,6-Naphthodione-Based Monomers and Polymers

Haichang Zhang, Jörg-Martin Neudörfl and Bernd Tieke*

Department of Chemistry

University of Cologne

Luxemburger Str.116

D-50939 Cologne

Germany

Corresponding Author

*E-mail: tieke@uni-koeln.de

Abstract

Novel 1,6-naphthodione monomers and π -conjugated polymers were synthesized and characterized. Monomeric 1,6-naphthodifuranones and -dipyrrolidones exhibit purple to blue colors with high extinction coefficients up to $4.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. As shown by X-ray crystal structure analysis, the naphthodipyrrolidone core is fully planar. 1,6-Naphthodione-based polymers exhibit low band gaps (1.20-1.41 eV) and broad absorption bands (400-1000 nm). Due to their interesting electronic and optical properties, and their planar structure, naphthodione-based monomers are promising building blocks for novel π -conjugated polymers with application potential in optoelectronics.

In order to develop new materials for optoelectronic applications, it is necessary to design and synthesize new conjugated polymers with suitable properties such as broad absorption range, low HOMO-LUMO gaps and high electron and hole mobility. A useful strategy in the design of such polymers is based on the incorporation of deeply colored organic chromophores, which are highly absorbing in the visible and near infrared region, into π -conjugated polymers.¹ Monomeric 1,6-naphthodifuranone (1,6-NDF) is a deeply purple to blue colored dye, which has attracted our attention.² The structure of 1,6-NDF is similar to 1,5-benzodifuranone (1,5-BDF)³ except that an additional benzene ring is incorporated in the **chromophore**, which increases the length of the conjugated π -system and causes a bathochromic shift of the absorption. 1,6-NDF clearly differs from the isomeric 1,10-naphthodifuranone (1,10-NDF)⁴, in which the additional benzene ring is only attached to the chromophore and does not cause a red-shift of the absorption. **1,6-Naphthodipyrrolidones (1,6-NDP) resemble 1,6-NDF except that the lacton units are replaced by N-alkylated lactam units.** Alkylation of these units increases the solubility of the chromophore strongly. 1,6-NDP is related to 1,5-benzodipyrrolidone (1,5-BDP)⁵ (see Figure 1), but contains an additional benzene ring, which enlarges the π -extension, and favours a bathochromic shift of the absorption.

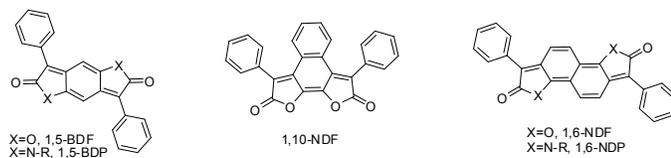
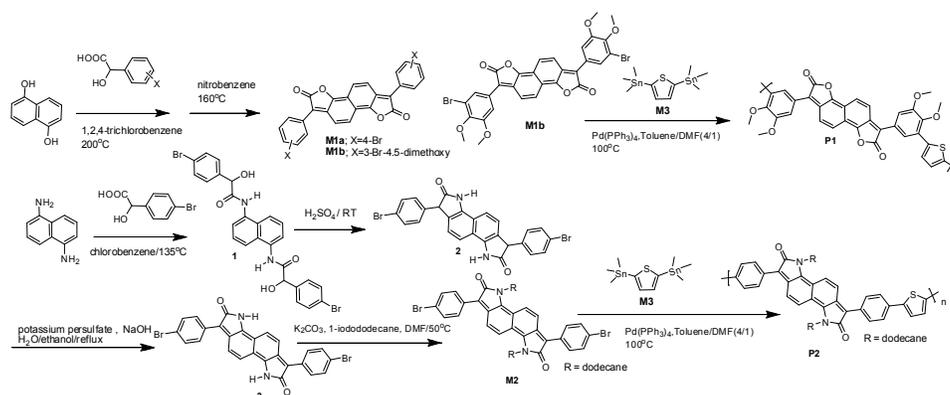


Figure 1. Structures of benzodiones and naphthodiones.

1,6-NDFs belong to a kind of electron-deficient chromophores, which have been developed in the last 30 years, and are prepared upon condensation of 1,5-dihydroxynaphthalene with derivatives of mandelic acid. The final deep color originates from the quinonoid structure of the central core unit, which is obtained upon oxidation of the naphthalene unit with nitrobenzene. To our knowledge, only few articles reported on derivatives of 1,6-NDF,² whereas 1,6-NDP and the polymers based on 1,6-NDF and 1,6-NDP are completely unknown. Here we report three new monomers 3,8-bis(4-bromophenyl)naphtho[1,2-*b*:5,6-*b'*]difuran-2,7-dione (**M1a**), 3,8-bis(3-bromo-4,5-dimethoxyphenyl)naphtho[1,2-*b*:5,6-*b'*]difuran-2,7-dione (**M1b**), and 3,8-di(4-bromophenyl)-1,6-bis-dodecyl-2,7-dioxo-1,2,6,7-tetrahydro-naphtho[1,2-*b*:5,6-*b'*]-dipyrrole (**M2**), and two polymers **P1** and **P2** based on **M1b** or **M2** and thiophene as comonomer, which exhibit a deep blue color and very low band gaps. The synthesis of the monomers is outlined in Scheme 1. **P1** and **P2** were obtained upon Stille coupling of **M1b** or **M2** with 2,5-bis-(trimethylstannyl)thiophene (**M3**) using Pd(PPh₃)₄ as catalyst in toluene/DMF (4/1) (Scheme 2). The polymers were characterized by ¹H-NMR and gel permeation chromatography (GPC). The weight-average molecular weights (*M_w*) were found to be 7.9 kDa (PDI: 1.5, **P1**) and 16.7 kDa (PDI: 2.2, **P2**).



Scheme 1. Synthetic routes towards **P1** and **P2**.

Single crystals of **M2** in a size of 0.3*0.04*0.02 mm were obtained upon slow evaporation of dichloromethane from solution at room temperature (concentration: 15 mg **M2** in 20 ml solvent). The crystal structure and the packing of the molecules are depicted in Fig. 2. The unit cell was found to be triclinic with space group P-1 (Figure 2a). The crystallographic center of symmetry is located at the midpoint of C11 and C11a (Figure 2b). The molecules adopt an intermolecularly slipped π - π stacking with the shortest distance being 3.38 Å, which is slightly shorter than for 1,5-BDP (3.56 Å).^{5a} There is a 24.9° dihedral angle between the phenyl substituent and the 1,6-NDP core, which is 13.1° smaller than for 1,5-BDP.^{5a} This indicates that **M2** is much more planar, which is advantageous for π -conjugation. Moreover, there is a short distance between the C=O group of the 1,6-NDP core and the hydrogen atom of the phenyl ring of the neighboring molecule of 2.52 Å (C2—H2---O1, Fig. 2c). The bond lengths and other information of the single crystal structure are given in the Supporting Information (**S2**).

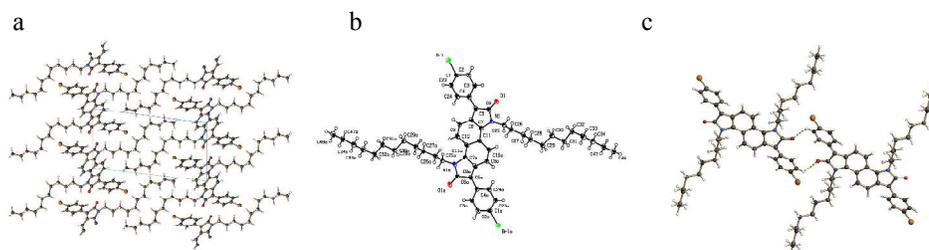


Figure 2. Single crystal structure of **M2**.

Solutions of **M1** and **M2** exhibit a purple to blue color and show a strong absorption in the visible. The optical data are listed in Table 1, the UV/vis absorption spectra are displayed in the Supporting Information (S1). **M1a** is not well soluble in common organic solvents, while **M1b** exhibits a better solubility. In dichloromethane, a deep blue solution with a high extinction coefficient of $2.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 588 nm is formed. Compared with **M1a**, the absorption of **M1b** is red-shifted by 25 nm because the two methoxy units attached to the benzene ring favor a bathochromic shift due to an increased donor-acceptor (D-A) character. **M2** is highly soluble in common organic solvents. In dichloromethane, a purple solution is formed with a high extinction coefficient of $4.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 567 nm. Compared with BDP,^{5a} the absorption maximum of NDP is red-shifted by about 80 nm. This can be ascribed to the larger size of the NDP chromophore and its more planar structure.

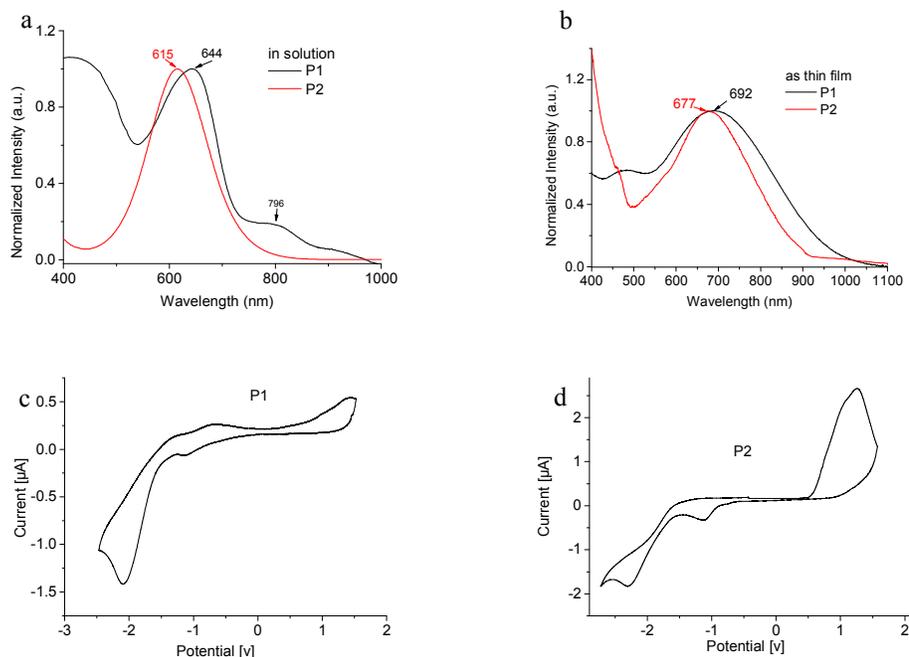


Figure 3. Optical and electrochemical properties of **P1** and **P2**. UV/vis absorption spectra of **P1** in 1,2,4-trichlorobenzene, and **P2** in dichloromethane (a) and as thin films on quartz substrates (b). Cyclic voltammograms of **P1** (c) and **P2** (d) as thin films on ITO-coated glass substrates. Solution: 0.1 M TBAPF₆/acetonitrile. Potential calculated versus ferrocene. Scan rate: 100 mV s⁻¹; T= 20 °C.

Table 1. Optical Properties of Monomers and Polymers and Band Gaps of Polymers.

Compounds	λ_{\max} [nm]		Extinct. Coeff. ϵ (λ_{\max}) [1*10 ⁴ L mol ⁻¹ cm ⁻¹]	$E_g^{\text{opt}}/E_g^{\text{ec}}$ [eV] ^c
	in solution	as thin film		
M1a	560 ^a	n.d.	n.d.	n.d.
M1b	588 ^a	n.d.	2.6	n.d.
M2	567 ^a	n.d.	4.6	n.d.
P1	644 ^b	692	1.9	1.25/1.30
P2	615 ^a	678	2.8	1.38/1.41

^a in dichloromethane; ^b in 1,2,4-trichlorobenzene; n.d.= not determined; ^c E_g^{ec} according to the following equation: $-E_{\text{LUMO}} = E_{\text{onset}(\text{red})} + 4.8 \text{ eV}$ and $-E_{\text{HOMO}} = E_{\text{onset}(\text{ox})} + 4.8 \text{ eV}$, where $E_{\text{onset}(\text{red})}$ and $E_{\text{onset}(\text{ox})}$ are the onset potentials for the oxidation and reduction processes vs. ferrocene.

The absorption spectra of the polymers are shown in Figs. 3a and 3b. The two polymers form deep green and blue solutions with maxima at 644 (P1) and 615 nm (P2), respectively. P1 is only moderately soluble in common organic solution, the extinction coefficients of the strongest bands being $1.9 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ in 1,2,4-trichlorobenzene. P2 is well soluble in common organic solvents such as dichloromethane, the extinction coefficient being $2.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 615 nm. The absorption maxima are 56 nm (P1) and 48 nm (P2) red-shifted with regard to the related monomers. This is due to strong D-A interactions between the 1,6-naphthodione core and the thienyl units giving rise to an enhanced intramolecular charge transfer (ICT). Polymer films were prepared upon spin coating from hot 1,2,4-trichlorobenzene (P1) and dichloromethane (P2) on a Si/SiO₂ substrate. The absorption spectra of the films show maxima at 692 nm for P1, and 678 nm for P2, respectively. They are about 50 nm red-shifted compared with the solution spectra, and the long-wavelength tails of the absorption bands are extended to the infrared. This indicates a gain of planar conformation and/or the presence of π - π interchain association in the solid state. The polymers show a very broad absorption from 400 to 1000 nm, which matches the solar photon most intense flux (that is in the 400-800 nm range).⁶ Thin film absorption coefficients of P1 and P2 are $4.2 \times 10^5 \text{ cm}^{-1}$ and $7.6 \times 10^5 \text{ cm}^{-1}$, respectively. Optical HOMO-LUMO energy gaps estimated from the onset of the film absorption are 1.25 eV for P1, and 1.38 eV for P2, respectively. The two polymers are very weakly luminescent with luminescence quantum yields below the detection limit.

The electrochemical properties of the polymers were investigated using cyclic voltammetry. The experimental details are described in the Supporting Information. It can be seen from Figs. 3c and 3d that the anodic oxidation of the polymers sets in at

low potentials of 0.33 V (**P1**) and 0.50 V (**P2**), respectively. Two anodic waves with maxima at 1.1 and 1.38 V (**P1**), and 0.8 and 1.21 V (**P2**) occur. This can be ascribed to formation of cation radicals and dications. The reductive cycle of **P1** exhibits two cathodic waves at -1.12 and -2.07 eV, which are reverted at -1.29 and -0.71 eV. The cathodic waves indicate the reduction of the quinonoid to a benzoic structure. The reversibility of the reduction indicates a high stability of the anion radical, which can possibly be explained with a stabilizing negative charge of the oxygen atoms in the carbonyl groups of both the lacton groups in the naphthodione units. For **P2** two cathodic waves at -1.09 and -2.30 V occur, which are reverted at -1.54 V. The polymers show low LUMO (-4.17 eV, **P1**; -3.96 eV, **P2**) and HOMO levels (-5.47 eV, **P1**; -5.37 eV, **P2**). Due to the low LUMO and HOMO energy level of the polymers, good electron injection and ambient stabilities of OFET devices and air stability can be expected.^{7,8} The polymers exhibit quite low HOMO-LUMO band gaps of 1.20 eV (**P1**) and 1.41 eV (**P2**), respectively. The electrochemical band gaps are larger than the optical ones due to the interfacial barrier for charge injection.⁹

In this article three novel deep purple to blue monomers and two π -conjugated polymers based on naphthodione units with low band gaps are described. Monomers **M1** and **M2** are well soluble in hot toluene and suitable for Suzuki and Stille coupling because of the bromine substituent groups. The three monomers show a broad absorption with maxima around 588 nm (**M1**), 567 nm (**M2**) and 560 nm (**M3**), respectively, with high extinction coefficients up to $4.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The X-ray

analysis of **M2** indicates a dihedral angle of 24.9° between 4-bromophenyl groups and the NDP core, which is about 13° smaller than for BDP, and a weak π - π stacking separated by the distance of 3.38 \AA , which is slightly shorter than for 1,5-BDP (3.56 \AA). This indicates that NDP units are more planar than BDP, which is advantageous for π -conjugation favoring a bathochromic shift. The polymers exhibit low band gaps (1.20 eV , **P1**; 1.41 eV , **P2**) and broad absorption bands (from $400\text{-}1000 \text{ nm}$) with high extinction coefficients up to 2.8×10^4 . This well matches the solar photon most intense flux. Due to their interesting electronic and optical properties, in addition to the planar structure, naphthodiones are promising building block for the development of novel π -conjugated polymers for optoelectronic applications. A detailed study on 1,6-naphthodione-based monomers and polymers is at hand and will be published shortly.

Supporting Information

Experimental details, ^1H NMR spectra, UV/vis absorption spectra of **M1-M2**, and crystal structure data of **M2**.

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Table of Contents Graphic

Deeply coloured 1,6-Naphthodifuranone-/1,6-naphthodipyrrolidone-based monomers and polymers are reported. The polymers exhibit a broad and strong absorption in the visible from 400 to 1000 nm, and low band gaps of 1.2-1.41 eV.

