



Synthesis and electrochemical properties of novel, donor–acceptor pyrrole derivatives with 1,8-naphthalimide units and their polymers



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ABSTRACT

A new class of bipolar monomers with pyrrole or thiophene–pyrrole–thiophene as electron donor and 1,8-naphthalimide as electron acceptor unit is reported. Donor–acceptor conjugated polymers were generated electrochemically. The synthesis of monomers, optical, electrochemical and spectroelectrochemical properties supported by theoretical calculations are presented. 1,8-naphthalimide units were attached directly to pyrrole in compounds **1a** and **2a** or by different bridges in the case of **1b** and **2b**. Intramolecular donor–acceptor interactions of the monomers and its polymers were investigated using cyclic voltammetry, in-situ UV–Vis–NIR, electron spin resonance (ESR) spectroelectrochemistry and fluorescence spectroscopy. Studied compounds present large discrepancy (up to 1.31 eV for **2a**) between energy gap values determined through electrochemical and optical measurements. The Time-dependent density functional theory (TDDFT) calculations help to explain this discrepancy. This is caused by weak HOMO to LUMO transition, 2000 times weaker than HOMO⁻² to LUMO or HOMO to LUMO⁺¹ transition. Altering the structure of monomers yields different stability and properties of obtained polymers. The p- and n-doping processes are separated. Anions are localized mainly on 1,8-naphthalimide units. Cations are localized mainly on pyrrole or thiophene–pyrrole–thiophene moiety and their polymer chains. Attachment of the additional thiophene units decreases the oxidation potential of the monomer and reduces the influence of the steric hindrance between 1,8-naphthalimide moiety and polymer/oligomers chain. This new class of model compounds is promising for use as a material with enhanced charge separation for wide range of optoelectronic, electrochromic and photovoltaic applications.

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1. Introduction

Organic electronics is a dynamically growing branch of materials science, attracting the attention of numerous researchers worldwide. Based on conductive molecules and macromolecules, such as conjugated polymers, the field introduces novel concepts, such as printable and flexible electronics. Furthermore, the operating parameters of such materials and devices can be tuned through structural modification of the electroactive layers, leading to a multitude of potential systems. Combining versatility with outstanding mechanical properties, organic materials are well equipped to compete with inorganic semiconductors in a bid for supremacy in commercial applications. A number of excellent reviews strive to

further this goal, discussing and systematizing existing developments in the field [1–4].

Recently, modification of conducting polymers' physicochemical properties, through the functionalization with a variety of chromophore groups has garnered considerable interest [5–7]. The reported, π -conjugated, semiconducting systems can be divided into p- or n-type, depending on the nature of the charge carriers occurring in each material. Initially, most works were concerned with p-type organic semiconductors. Lately, however, the study of n-type systems has achieved significant progress as reflected in most recent reports. The importance of improvements in design and synthesis of such semiconductors is not to be underestimated, as they are essential for the construction of an array of electronic devices, including organic photovoltaic cells (OPVs) [8], organic light-emitting diodes (OLEDs) [9] and organic field-effect transistors (OFETs) [3,10].

Among known, n-type organic materials, aromatic imides are acclaimed as one of the most stable, demonstrating relatively high electron affinity and electron mobility [10]. They are a versatile

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material building block, useful for supplementing materials with electron-withdrawing properties, due to their planar, conjugated structure, substituted with one or two π -accepting imide groups [11–13]. 1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione, imide of 1,8-naphthalenedicarboxylic acid is a relatively simple representative of aromatic imides. The compound has been successfully used in the construction of OPVs [14], white polymer light emitting diodes (WPLEDs) [15], fluorescent probes for analytical sensing and optical imaging [16], DNA intercalators [17] as well as colorimetric and fluorescent anion sensors [18].

p-Type conjugated polymer semiconductors, on the other hand, are well-represented by polypyrrole and its substituted derivatives. The nature of the substituent, in such systems, determines the properties of the polymer, predestining it for application in a given type of devices, such as electrochromics [19], sensors [20] and solar cells [21,22]. For N-substituted pyrroles, large groups may stabilize the radical cation generated during electrochemical polymerization, possibly inhibiting the process. Steric interactions in resultant polymers are particularly important, as they may induce a loss of conjugation across the polymer backbone, leading to lower conductivity of the material [23].

Building upon the highlights of both p- and n-type polymer semiconductors, the donor–acceptor (D–A) approach, introduced by Havinga et al. [24] creates a new quality. The importance of structural modification is retained and supplemented as HOMO and LUMO energy levels of the material may be individually tuned. Two distinct strategies for D–A semiconductors have been reported, composed of either a D–A copolymeric chain [25] or a homopolymer donor chain substituted with acceptor pendant groups [26,27]. The first architecture allows for better band gap control, while the second exhibits improved charge separation, both features well sought after [8].

Adhering to the above approach, monomers composed of an n-type, aromatic imide acceptor core and a p-type, pyrrole-based moiety have been envisioned. For the exploration of this new class of D–A systems, a simple 1,8-naphthalimide was chosen as the acceptor core. D–A monomers were prepared either through a direct N–N linkage between donor and acceptor moiety or through the use of a linking group (Fig. 1), similar to previously reported systems, where 1,8-naphthalimide was used as a pendant group of a conducting polymer [15,28].

2. Experimental

2.1. Materials

All used reagents were purchased from Aldrich or Alfa Aesar. Solvents were used without further purification. Ethyl alcohol and toluene were dried with molecular sieves of 4 Å prior to use. Column chromatography was performed using silica gel 60 (0.040–0.063 mm) purchased from Merck. NMR spectra were recorded at 600 MHz for ¹H NMR and 151 MHz for ¹³C NMR on a Varian Mercury Plus 600 MHz spectrometer; δ values are in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on ESI Mass Spectrometer ABSciex System 4000 QTRAP® at positive and negative modes of ionization. Melting points were measured with a Boetius apparatus (Franz Kustner Nachf. KG Dresden HMK) and are uncorrected.

2.2. Preparation of monomers

2.2.1. 2-amino-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione(**1**)

To the suspension of 1,8-naphthalic anhydride (0.99 g, 5 mmol) in chloroform (40 mL), hydrazine monohydrate (0.75 mL, 10 mmol) was added. The reaction mixture was heated under reflux for 4 h.

After completion of the reaction (progress was monitored by means of TLC: MeOH:CHCl₃ 10:90 v/v), the mixture was cooled to room temperature, the obtained precipitate was filtered off and purified by column chromatography to give yellow solid. Yield: 87% (0.92 g). *Mp* 263–264 °C; ¹H NMR (600 MHz, DMSO-*d*₆, δ): 8.50 (dd, *J* = 7.4, 0.7 Hz, 2*H*, Ar–H), 8.45 (dd, *J* = 8.2, 0.7 Hz, 2*H*, Ar–H), 7.87 (dd, *J* = 8.2, 7.4 Hz, 2*H*, Ar–H), 5.80 (s, 2*H*, NH₂); ¹³C NMR (151 MHz, DMSO-*d*₆, δ): 160.422, 134.42, 131.21, 130.71, 127.21, 125.95, 121.63. ESI–MS (*m/z* (%)): 213.2 (100) [M+H]⁺, 235.2 (40) [M+Na]⁺, 229.2 (100) [M+OH]⁺.

2.2.2.

2-(2-aminoethyl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione(**2**)

To the solution of 1,2-diaminoethane (0.6 g, 10 mmol) in EtOH (100 mL) catalytic amount of DMAP 4-dimethylaminopyridine was added (0.005 g). The mixture was stirred under reflux for 1 h while the naphthalic 1,8-anhydride (0.99 g, 5 mmol) was added in portions. The mixture was refluxed for additional 4 h. The course of the reaction was monitored by means of TLC (MeOH:CHCl₃:NH₃, 20:80:1 v/v/v). After completion of the reaction the mixture was cooled and the precipitate was filtered off. The filtrate was concentrated under reduced pressure and the residual was purified by column chromatography to give pale yellow solid. Yield: 59% (0.71 g). *Mp* 140–141 °C; ¹H NMR (600 MHz, CDCl₃, δ): 8.61 (dd, *J* = 7.3, 1.0 Hz, 2*H*, Ar–H), 8.22 (dd, *J* = 8.2, 1.0 Hz, 2*H*, Ar–H), 7.76 (dd, *J* = 8.2, 7.3 Hz, 2*H*, Ar–H), 4.29 (t, *J* = 6.7 Hz, 2*H*, CH₂N(CO)₂), 3.08 (t, *J* = 6.7 Hz, 2*H*, CH₂NH₂), 1.30 (bs, 2*H*, NH₂); ¹³C NMR (151 MHz, CDCl₃, δ): 164.48, 133.99, 131.60, 131.33, 128.23, 126.94, 122.60, 43.18, 40.55. ESI–MS (*m/z* (%)): 241.4 (70) [M+H]⁺, 481.4 (100) [2M+H]⁺, 721.8 (70) [3M+H]⁺.

2.2.3.

2-(1*H*-pyrrol-1-yl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione(**1a**)

N-Amino-1,8-naphthalimide (0.106 g, 0.5 mmol) and 2,5-dimethoxytetrahydrofuran (0.06 mL 0.5 mmol) were refluxed in acetic acid (6 mL) for 3 h. Acetic acid was evaporated under reduced pressure. The crude residue was purified by column chromatography (MeOH:CHCl₃ 5:95, v/v) to give pale brown solid. Yield: 50% (65 mg). *Mp* 304–306 °C; ¹H NMR (600 MHz, CDCl₃, δ): 8.69 (dd, *J* = 7.3, 1.0 Hz, 2*H*, Ar–H), 8.31 (dd, *J* = 8.3, 1.0 Hz, 2*H*, Ar–H), 7.82 (dd, *J* = 8.3, 7.3 Hz, 2*H*, Ar–H), 6.77–6.77 (m, 2*H*, Ar–H), 6.40 (t, *J* = 2.3 Hz, 2*H*, Ar–H); ¹³C NMR (151 MHz, CDCl₃, δ): 162.45, 135.08, 132.39, 131.94, 128.13, 127.21, 122.14, 121.29, 108.58; IR: ν = 3078 (C–H Ar), 1716 (C=O), 1688 (C=O), 1585 (C–C Ar), 1359 (C–N–C), 1071 (C–H Het) cm^{−1}; ESI–MS (*m/z* (%)): 263.2 (45) [M+H]⁺, 284.8 (100) [M+Na]⁺.

2.2.4. 2-(2-(1*H*-pyrrol-1-yl)ethyl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione(**1b**)

Synthesis was performed according to the same procedure as 1a. Yield 81% (117 mg), pale yellow solid. *Mp* 160–162 °C; ¹H NMR (600 MHz, CDCl₃, δ): 8.59 (dd, *J* = 7.3, 1.0 Hz, 2*H*, Ar–H), 8.23 (dd, *J* = 8.2, 1.0 Hz, 2*H*, Ar–H), 7.76 (dd, *J* = 8.2, 7.3 Hz, 2*H*, Ar–H), 6.74 (t, *J* = 2.1 Hz, 2*H*, Ar–H), 6.12 (t, *J* = 2.1 Hz, 2*H*, Ar–H), 4.56–4.52 (m, 2*H*, CH₂N(CO)₂), 4.26–4.22 (m, 2*H*, CH₂N(CH₂)₂); ¹³C NMR (151 MHz, CDCl₃, δ): 163.97, 134.21, 131.64, 131.42, 128.21, 127.00, 122.32, 121.01, 108.51, 46.78, 41.05; IR: ν = 3072 (C–H Ar), 1692 (C=O), 1655 (C=O), 1589 (C–C Ar), 1440 (C–H Pyr), 1384 (C–N–C), 1074 (C–H Pyr), 1048 (C–H Pyr), 1033 (C–H Pyr), 943 (C–H Pyr) cm^{−1}; ESI–MS (*m/z* (%)): 291.4 (80) [M+H]⁺, 313.4 (80) [M+Na]⁺, 531.6 (35) [2M+H₃O+MeOH]⁺, 603.6 (100) [2M+Na]⁺.

2.2.5. 2-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione(**2a**)

Synthesis of the monomer was carried out in two steps. The first one was acylation of thiophene with succinyl dichloride

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