



Unusual loss of electron mobility upon furan for thiophene substitution in a molecular semiconductor

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ABSTRACT

Furan has often been considered as a more sustainable alternative to thiophene in organic electronics. Herein we demonstrate that replacing thiophene with furan in a phthalimide based molecular semiconductor results in a complete loss of electron mobility when evaluated using organic thin film transistors (OTFTs). Although optical, electronic, thermal, and structural characterization show subtle effects substituting furan for thiophene, theoretical dimer modeling employing the respective single crystal structures of the two molecules reveals a loss of degeneracy between the lowest unoccupied molecular orbital (LUMO) and LUMO+1 molecular orbitals in the bifuran-containing molecule. These results demonstrate that minor changes to molecular structure can result in large differences in device performance.

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Organic small molecule and polymer semiconductors have paved the way for next-generation flexible, light-weight and renewable electronic materials which continue to attract commercial interest [1,2]. In particular the design and synthesis of new organic building blocks and molecular and polymeric architectures are the focus of many research groups and have led to significant improvements in device performance [3–5]. Thiophene, a low-cost and readily available heterocycle, is one of the most widely used and well-studied building blocks in many high performance organic π -conjugated materials [6,7–9]. More recently in the field of organic electronics, reports illustrate the need for sustainable materials [10–12,13]. Towards this end, furan is currently being explored as a more sustainable alternative to thiophene due to its structural

similarity, availability from renewable biological feedstocks, and ease of decomposition, making it an attractive building block in ‘green’ materials [10,11,14,15]. When replacing thiophene for furan it is important that the effects of this substitution are predictable and that device performance is not compromised in trying to obtain a more sustainable material.

Previously, we reported on the synthesis of a simple molecular semiconductor which consisted of a bithiophene core flanked by phthalimide end-capping units. This compound was shown to exhibit a high electron mobility of $\sim 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when utilized as an evaporated active layer in thin-film transistors [16]. In the present study we replaced the bithiophene unit in this architecture with the relatively more sustainable bifuran building block. It was our hypothesis that the optical and electronic properties would be minimally affected by this change and that a more sustainable material with equal performance would result. The chemical structures of the materials of interest are shown in Fig. 1. Compound 2 was synthesized in a

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similar fashion to **1** using a combination of Stille and direct hetero-arylation carbon–carbon bonding forming reactions. Full details can be found in the [Supporting Information](#).

In order to compare small molecules **1** and **2**, we investigated their respective photophysical, thermal, and electronic properties using a combination of absorption and emission spectroscopy, differential scanning calorimetry, cyclic voltammetry, and ultraviolet photoelectron spectroscopy. UV–Visible spectroscopy was used to examine the absorbance profiles of both **1** and **2** in CHCl₃ solution and as evaporated thin films. Spectra are shown in [Fig. 2](#). The solution spectra of compounds **1** and **2** display little fine structure in their absorbance profiles and have absorbance maximum at 425 nm and 432 nm, respectively. The absorbance onsets for **1** and **2** in CHCl₃ solution are 486 nm and 488 nm, respectively. The minimal change in absorbance spectra observed between **1** and **2** indicate that the substitution of thiophene (**1**) for furan (**2**) had little effect on the intramolecular electronic structure. The evaporated films of **1** displayed a blue shifted absorbance maximum ($\lambda_{\text{max}} \sim 384$ nm). Similarly, evaporated films of **2** display a blue shifted absorbance maximum ($\lambda_{\text{max}} \sim 377$ nm) when compared to the solution spectrum, thus indicating that both **1** and **2** form H-aggregated structures in the solid state [17,18]. Again there are no significant differences in the evaporated film absorbance profiles between **1** and **2**. The emission spectra of compounds **1** and **2**, shown in [Fig. 2](#), show similar behavior in solution. Compound **1** exhibits a Stokes shift of 90 nm and has an emission maximum at 515 nm, while compound **2** exhibits a Stokes shift of 98 nm and has an emission maxima at 530 nm. In contrast, the emission profile of **2** as an evaporated film shows the emergence of a longer wavelength shoulder and a smaller Stokes shift by approximately 24 nm ([Fig. 2B](#)). Such differences can be attributed to **2** having a more rigid and planar π -conjugated backbone structure afforded by the smaller size of the furan vs thiophene heterocycle, a trend eloquently described by Bendikov and co-workers [19]. The minimal change in planarity of **2** upon transition to the solid state results in a smaller change in vibrational energy loss upon photoexcitation, maintaining the hypsochromic shift observed in the emission spectra. The larger degree of conformational changes in **1** upon adopting a planar structure in thin films, as observed in the single crystal structure (*vide infra*), results in greater vibrational losses upon excitation and an observed bathochromic shift of the emission spectra. The larger degree of vibrational coupling also broadens

the emission spectra and leads to a lower degree of fine structure in **1** compared to **2**. A summary of optical data for **1** and **2** can be found in [Table 1](#).

Further comparing the effects of furan for thiophene substitution the electrochemical properties of **1** and **2** were investigated using cyclic voltammetry ([Fig. 3A](#), [Table 1](#)). Both compound **1** and compound **2** exhibited fully reversible oxidation and reduction peaks. The onset of oxidation and reduction for **2** occurred at approximately 0.68 V and -1.82 V, respectively, slightly lower values when compared to **1**, indicating that furan substitution increases the electron density of the small molecule. This is not unexpected, and matches other observations that have been made when comparing α -oligofurans to α -oligothiophenes [19,20]. To gain a better handle of the electronic energy levels of the two compounds, the solid state ionization energies (IE) of evaporated thin films of compounds **1** and **2** were measured using ultraviolet photoelectron spectroscopy ([Fig. 3B](#)). The IEs for compounds **1** and **2** were found to have the same value of ~ 6.0 eV ([Table 1](#)). Thus, the slight differences in the CV values might be attributed to distortions along the π -conjugated backbone giving rise to differences in delocalized electron density, with compound **1** being affected the most due to the large size of the thiophene rings, whereas in the evaporated thin films we expected the molecules to adopt a more planar conformation and thus similar electronic energy levels are easily rationalized.

The thermal properties of both **1** and **2** were investigated using differential scanning calorimetry in order to compare the properties of the bulk solids. In general, **1** and **2** display high melting and crystallization transitions, with sharp peaks and transitions occurring above 200 °C. Melting transitions for **1** and **2** were observed at 231 °C and 257 °C, respectively, and crystallization transitions were observed at 215 °C and 238 °C, respectively. The slight increase in melting and crystallization temperatures can be indicative of a more planar structure and increased π – π interaction between adjacent molecules for **2** than for **1** [21–23], which is consistent with the small Stokes shift observed. The DSC traces for the melting and crystallization transitions are shown in [Fig. 4](#) and the data are presented in [Table 1](#).

Considering compound **1** showed good charge carrier mobility in n-channel thin-film transistors (TFTs) [16], we initially set out to evaluate the electron mobility of **2**. Owing to their similar optical and electronic properties, but **2** appearing to adopt a more planar π -conjugated backbone, we anticipated that **2** might exhibit better TFT

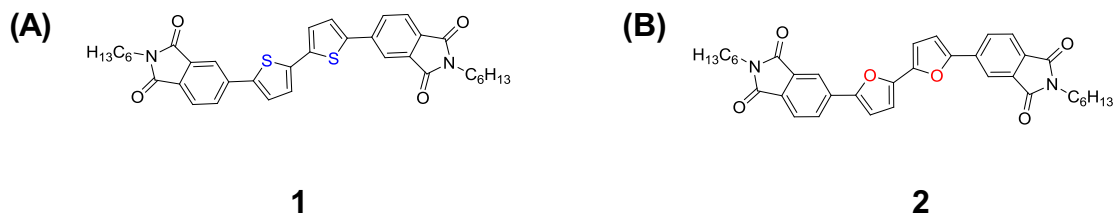


Fig. 1. Chemical structure of small molecules (A) **1**, (B) **2**.

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