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New bridged oligofuran for optoelectronic applications

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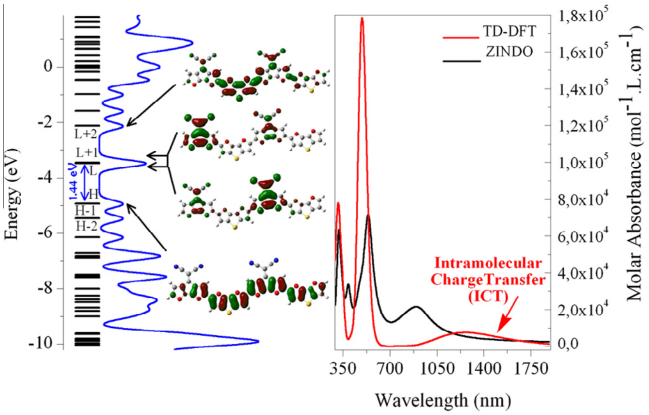
HIGHLIGHTS

- Designed new oligofuran-bridged systems for organic electronic devices.
- Band gap, HOMO, LUMO electron distributions and optical spectrum were analyzed for each molecule.
- Varied and interesting physical properties of the studied materials.

GRAPHICAL ABSTRACT

Designed new small band gap of FuC=C(CN)$_2$FuS oligomer for organic bulk heterojunction photovoltaic cell (OPC).



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ABSTRACT

Based on density functional theory (DFT) calculations, we have investigated the structural and optoelectronic properties of oligofuran (OFu)-bridged systems via useful electron donating groups (>S, >CH$_2$, >SiH$_2$ and >NH) and electron accepting ones (>C=C(CN)$_2$, >C=O, >C=S and >C=CH$_2$). The results were then discussed and compared with those obtained with the corresponding unbridged form. It was found that the optical band gap of OFu decreases significantly when it is bridged by >NH group arranged through an alternating way with >C=S or >C=C(CN)$_2$ group, which gives bridged polyfuran (PFu) with desirable opto-electronic properties. Further, an intra-molecular charge transfer for the systems was undertaken in support of time-dependent DFT (TD-DFT) and semi-empirical ZINDO calculations. In this frame, we have shown that >C=C(CN)$_2$ and >S bridging groups leads to a new oligomer possessing favorable optoelectronic parameter for its use as an active layer in organic photovoltaic cells.

Introduction

Due to their electro-conducting properties, polyheterocyclic polymers or oligomers continue to attract considerable attentions [1]. Therefore, intensive efforts have been undertaken to enhance their physicochemical properties by developing new synthesis ways [2,3] and doping processes [4]. Furthermore and recently, it was demonstrated that bridging procedure is considered as a new way to modulate optoelectronic properties of several pentacyclic polymers such as polythiophene (PTh) and polypyrrole (PPy) [5]. In fact, electronic properties of bridged oligomers are sensitive

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to the chemistry of the electron donating or accepting behaviours [6]. On the other hand, it has been shown in several studies that the insertion of spacer groups could enhance the charge carrier's transfer in the polymer [7]. In this context, among polyheterocyclic polymers, polyfuran (PFu) is an heteroatomic polymer having a several limitations due to its poorly defined structure, low aromaticity and high level of disorder [8]. In other words, it is difficult to obtain homo-polymer structure due to the significant cleavage of the furan rings occurred during the polymerization process, leading to some functional groups [9]. In order to explore and to improve the properties of PFu, we have developed a study focused on the bridging effect on the properties of this polymer. Thus, new variety of these polymers has been developed in order to improve their photo-physical properties and in particular to define precisely their structure–property relationship. In parallel, it is well known that theoretical calculations on oligomers help to understand their structure–property relationship and then constitute a model control of the charges' transport and optical properties in such materials [10]. Accordingly, through the density functional theory (DFT) calculations, we have theoretically investigated the main properties of bridged oligofuran by electron accepting groups and electron donating groups [11]. We also examined the ethylene group effect on the electronic properties of bridged OFu. On the second part, all the theoretical results derived from optimized structure were discussed in order to select the optimal one which could be used in optoelectronic devices.

Computational details

All calculations were carried out using density functional theory (DFT) implanted in GAUSSIAN (09) program [12] for isolated gas-phase molecules in their ground states. The geometric structure of each molecule was optimized using the most popular Becke's three parameters hybrid functional, B3 [13], with non-local correlation of Lee–Yang–Parr, LYP, abbreviated as B3LYP hybrid functional [14]. DFT calculations with B3LYP were performed with the 6-31G(d) level of theory. The energy of the highest occupied molecular orbital (ε_{HOMO}) and the lowest unoccupied molecular orbital (ε_{LUMO}) as well as the HOMO–LUMO energy difference (Δ_{H-L}) were also elucidated for all the studied compounds. The DFT//B3LYP/6-31G(d) method has been successfully applied to other conjugated oligomers [15,16]. Therefore, the optimized geometries were calculated for cationic and anionic charged states. Hence, the energies for the different charged states in the relevant geometries were obtained for calculating ionization potential (IP) and electronic affinity (EA). The force constants of each structure of bridged OFu were carried out using Mopac 2000 program [17]. We also plotted the contour maps of frontier molecular orbital with the help of "GaussView" program [18]. As for theoretical optical properties, time dependent density functional theory (TD-DFT) and semi-empirical ZINDO calculations were employed to predict the optical absorption spectra on optimized ground-state structures [19].

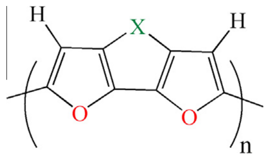

Fig. 1. Molecular structure of bridged octafuran.

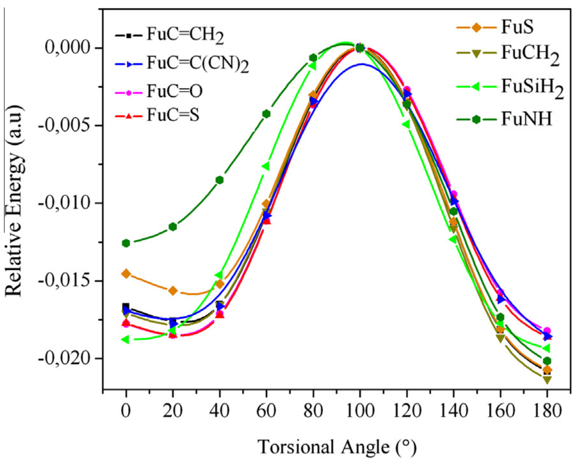

Fig. 2. Conformational analysis of different bridged octafuran.

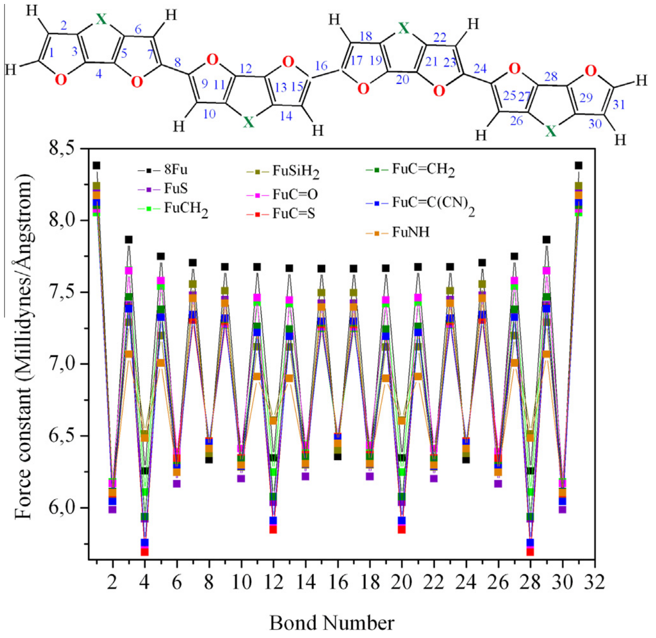

Fig. 3. Force constants of octafuran in bridged and unbridged forms. The horizontal axis label represents the individual bond in the numbering sequence, as shown at the top.

Electronic transitions assignments and oscillator strengths were also calculated using the same method of calculations. The theoret-

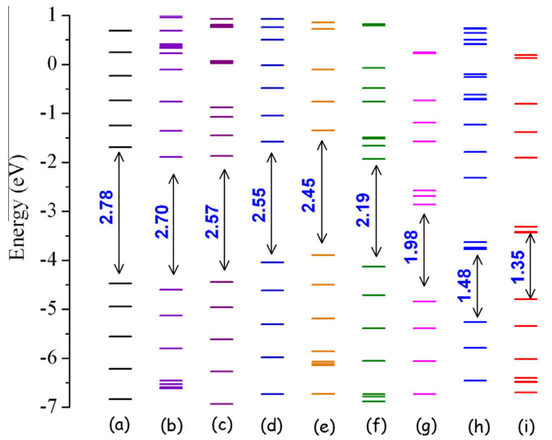

Fig. 4. The DFT//B3LYP/6-31G(d) electronic structures of octafuran in unbridged form [*8Fu (a)*] and bridged forms [*FuS (b), FuSiH$_2$ (c), FuNH (d), FuCH$_2$ (e), FuC=CH$_2$ (f), FuC=O (g), FuC=C(CN)$_2$ (h) and FuC=S (i)*].