

Substituent effects on furan-phenylene copolymer for photovoltaic improvement: A density functional study

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ABSTRACT

The structural, electronic and photovoltaic properties of furan-phenylene copolymer ((Fu-co-Ph)₄) and its derivatives were evaluated using density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The calculated band gaps of pristine furan and phenylene are in good agreement with the available experimental data. The lower band gap value of 2.72 eV was obtained from -NO₂ and -NHCH₃ substituents, leading to broader solar absorption range. With respect to the reorganization energy, -OCH₃, -NHCH₃, -OH, -SCH₃, -CH₃, -CF₃, -NO₂, and -F substituted (Fu-co-Ph)₄ structures were classified as better electron donor materials. For combination with PC₆₁BM, -NO₂, -CN, -CF₃ and -F functionalized copolymers demonstrated significantly higher open circuit voltage (V_{oc}) values ranging from 1.07 to 2.10 eV. Our results revealed that electron withdrawing group substitution on furan-phenylene copolymers was an effective way for improving electronic and optical properties of donor materials used in photovoltaic applications.

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1. Introduction

Conducting polymers (CPs) are extensively used as the donor material in bulk-heterojunction (BHJ) of polymer solar cells due to their favorable properties such as low cost of fabrication, light weight devices, mechanical flexibility, good electrical transport and solar absorption. For maximizing power conversion efficiency of polymer solar cells, the relevant parameters such as open-circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) are needed to be optimized by adjusting molecular energy levels of donor and acceptor incorporated at BHJ [1]. For acceptor, fullerene derivative of C₆₀ is the well-known electron transport species, while various new donor compounds based on conducting polymer were vastly introduced [2–6]. During the last decade, numerous experimental [7–22] and theoretical [23–27] studies were carried out for achieving higher efficient polymer solar cells. Among such researches, the concept of structural modifications was widely applied including substitution of functional groups onto polymer backbone and copolymerization of alternated electron withdrawing and electron donating monomers. It was reported that an introducing electron withdrawing group into backbone of conjugated

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polymers such as fluoro (-F) substituted poly(benzodithiophene-thienothiophene) [14], carbonyl groups (R-O-R') substituted 2D-conjugated polymer with alkylthio side-chain [15], cyano (-CN) and nitro (-NO₂) substituted phenylenevinylene [17], carboxylate (-COO-) substituted polythiophene [20], fluorine (-F), ester (RCOOR'), carbonyl (R-O-R'), sulfonyl (R-S(=O)₂-R') and cyano (-CN) substituted benzodifuran-alt-thienothiophene [22] given smaller band gap material with higher V_{oc} and PCE values, resulting to broader absorption range. Similar results were also found from attachments of alkoxy groups on backbone or side chain of thieno[3,4-*b*]thiophene and benzodithiophene copolymer [19] and benzodithiophene-based copolymer [16]. Recently, poly(furan-co-phenylene) was synthesized by electrochemical technique in the cholesteric liquid crystal medium, demonstrating the specific applications for optical filters, display devices, and optical diffraction devices [28]. However, a detailed understanding of electronic effects including charge analysis and optical properties is not well-described, especially for their functionalized structures. In addition, structural modification of poly(furan-co-phenylene) for photovoltaic application is still questioned. For theoretical analysis, substituent effects in different positions of block-copolymer seem not to be complicated since density functional theory (DFT) was successfully employed for describing electronic properties of various systems [29,30], especially for π -conjugated structures [31–33]. It was revealed that the predicted trends derived from

such method are similar to those determined from experiments [34–36].

In the present study, density functional theory (DFT) and time-dependent functional theory (TD-DFT) methods were performed for evaluating substituent effects of small functional groups including various electron donating groups (EDG) and electron withdrawing groups (EWG) on structural, electronic and optical properties of furan-phenylene copolymers ((Fu-co-Ph)₄). The hydrogen atoms situated at the 1st and 4th positions of the phenylene unit of the (Fu-co-Ph)₄ copolymers were replaced by several substituents (-X) such as -CH₃, -OCH₃, -CH₂OCH₃, -NHCH₃, -NH₂, -N(CH₃)₂, -SCH₃, -OH, -F, -CN, -NO₂, and -CF₃. For describing electronic properties, HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), HOMO-LUMO gap (E_g), ionization potential (IP), electron affinity (EA) and reorganization energy (λ) were calculated using the B3LYP/6-31G(d) method, while the excitation single state was estimated from TD-B3LYP/6-31G(d) calculations. Finally, hole and electron transport properties of the pristine (Fu-co-Ph)₄ and its derivatives ((Fu-co-Ph)₄-X) were evaluated for characterizing donor and acceptor behavior of the functionalized materials. To our best knowledge, a detailed description on structural, electronic, and optical properties of the functionalized furan-phenylene copolymers has not been addressed. Finally, the novel donor materials designed for better photovoltaic were proposed.

2. Computational method

The chemical structures of the pristine (Fu-co-Ph)₄ and its derivatives ((Fu-co-Ph)₄-X) investigated in this work are depicted in [scheme 1](#). Various electron donating groups: -CH₃, -OCH₃, -CH₂OCH₃, -NHCH₃, -NH₂, -N(CH₃)₂, -SCH₃, -OH and electron withdrawing groups: -F, -CN, -NO₂, -CF₃ substituents (-X) were attached to the 1st and 4th positions of the phenylene rings in the (Fu-co-Ph)₄ copolymers. It is noted that no structural data of furan-phenylene copolymer was experimentally obtained. The tetramer was chosen as a model for quantum calculation, according to the previous study of thiophene-phenylene copolymer [37]. In addition, such oligomeric size was successfully applied in other calculations of copolymers [38–40].

Structures of (Fu-co-Ph)₄ copolymer and its derivatives were optimized using the Becke's three-parameter hybrid, B3 with non-local correlation of Lee-Yang-Parr, the LYP (B3LYP) method [41] in conjunction with the 6-31G(d) basis set [42] since such method has been successfully applied for several relevant systems [33,43–47]. It was reported that B3LYP and CAM-B3LYP given the best results in comparison with experimental data, while B3LYP predicted better the energies of the frontier electronic levels [43]. The vibrational frequencies were also evaluated in order to ensure located minimum point of all optimized structures with no imaginary frequencies. The neutral, cationic, and anionic forms of (Fu-co-Ph)₄ structure including functionalized copolymers were calculated for elucidating the ionization potential energy (IP),

electron affinity (EA) and reorganization energy (λ_{total}) for hole (λ_{hole}) and electrons ($\lambda_{\text{electron}}$). Their corresponding equations are shown in Eqs. (1)–(4) [48].

$$IP_V = E_0^+ - E_0 \quad \text{and} \quad IP_A = E^+ - E_0 \quad (1)$$

$$EA_V = E_0 - E_0^- \quad \text{and} \quad EA_A = E_0 - E^- \quad (2)$$

$$\lambda_{(\text{hole})} = (E_0^+ - E_0) - (E_+ - E_0^+) \quad (3)$$

$$\lambda_{(\text{electron})} = (E_0^- - E_-) - (E_0 - E_0^-) \quad (4)$$

The subscripts V and A onto the ionization potential and electron affinity shown in (1) and (2) referring vertical and adiabatic approach in the calculations. $E_0^{+(-)}$ being the energy of cation (anion) evaluated from the optimized structure of neutral molecule. $E_{+(-)}^0$ representing the energy of neutral molecule examined at cationic (anion) state. E_0 , E_+ and E_- meaning the energies derived from the neutral, cationic, and anionic ground state structures, respectively. The efficiency of hole creation in donor material is directly related to the ionization potential, while the capability of electron injection is predicted from electron affinity. In addition, the power conversion efficiency (PCE) of solar cells is proportional to the open circuit voltage (V_{oc}), the short-circuit current density (J_{sc}) and the fill factor (FF) as defined by following formula [49].

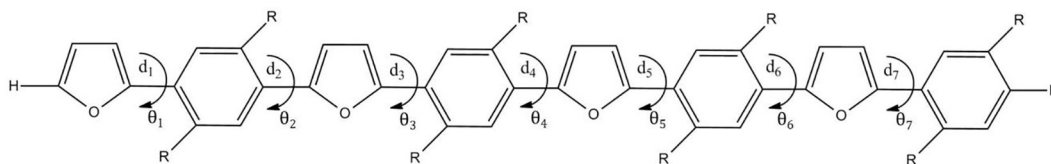
$$PCE = \frac{FF \cdot V_{oc} \cdot J_{sc}}{P_{in}} \quad (5)$$

where FF is the fill factor, V_{oc} is the open circuit voltage, J_{sc} is the short-circuit current and P_{in} is the incident power density. In order to theoretically estimate the performance of bulk hetero-junction (BHJ), the open circuit voltage (V_{oc}) based on the Scharber's model [50] is defined as following equation

$$V_{oc} = \frac{1}{e} |E_{\text{HOMO}}(\text{donor})| - |E_{\text{LUMO}}(\text{acceptor})| - 0.3V \quad (6)$$

$$\Delta E_{LL} = |E_{\text{LUMO}}(\text{acceptor})| - |E_{\text{LUMO}}(\text{donor})| \quad (7)$$

where e is the elementary charge, $E_{\text{HOMO}}(\text{donor})$ is the HOMO energy of the donor, $E_{\text{LUMO}}(\text{acceptor})$ is the LUMO energy of the acceptor (PC₆₁BM) and $E_{\text{LUMO}}(\text{donor})$ is the LUMO of the donor. The value 0.3 V is an empirical value of deviation between built-in potential and open circuit voltage. Optical properties including UV-Vis spectra, excitation energies, and oscillator strengths were simulated using the TD-B3LYP/6-31G(d) method. All calculations were performed using Gaussian 09 package [51] with the default temperature and pressure of 298.15 K and 1 atm, respectively. The molecular structures and frontier molecular orbital plots were displayed by Gaussview 4.1 program [52].



R = EDG: -OCH₃, -NH₂, -NHCH₃, -N(CH₃)₂, -OH, -SCH₃, -CH₃, -CH₂OCH₃
R = EWG: -CF₃, -CN, -NO₂, -F

Scheme 1. Sketch map of the structure, inter-ring bond and dihedral angle.

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