

Unraveling the Impact of Non-Covalent Interactions and Different Donor Moieties on Charge Transport in DPPT-Based Polymers

Jinyang Luo¹, Jiawei Dong², Guo Wang¹, Linjun Wang^{2,*} and Hua Geng^{1,*}

¹*Department of Chemistry, Capital Normal University, Beijing 100048, China;*

²*Zhejiang Key Laboratory of Excited-State Energy Conversion and Energy Storage, Department of Chemistry, Zhejiang University, Hangzhou 310058, China*

* Corresponding authors: hgeng@cnu.edu.cn

Received on 21 March 2025; Accepted on 23 April 2025

Abstract: The integration of both rigid and flexible components holds great potential to significantly enhance the overall performance of organic electronic devices. Non-covalent interactions are frequently harnessed to augment the planar conjugation of polymers, consequently elevating the rigidity of these polymers. However, the influence of the dihedral angle distortion between donor and acceptor units, which is induced by the flexibility inherent in donor-acceptor copolymers, on charge transport remains poorly understood. In this study, we systematically investigate intra-chain charge transport parameters and charge mobility for the 3,6-bis(thiophen-2-yl) diketopyrrolopyrrole (DPPT) conjugated with various donor moieties. Combining with density functional theory (DFT) and the Su-Schrieffer-Heeger (SSH) model, we find that when the non-covalent interactions between the donor and acceptor units are enhanced (as exemplified by DPPT-FT and DPPT-BO), the coupling between electrons and low-frequency vibrations is significantly suppressed. Simultaneously, the intra-chain electronic coupling increases owing to substantial orbital overlap. Surface hopping simulations are utilized to study the charge transport properties. For DPPT-T, DPPT-FT, and DPPT-BT, weaker molecular rigidity and disordered chain packing lead to thermally activated hopping transport (low electronic coupling and high reorganization energy). In contrast, the enhanced structural rigidity of DPPT-BO facilitates charge delocalization, leading to an initial improvement in carrier mobility under low-temperature conditions, and thermal fluctuation effects induce a band-like behavior at high temperature.

Key words: charge transport, Diketopyrrolopyrrole copolymers, torsional stiffness, non-covalent interactions, Su-Schrieffer-Heeger model.

1. Introduction

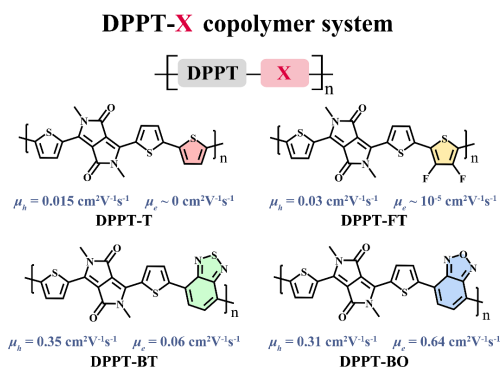
Conjugated donor-acceptor (D-A) polymers as organic semiconductor materials have attracted much attention due to their promising applications in organic electronic devices [1,2].

The performance of these devices heavily depends on the charge transport properties of the D-A conjugated polymers. For these kind of polymers, covalent interactions establish main-chain backbone, determining its fundamental charge transport capability, while non-covalent interactions (including hydrogen bonds, van der Waals forces, π - π stacking, electrostatic

interactions, etc.) modify the backbone, regulating intra-chain and inter-chain behavior as well as macroscopic properties (such as charge mobility and flexibility) [3-6]. With respect to inter-chain charge transport, it is more susceptible to the solvent used during device fabrication, the film preparation process, and the impact of side chains [6-8]. Intra-chain charge transport better reflects the intrinsic transport properties.[9-11] Through designing different donor-acceptor unit combinations within the polymer chain, remarkable high charge mobility has been obtained [11-14].

It is difficult to fully understand the influence of intra-chain non-covalent interactions on charge transport dynamics, since intra-chain non-covalent interactions have multiple impacts [4,6] [i] Intra-chain non-covalent interactions induce coplanar chain conformation, which facilitates π -orbital overlap, increases electronic coupling (V) and narrows the bandgap (E_g). The smaller Donor-Acceptor dihedral, the larger electronic coupling [15-17]. [ii] Intra-chain non-covalent interactions can restrict torsional freedom, promoting planar or folded conformations that minimize geometric disorder. By stabilizing chain geometry, intra-chain interactions decrease the reorganization energy (λ) required for charge transfer, enhancing the exponential term in Marcus theory [4]. [iii] Intra-chain non-covalent interactions can lower thermal activation barriers, enabling more efficient charge transport, especially at low temperatures [4,15]. However, excessively strong intra-chain interactions may create deep energy traps, capturing charge carriers, and increases trap density, reducing overall mobility [11, 12].

On the other hand, diketopyrrolopyrrole (DPP) based copolymers have attracted widely attention due to excellent ambipolar charge transport properties [1,18]. The measured values of charge mobility vary significantly under different experimental conditions. When DPPT, the derivative of DPP, is combined with different donor moieties, i.e., thiophene (T), 3,4-difluorothiophene (FT), benzothiadiazole (BT), benzoxadiazole (BO) then copolymerized, four D-A copolymers labeled as DPPT-T, DPPT-FT, DPPT-BT, DPPT-BO are obtained, the charge mobilities of these molecules range from 10^{-5} to $9.24 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ under different experimental conditions [19-23]. But for the purpose of comparison, we select the results obtained under same device structure (in a bottom-gate top contact (BG-TC) with SiO_2 as the dielectric) [22,23], and their charge mobilities in organic thin-film transistors have been reported ranging from 10^{-5} to $0.64 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (see **Scheme 1**).



Scheme 1. Investigated systems for DPPT-T, DPPT-FT, DPPT-BT and DPPT-BO copolymers, μ_h (μ_e) is the experimentally measured hole (electron) mobility [22, 23].

To unravel the impact of non-covalent interactions and different donor moieties on charge transport in DPPT-based polymers, we constructed the molecular structures for the copolymers of DPPT-T, DPPT-FT, DPPT-BT, DPPT-BO, as seen in Scheme1. Based on charge transport parameters and the Su-Schrieffer-Heeger (SSH) model [24], we find that strengthening non-covalent interactions between donor and acceptor units markedly reduces the coupling between electrons and low-frequency vibrations. Simultaneously, intrachain electronic coupling is enhanced. As the rigidity of DPPT copolymers increases, charge mobility obtained by surface hopping simulation exhibits a steeper rise with temperature. This behavior suggests diminished energy loss from charge relaxation due to intramolecular vibrations, thereby promoting efficient intra-chain charge transport.

2. Theoretical methodology

To study charge transport properties and to calculate intra-chain electron and hole mobilities, the DPPT copolymers were coarse-grained as one-dimensional arrays of DPPT and X units, based on tight-binding Su-Schrieffer-Heeger model, which considers both local and non-local electron-phonon (e-ph) couplings.[24] Thus, the electronic structure of these polymers can be described by the following total Hamiltonian [10,25],

$$H = H_e + H_n \quad (1)$$

with the electronic part written as

$$H_e = \sum_{k=1}^N (\epsilon_k + \alpha_{k,1}x_{k,1} + \alpha_{k,2}x_{k,2}) |k\rangle\langle k| + \sum_{k=2}^N J |\cos \theta_{k,k-1}| [|k\rangle\langle k-1| + |k-1\rangle\langle k|] \quad (2)$$

and the nuclear part as

$$H_n = \sum_{k=1}^N \frac{1}{2} \left(m_{k,1}v_{k,1}^2 + K_{k,1}x_{k,1}^2 + m_{k,2}v_{k,2}^2 + K_{k,2}x_{k,2}^2 + I_k\omega_{k,3}^2 \right) + \sum_{k=2}^N \frac{K_\theta}{2} (\theta_{k,k-1} - \theta_{eq})^2 \quad (3)$$

Here, ϵ_k represents the on-site energy of the donor/acceptor moiety in the neutral ground-state equilibrium geometry. J is the electronic (hole or electron) coupling modulated by a cosine function with angle $\theta_{k,k-1}$ describing the torsion between the DPPT and X units.[10, 25] The nuclear dynamics is described by three effective, classical, harmonic vibrational degrees of freedom: $x_{k,1}$, $x_{k,2}$, and $\theta_{k,k-1}$. The first two represent a high- and low-frequency intra-monomer mode, respectively, and account for the change in monomer geometry upon addition of excess holes or electrons. The k -th monomer energy is linearly modulated with these parameters by a local electron-phonon coupling constant ($\alpha_{k,1}$ and $\alpha_{k,2}$). This, in turn, is related to the relaxation energy $\lambda_{k,1(2)}$ by $\alpha_{k,1} = \sqrt{2K_{k,1(2)}\lambda_{k,1(2)}}$. The force constant of the harmonic oscillator is $K_{k,1(2)} = m_{k,1(2)}\omega_{k,1(2)}^2$,