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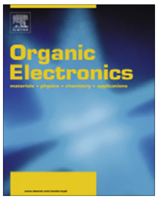

# Charge transport properties in a series of five-ring-fused thienoacenes: A quantum chemistry and molecular mechanic study

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ABSTRACT

The charge transport properties in a series of five-ring-fused thienoacenes are detailedly investigated here. With both high 3-D hole mobilities and good oxidative stability, the thiophene–benzene alternate structures in series B should be better than other two series as *p*-type organic semiconductors. In addition, a theoretical explanation for the difference between experimental hole mobilities in B-3 and B-3* is provided based on crystal structure prediction. The role of dynamic disorder in C-3 is also investigated here and the results indicate that dynamic disorder plays a crucial role both in the 1-D and 2-D carrier transporting process.

## 1. Introduction

Organic semiconductors based on π-conjugated materials are of great interests for their applications in optoelectronic and microelectronic devices, for instance, organic light-emitting diodes (OLEDs) [1,2], organic field-effect-transistors (OFETs) [3–5] and organic photovoltaic devices (OPVs) [6,7]. Pentacene [8–13] and oligo/polythiophenes [14,15] are the representative *p*-type organic semiconductors in the last twenty years. Pentacene, its experimental hole mobility within the range from 0.25 to 35 $cm^2\ V^{-1}\ s^{-1}$ [16–23], suffers from the oxidative instability and poor solubility [24,25]. Many investigations based on modified pentacene have been widely carried out for developing OFET materials which possess not only high carrier mobilities but also excellent stability in ambient atmosphere. Notably, introducing thiophene rings into pentacene to yield new five-ring-fused thienoacenes has attracted much attention [26–31].

Up to now, a great number of five-ring-fused thienoacenes have been synthesized in experiments. As the different combinations of thiophene rings and benzene rings, these five-ring-fused heteroacenes can be divided into three series: acene[n]thiophenes(Ac[n]Ts, series A) [32–34], benzene–thiophene alternating molecules (BTAs, series B) [35–38] and [n]thienoacenes([n]TAcs, series C) [39–43]. Moreover, each series consists of several members according to the number of thiophene rings or cis–trans isomerism (see Fig. 1). Some work in experimental have found that introducing thiophene rings into the fused oligoacenes widens the HOMO–LUMO gaps and hence improves the oxidative stability [44]. However, the influence of different combinations on their stability and carrier transport properties was not mentioned. Neckers et al. demonstrated that the carrier mobility was related to the thiophene orientation (B-3 and B-3* in Fig. 1). Their research results indicated that B-3* exhibited higher hole mobility than B-3 by one order magnitude [35]. Anthony considered that it was likely due to the difference in grain sizes observed upon AFM analysis of the thin films [29]. In the theoretical investigation, Bredas et al. detailedly

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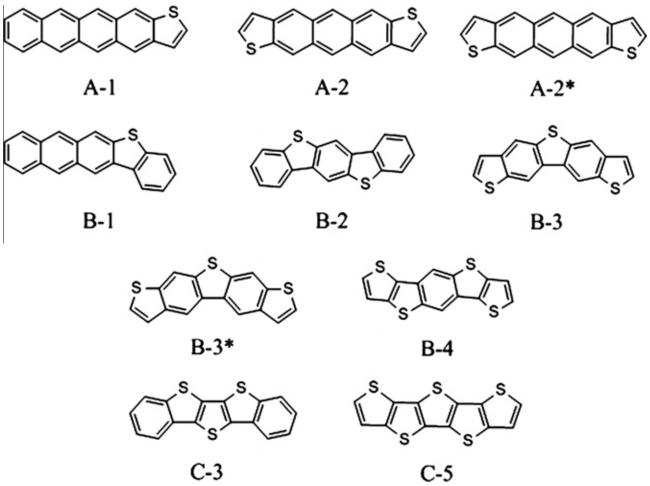

**Fig. 1.** Chemical structures of five-ring-fused molecules investigated in this study. A, B, and C refer to Ac[n]Ts, BTAs and [n]TAcs respectively. The numbers refer to the number of thiophene rings and (*) means cis-isomer.

investigated the vibrational coupling in B-3 and B-3*. Their results showed that the hole-vibrational couplings between these two isomers were remarkably different [45]. To explain this, a better understanding of the relation between intrinsic hole mobilities and molecular structures in five-ring-fused thienoacenes is needed. Hu et al. have reported that the [n]TAcs (C-3 and C-5 in Fig. 1) should be promising candidates for *p*-type organic electronics [39,42]. Especially for C-3, its anisotropic hole mobility in single crystal device was up to 1.8 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Here comes the question: which kind of combination in these three series five-ring-fused thienoacenes has the most advantage as *p*-type organic semiconductors?

The objective of the present work is to investigate the influence of the intrinsic electronic structure and topography of these three series five-ring-fused thienoacenes on their stability and carrier transport properties. Therefore, a quantum chemistry and molecular mechanic combined approach is applied here to investigate the energy levels, the reorganization energies, the molecular stacking arrangement, the transfer integrals and the carrier mobilities of those molecules. Through our study, the effect of different combination in five-ring-fused thienoacenes on stability and transport parameters is revealed, which can provide theoretical support and useful information for molecular design and synthesis of the promising organic semiconductors.

## 2. Theoretical and computational approaches

In general, there are two types of carrier motion in organic solid materials: the coherent band mechanism and the incoherent hopping mechanism [46–49]. The former is suitable for highly ordered organic crystals at low temperature, where carrier motion occurs as a delocalized plane wave in energy band [46]. The interaction between the nearest molecules is comparable with the dynamic disorder, for example, reorganization energies are resulting from the charge transfer process between the nearest dimers [50,51]. When it comes to the high temperatures (maybe room temperature) or less-ordered system (or polycrystalline system), interactions of organic molecules are mainly from weak van der Waals forces, in which charge carriers are expected to be strongly localized over one molecule due to the dynamic structure disorder. Thus, the coherent band mechanism is not suitable in this case and the incoherent hopping mechanism is often employed [46]. In this study, the hopping mechanism is adopted as the transport mechanism.

The hopping mechanism can be described as a self-exchange reaction $M + M^{\pm} = M^{\pm} + M$ in which an electron or hole jumps from one charged molecule to another adjacent neutral molecule. The hopping rate can be expressed by Marcus theory via the following equation:[52]

$$k_{ct} = \frac{V^2}{\hbar}\left(\frac{\pi}{\lambda k_B T}\right)^{1/2} \exp\left\{-\frac{\lambda}{4k_B T}\right\} \tag{1}$$

where $\lambda$ is the reorganization energy, $V$ the intermolecular charge transfer integral, $T$ the temperature, and $k_B$ the Boltzmann constant. Eq. (1) is applicable for $V \ll \lambda$. It can be seen from Eq. (1) that the charge transfer rate is mainly determined by two major parameters: the reorganization energy ($\lambda$) and the intermolecular charge transfer integral ($V$).

The reorganization energy ($\lambda$) consists of intramolecular reorganization energy and intermolecular reorganization energy. However, intermolecular reorganization energy is much smaller than intramolecular one in organic solid [50]. Thus, the intramolecular reorganization energy, which reflects the deformation of the molecular geometry in charge transfer process, is only considered in this study. The intramolecular reorganization energy can be obtained in two ways: (1) from the adiabatic potential surfaces (AP) of neutral/charged species (see Fig. 2) [53,54] and (2) from the normal mode analysis (NM) [55–57]. Latter principle is that intramolecular reorganization energy of a molecule is dominated by its intrinsic vibrations, contribution of every