Theoretically Rational Designs of Transport Organic Semiconductors Based on Heteroacenes

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A Marcus electron transfer theory coupled with an incoherent polaron hopping and charge diffusion model in combining with first-principle quantum chemistry calculation was applied to investigating the effects of heteroatom on the intermolecular charge transfer rate for a series of heteroacene molecules. The influences of intermolecular packing and charge reorganization energy were discussed. It was found that the sulphur and nitrogen substituted heteroacenes were intrinsically hole-transporting materials due to the reduced hole reorganization energy and the enhanced overlap between HOMOs. For the oxygen-substituted heteroacene, it was found that both the electronic couplings and the reorganization energies for holes and electrons were comparative, indicating the application potential of ambipolar devices. Most interestingly, for the boron-substituted heteroacenes, theoretical calculations predicted a promising electron-transport material, which is rare for organic materials. These findings provide insights into rationally designing organic semiconductors with specific properties.

Keywords   organic field-effect transistor, charge transfer, theoretical design of transport material

Introduction

Conjugated organic materials with high charge carrier mobility and good stability in ambient condition are highly desirable in optical and electronic devices[1-8] because they show the advantages of being relatively low-cost, flexible and having tunable electronic properties. Charge transport properties are the key issue for the realization of these applications. Most of organic semiconductors are hole transport materials, because usually the hole mobility is much higher than the electron mobility as well as many electron trap centers present. It is highly desirable for designing both ambipolar organic materials in which both hole and electron can transport in equilibrium, and the electron transport materials. Recently, there has been great progress in obtaining hole-transporting (p-type) organic semiconductors showing high mobilities (larger than 1.0 $cm^2•V^{-1}•s^{-1}$).[9-11] In contrast, relatively rare efficient electron-transporting (n-type) organic semiconductors were reported. To date, one approach to find n-type materials is substituting p-type compounds with strongly electronegative groups, and the other way is to use electron-deficient π-conjugated cores.[12-17]

Acene molecules have been demonstrated as high-performance p-type semiconductors.[18] Recently, Wakim *et al*[19] and Kawaguchi *et al*[20] have synthesized some heteroacenes containing N and O atoms. Nitrogen-substituted acenes have also shown hole-transporting.[11]

In this work, we will theoretically investigate the effects of different heteroatoms on the charge-transfer properties in heteroacenes in order to shed light on how to design ambipolar materials and electron transport materials.

Computational methods

There are two kinds of mechanisms of charge transfer in materials: (i) the coherent band model, which is usually suitable for highly ordered inorganic semiconductors and organic single-crystal systems at very low temperatures and (ii) the hopping-type mechanism.[21] Near room temperature, organic conjugated molecules can be described with a hopping mechanism due to the dynamic structure disorders usually present in organic materials.[22]

In this model, the charge-transfer rate for hole or electron transport between two neighbouring molecules at a fixed temperature (T) is described by Marcus theory as,[23-25]

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

where $\hbar$ is the Planck constant and k_B the Boltzmann constant. There are two key parameters governing the incoherent hopping transport: the reorganization energy (λ) and the transfer integral between neighboring mole-

1006 *Chin. J. Chem.*, 2008, Vol. 26, No. 6

HE *et al.*

cules (*V*).

The reorganization energy reflects the energy difference arising from the structure relaxation of the two neighboring molecules upon charge transfer. For a p-type molecular semiconductor, λ is calculated as,[25,26]

$$\lambda_h = E^+(Z) - E^+(Z^+) + E(Z^+) - E(Z) \quad (2)$$

where $E^+(Z)$ is the energy of the cationic molecule in an optimized neutral geometry, $E^+(Z^+)$ the optimized energy of the cationic molecule, $E(Z^+)$ the energy of the neutral molecule in the optimized cationic geometry, and $E(Z)$ the optimized energy of the neutral molecule. Similarly, for an n-type semiconductor, the reorganization energy reads:

$$\lambda_e = E^-(Z) - E^-(Z^-) + E(Z^-) - E(Z) \quad (3)$$

where $E^-(Z)$ is the energy of an anionic molecule in the neutral geometry, $E^-(Z^-)$ the optimized energy of the anionic molecule, and $E(Z^-)$ the energy of the neutral molecule in the anionic geometry.

According to the method proposed by Valeev and co-workers,[27,28] we can evaluate the hole (electron) transfer integral by the effective electronic coupling matrix element between the highest occupied molecular orbitals, HOMOs (lowest unoccupied molecular orbitals, LUMOs) of the two neighboring monomers, which is expressed as,

$$V = \frac{H_{12} - \frac{1}{2}(H_{11} + H_{22})S_{12}}{1 - S_{12}^2} \quad (4)$$

The *H* matrix elements are calculated by

$$H_{ij} = \langle \Phi_i | F | \Phi_j \rangle \quad (5)$$

where Φ_i and Φ_j represent the HOMOs (for hole transport) or LUMOs (for electron transport) of the isolated molecule in the dimer. *F* is the self-consistent Fock matrix of the dimer. S_{12} is the overlap integral between Φ_1 and Φ_2.

All the calculations were carried out at the hybrid density functional theory (DFT) level using the B3LYP functional coupled with 6-31G* basis set with Gaussian 03 package.[29] The optimized molecular geometries for all molecules (see Figure 1) exhibit planar structures (*xy* plane). We have validated our computational approaches by performing calculations with different basis sets under the same hybrid functional (B3LYP) on the boron-substituted acene. Table 1 presents the hole and electron transfer integrals and reorganization energies for different basis set. The transfer integrals were derived from the intermolecular packing mode that the two monomers were separated along *z*-axis at a distance of 3.5 Å. We can see that the dependence on basis set is minor and the influence on the results is not significant. Thus, the choice of 6-31G* can satisfy our requirements on analyzing the structure-property relationship in terms of dominant charge carrier type: electron or hole.
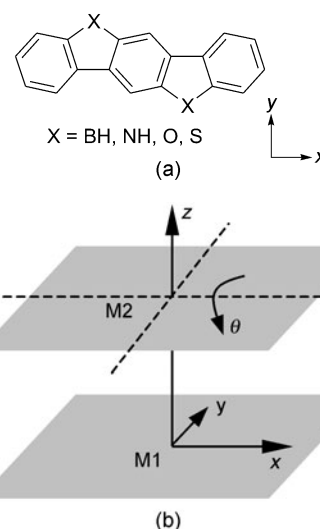

Figure 1 Molecular structures of the studied heteroacences and *xyz* coordinates (a) and molecular packing mode of the dimer (b).

Table 1 Dependence of the hole and electron transfer integrals (*V*) and the reorganization energies (λ) on basis set

		Basis				
		6-31G	6-31G*	6-31G**	6-311G	6-311G*
V/eV	Hole	0.337	0.336	0.336	0.333	0.335
	Electron	0.510	0.509	0.509	0.496	0.498
λ/eV	Hole	0.234	0.240	0.240	0.243	0.243
	Electron	0.157	0.175	0.173	0.168	0.173

Results and discussion

From Eq. 1, we know that the reorganization energy provides a transport barrier with thermal activation energy $\lambda/4$. The transfer integral (*V*) provides the necessary coupling for charge to diffuse. Our purpose is to investigate how heteroatoms affect these two parameters.

We first discuss the influence of heteroatom on the HOMO and LUMO of an isolated molecule. Figure 2 depicts the schemes of HOMOs and LUMOs for the different heteroacene molecules. We note that the HOMOs of the B-, O-, N- and S-substituted heteroacenes are similar in shape. The electron densities at the B and O atoms are zero, meaning that there is no contribution to the hole transfer integral from the heteroatom for B or O substitution. However, for N- or S-substituted acenes, the electron density at N and S atoms, especially at S, is relatively large. Consequently, the relative orientations of the heteroatoms of the neighboring heteroacenes have great effects on the hole transfer integral for N- and S-acenes.

It is important to note that the LUMO of the molecules with electron-deficient B atoms is very different from other three substitutions, and the latter have similar electronic distributions. The electronic distribution of LUMO for the B-substituted heteroacene is more local
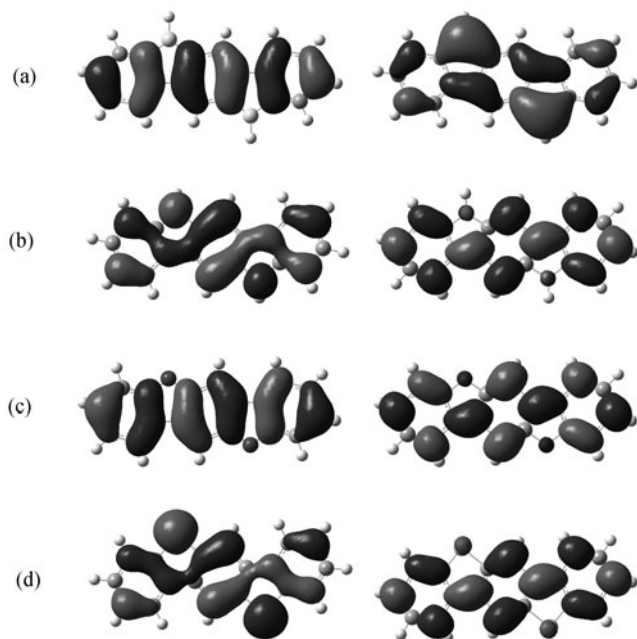
Charge transfer

Chin. J. Chem., 2008 Vol. 26 No. 6 **1007**

Figure 2 B3LYP/6-31G* calculated HOMOs (left) and LUMOs (right) for (a) B-, (b) N-, (c) O-, and (d) S-substituted acenes.

and concentrated at the B atoms, whereas there is almost no charge density at the heteroatoms for the other three heteroacenes. Thus it can be anticipated that boron-substitution can strongly influence the electron transport.

The intermolecular electronic coupling depends on the relative orientations and solid-state packing. Figures 3—6 show the evolutions of the transfer integrals for

electron (LUMO) and hole (HOMO) with respect to the sliding distances along *z*-, *x*- and *y*-axes and the rotation angles between two heteroacene molecules.

From Figure 3, we find that the transfer integral decreases sharply with the π-π stacking distance (along *z*-axis) and approaches zero at a distance of *ca.* 6 Å, which is shorter than twice of π-π interaction distance (usually set to be 3.5 Å). That means charge transfer can happen only between two neighbouring molecules in organic semiconductors. Along the *z*-axis, the hole transfer integral for the S-substituted acene is larger than the electron counterpart. Together with the smaller reorganization energy λ_h for hole (see Figure 7), Eq. 1 leads to much higher value for hole transfer than electron transfer. This is in agreement with experiment that S-substituted acenes are hole-transporting materials.[9]

Most interestingly, the transfer integral for electron in B-substituted acenes is larger than that for hole, whereas λ_e is smaller than λ_h (see Figure 7). This theoretical finding indicates that the B-acene based materials can be suitable for n-type semiconductors, which is highly demanding.

Along the *x*-axis, the transfer integrals exhibit damped oscillations with intermolecular separation (see Figure 4). The maximal and minimal values of the transfer integrals correspond to the positions where the HOMOs/LUMOs of the two isolated molecules have maximal and minimal overlaps. From Figure 5, the hole transfer integrals for B- and O-substituted acenes always decrease with increasing the distance between the two monomers along the *y*-axis. For the rest of transfer integrals along the *y*-axis, similar evolutions as along the
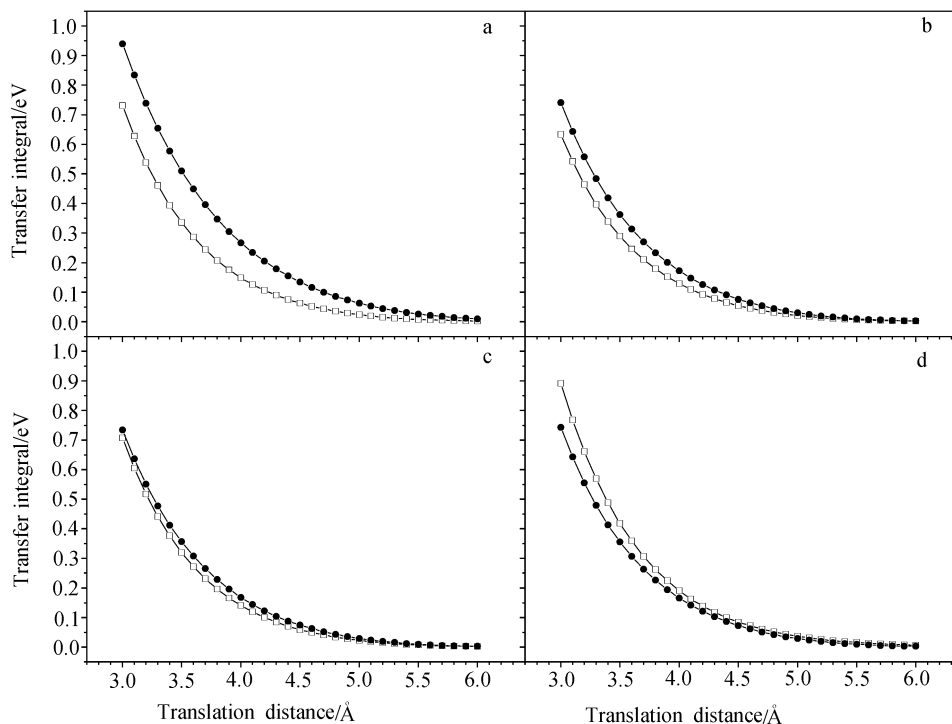

Figure 3 Evolution of hole (□) and electron (●) transfer integral with the translation distance along the *z*-axis for (a) B-, (b) N-, (c) O- and (d) S-substituted heteroacenes (translations along *x*- and *y*-axes are set to zero).
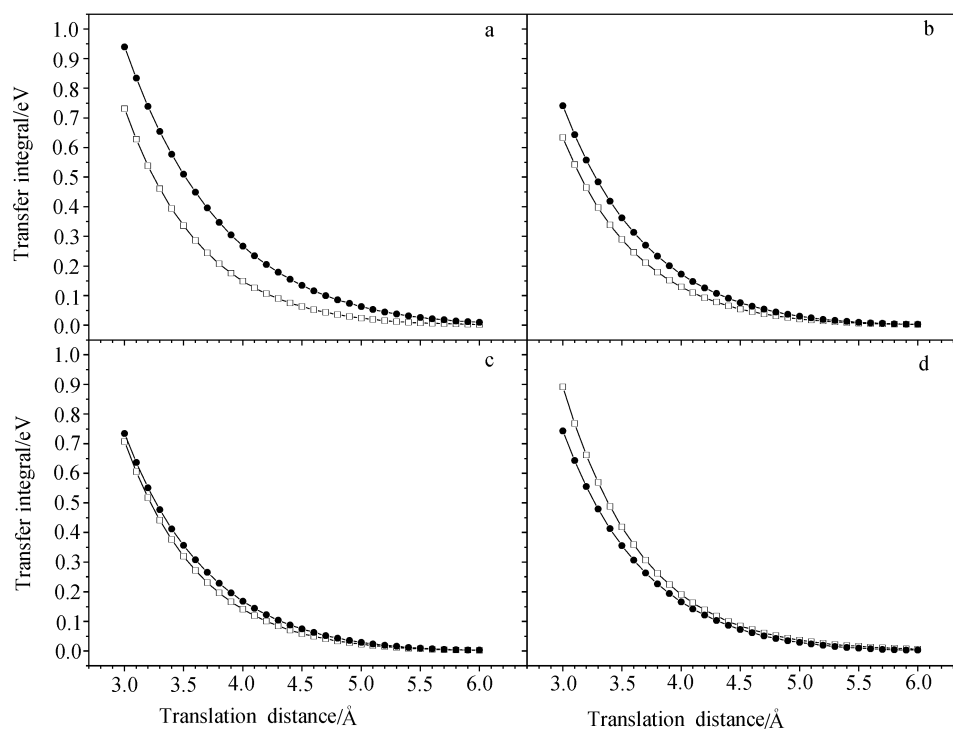
Figure 4 Evolution of hole (□) and electron (●) transfer integral with the translation distance along the *x*-axis direction for (a) B-, (b) N-, (c) O- and (d) S-substituted heteroacenes (translation along *y*-axis is set to zero and the separation in *z*-axis is set to be 3.5 Å).
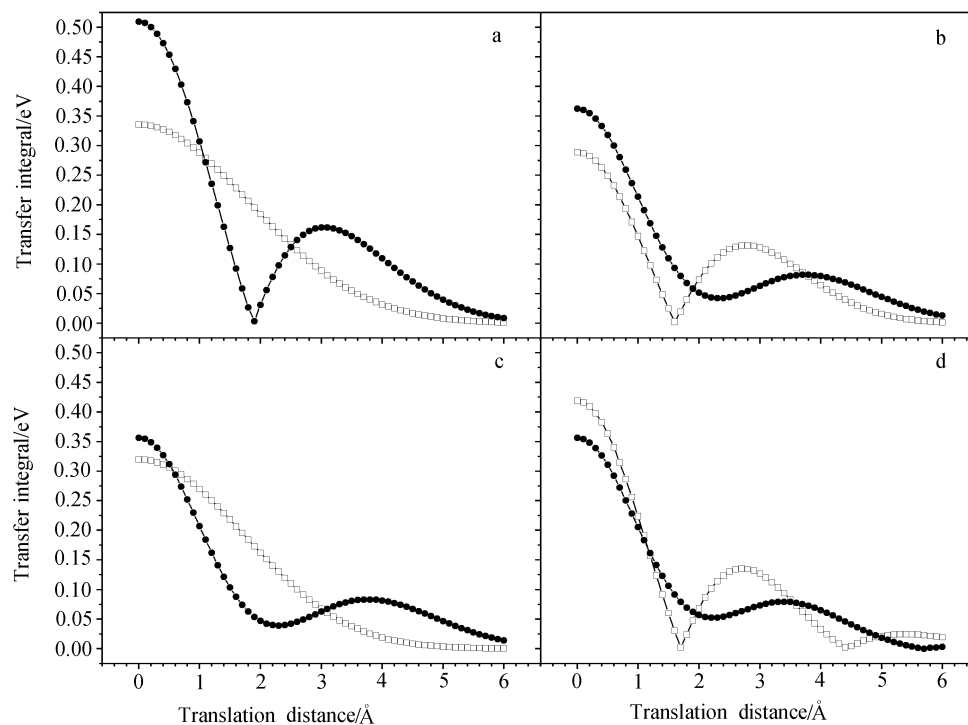
Figure 5 Evolution of hole (□) and electron (●) transfer integral with the translation distance along the *y*-axis direction for (a) B-, (b) N-, (c) O- and (d) S-substituted heteroacenes (translation along *x*-axis is set to zero and the separation along *z*-axis is 3.5 Å).

x-axis are found, but with much less oscillations.

Now, we investigate the evolution of the transfer integral with respect to the relative orientation angle (see Figure 6). We find that the heteroatoms have special influences on the transfer integral. If the heteroatoms have large electronic distribution in the HOMOs (for N- and S-acenes) or LUMOs (for B-acene), the transfer integrals will increase when the two heteroatoms in the different monomers approach each other by rotating one of the two molecules. If the heteroatoms are not present at the frontier orbitals, then the transfer integral is not influenced even when they get
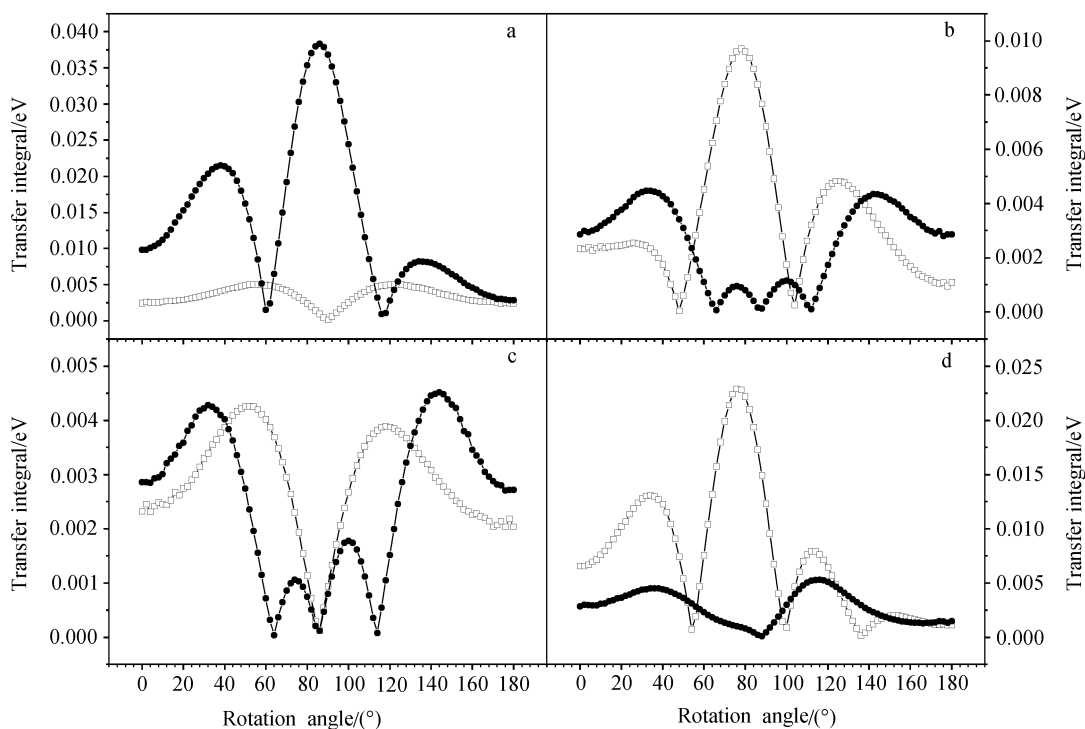
Charge transfer

Chin. J. Chem., 2008 *Vol. 26 No. 6* **1009**

Figure 6 Evolution of hole (□) and electron (●) transfer integral with the rotation angle for (a) B-, (b) N-, (c) O- and (d) S-substituted heteroacenes (translations along *x*- and *y*-axes are set to zero and the separation along *z*-axes is 5.0 Å).

closer during the rotation. Especially, when the heteroatom of one monomer is nearest to the other monomer (rotation angle is *ca.* 90°), the value of hole transfer integral for N- and S-acenes and electron transfer integral for B-acene will reach the maximum due to the maximal orbital overlap. If there is no electronic distribution in the edge heteroatom, the transfer integrals will reach a minimum or a very small value in such an angle.

Figure 7 shows the DFT calculated reorganization energies and energies of HOMO and LUMO levels for all the heteroacene molecules. For S- and N-substituted acenes, especially for S-acene, λ_h is much less than λ_e, resulting in predominant hole-transporting characteristics in these materials. For O-acene, λ_e is somewhat smaller than λ_h, and the transfer integrals for hole and electron along *z*-axis are comparative (see Figure 3), so we can expect an ambipolar behavior. The B-substituted acenes typically present a smaller electron reorganization energy and higher electronic coupling terms for appropriate intermolecular packing, indicating that the boron-substituted acenes can be promising electron transport materials.

Conclusion

To summarize, through quantum chemistry calculations within the framework of Marcus electron transfer theory, we found that the heteroacenes provided a very rich chemistry for materials. For the nitrogen- and sulphur-substitutions, we found that it was the hole that dominated the charge transport because of the small hole reorganization energy and large intermolecular
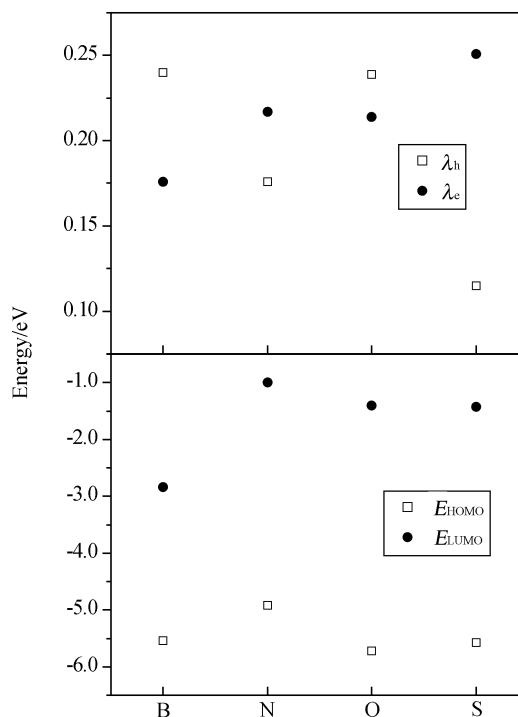

Figure 7 B3LYP/6-31G* calculated reorganization energies for hole λ_h and electron λ_e (top panel) and HOMO and LUMO energies (E_{HOMO} and E_{LUMO}) of the studied heteroacenes (bottom panel).

HOMO coupling. For the oxygen-substitution, a possible ambipolar behavior was predicted. Namely, hole and electron could transport in equilibrium. For the boron-substitution, the electron was found to be the dominant

charge carriers. This is rare because most of organic materials are hole transporting. These results provide rich insights into designing organic semiconductors for the electronics applications.

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