

Toward High Performance Ambipolar Transport from Super-exchange Perspective: Theoretical Insights for IID-based Copolymers

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 Electronic Supplementary Information

Abstract High-performance ambipolar charge transport materials can reduce the manufacturing cost of OFET and OPV devices, and simplify circuit design and device structure. In order to obtain ambipolar donor-acceptor (D-A) polymer, many efforts have been made through different donor and acceptor combination, halogenation or heteroatom substitution. However, the influencing factor for charge transport polarity is still much complicated. Based on intra-chain super-exchange mechanism for D-A polymer, we found that the energy alignment of donor and acceptor moiety has large impact on charge transport polarity. When the HOMO-LUMO (H-L) gap of the acceptor moiety is narrow, its HOMO/LUMO energy level both lie between the HOMO and LUMO of the donor moiety (sandwich-type energy alignment), and the corresponding D-A copolymers will be more likely ambipolar transport. And thus, take a narrow H-L gap thiazoleisoindigo (TzIID) acceptor as an example, we demonstrated that a series of TzIID based copolymers combined with wide H-L gap donor moieties can reveal ambipolar transport. We further predict several high performance ambipolar D-A copolymers (TzIID-TT etc.) with balanced electron and hole transport, whose effective mass ($m_e^* = 0.146$ and $m_h^* = 0.128$) is one of the smallest effective masses among ambipolar materials.

Keywords D-A copolymer; Ambipolar; Super-exchange mechanism; Charge transport

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INTRODUCTION

Donor-acceptor (D-A) conjugated polymers are widely used in optoelectronic devices such as organic photovoltaic (OPV)^[1–6] and organic field effect transistor (OFET)^[7–10] because of their solution processability, flexibility and temperature stability. Balanced ambipolar charge transport materials are conducive to simplifying the device structure and reducing manufacturing costs.^[11,12] Therefore, it is necessary to further design and develop new ambipolar transport materials with high charge carrier mobility.

The charge transport performance and polarity of D-A copolymers are affected and limited by many factors, such as side chains, molecular weight, solubility, microstructure, charge injection, and inter-chain or intra-chain charge transport.^[13,14] With respect to molecular design, combining different donor and acceptor moieties in copolymer is an effective strategy for experimentally obtaining ambipolar materials,^[15–20] such as changing the ratio of donor or acceptor moiety, heteroatom substitution or halogenation.^[20–23] IID based copolymers usually exhibit hole dominant transport or

ambipolar transport properties with relatively low charge mobility.^[20] Through introducing heteroatoms or fused rings into the backbone of copolymers, the charge transport polarity can be modulated and corresponding charge mobility was improved.^[24–26] Combining with different donor moieties, the copolymers based on azaisoindigo (AzIID)^[27,28] and thiaisoindigo (ThIID)^[21,29,30] have been reported with much higher hole mobility than that of IID based copolymers. While the thiazoleisoindigo (TzIID) moiety is combined with different donor moieties, corresponding copolymers have been found to be ambipolar transport properties with high mobility.^[31,32] And thus, minor chemical modification has a large effect on the charge transport polarity and mobility performance. Due to the structural complexity of conjugated polymers, the dynamic evolution of the geometric structure considering static and dynamic disorder have been investigated by many scientists.^[33–35]

With the advancement of material processing technology, one-dimensional (1D) nanowires with high charge mobility have been successfully obtained.^[36–39] The charge transport along the polymer main chain has been found to play a major role.^[40–45] However, there still exists great controversy in intra-chain transport in D-A copolymer.^[46–49] Although D-A co-crystal requires large intermolecular HOMO-LUMO (H-L) coupling for ambipolar characteristics, the D-A co-polymer

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does not.^[50,51] Since intermolecular donor acceptor interactions have large difference with bond-mediated D-A copolymers,^[51] the D-A copolymer presents different characters. The linkage sites and energy alignment between donor and acceptor moieties play important roles in the charge transport of the D-A copolymers.^[52–54]

Herein, we calculated electronic structures for a series of IID-based copolymers, as shown in Scheme 1. Based on the intra-chain bond-mediated super-exchange (SE) mechanism, we found that the energy alignment of the donor and acceptor moieties has a large impact on the charge transport polarity. When the acceptor moiety with narrow H-L gap combines the donor moiety with wide bandgap, the HOMO/LUMO energy level of the acceptor moiety both lie between the HOMO and LUMO of the donor moiety, the corresponding copolymer will more likely be ambipolar transport material. Take narrow H-L gap TzIID moiety as an example, we constructed TzIID based copolymers with a series of wide H-L gap donors (as shown in Scheme 1b), and predicted several high-performance ambipolar D-A copolymers with balanced electron and hole transport, whose effective mass ($m_h^*=0.128m_0$ and $m_e^*=0.146m_0$) is one of the smallest effective masses among ambipolar materials.

COMPUTATIONAL DETAILS AND MODEL

The electronic structure are calculated at B3LYP/6-31G(d) level with the GAUSSIAN09 code.^[55] In order to simplify the calculation, the side chain is replaced with a methyl group. The geometric structure of the 1D periodic polymer chain were optimized at PBE (Perdew-Burke-Ernzerhof) level with the VASP code.^[56] Uniform $21 \times 1 \times 1$ Monkhorst-Pack k-point mesh was employed for all D-A copolymers. We calculated 41 k-points between the gamma point (centre of the Brillouin Zone, BZ) and the edge of the first BZ to obtain the band structure along the direction of the copolymer's main chain. The effective mass for 1D crystal is obtained from the second order derivative of band energy.

The intra-chain SE coupling can be evaluated from Larsson partition approach. Based on the Hamiltonian and overlap matrix of triad system, which can be projected to the fragment molecular orbitals of donor, acceptor and bridge are as follows:

$$H = \begin{pmatrix} \varepsilon_1 & V_{12} & V_{1B} \\ V_{21} & \varepsilon_2 & V_{2B} \\ V_{B1} & V_{B2} & \varepsilon_B \end{pmatrix} \quad (1)$$

$$S = \begin{pmatrix} 1 & S_{12} & S_{1B} \\ S_{21} & 1 & S_{2B} \\ S_{B1} & S_{B2} & 1 \end{pmatrix} \quad (2)$$

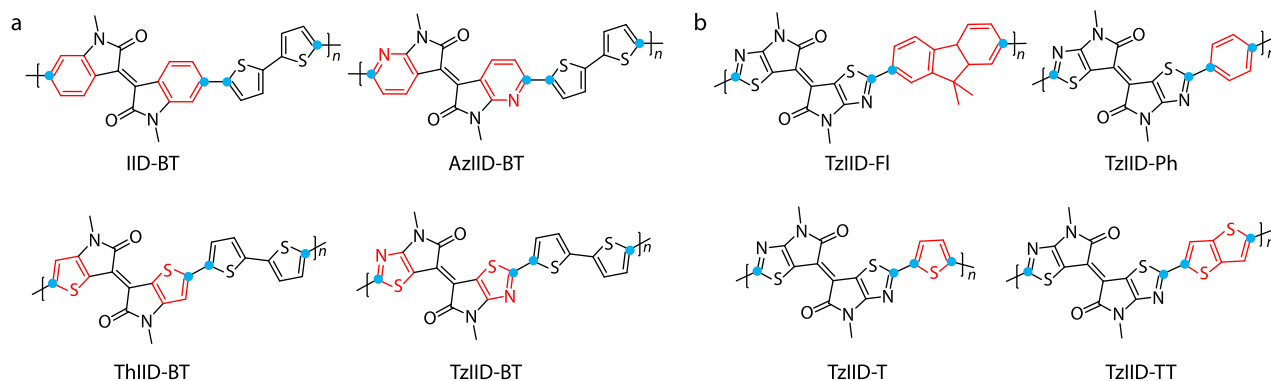
where, the matrix element $\varepsilon_i = \langle \psi_i | H | \psi_i \rangle$, $V_{ij} = V_{ji} = \langle \psi_i | H | \psi_j \rangle$ and $S_{ij} = S_{ji} = \langle \psi_i | \psi_j \rangle$. The fragment molecular orbital ψ_{ij} as basis set were normalized without hydrogen, which denotes the oligomer triad orbitals localized on donor or acceptor fragments. For hole (electron) transport, ψ_1 and ψ_2 are the HOMO (LUMO) of D1 (A1) and D2 (A2), respectively, and ψ_B represents the molecular orbitals of the bridge A (D) fragment. By means of Löwdin's symmetric transformation, site energy corrected from polarization can be considered as follows:

$$\tilde{H} = S^{-1/2} H S^{-1/2} = \begin{pmatrix} \tilde{\varepsilon}_1 & \tilde{V}_{12} & \tilde{V}_{1B} \\ \tilde{V}_{21} & \tilde{\varepsilon}_2 & \tilde{V}_{2B} \\ \tilde{V}_{B1} & \tilde{V}_{B2} & \tilde{\varepsilon}_B \end{pmatrix} \quad (3)$$

Next, using Larsson partition technique in connection with perturbation scheme, we obtain the effective electronic coupling:

$$V^{\text{eff}} = V^{\text{im}} + \sum_{b \in B} \frac{\tilde{V}_{1b} \tilde{V}_{b2}}{E - \tilde{\varepsilon}_b} \quad (4)$$

The $\tilde{V}_{12}$ is obtained through projection Hamiltonian of triad system on orthogonalized fragment basis and substantially weaker than the second term. $\tilde{V}_{1b}$ and $\tilde{V}_{b2}$ denote the coupling of the bridge orbital (b) with the frontier orbitals of the two adjacent fragments (1 and 2); E and $\tilde{\varepsilon}_b$ correspond to the energies of the adiabatic and bridge levels in the triad oligomer, respectively. Based on above Larsson partition approach, both site energy correction and all of bridge orbital contributions can be accounted. According to Eq. (4), the SE coupling is relative to the direct coupling between the donor and acceptor moieties, since the donor and acceptor moieties are connected by covalence bond interaction. In order to clarify the relationship of SE coupling and the charge density at linkage sites, we simplified Eq. (4) based on the tight binding Hückel approximation as follows:^[23,52]



Scheme 1 Investigated systems for (a) nIID-BTs (IID-BT, AzIID-BT, ThIID-BT and TzIID-BT) and (b) TzIID-donors. The linkage sites in both donor and acceptor moieties are marked by circles.

$$V_{\text{Hole/Elec}}^{\text{eff}} \propto C^{D1(A1)} C^{Dn(An)} \cos(\phi_{DA}) \cos(\phi_{AD}) \sum_{v \in A(D)} \frac{C_v^{A1(D1)} C_v^{An(Dn)}}{E - \epsilon_v^{A(D)}} \quad (5)$$

where C is molecular orbital coefficient, $D1$ ($A1$) and Dn (An) are the left and right linkage sites of the donor (acceptor) moieties, respectively. ϕ_{DA} denotes the torsional angle between π -orbital of the donor and the acceptor moiety. The summation runs over all molecular orbitals of the bridge, $C_v^{A1(D1)} C_v^{An(Dn)}$ is the molecular orbital coefficient of the left and right linkage sites of the bridge moiety. When the molecular coefficient at two linkage sites are equal $C^{A1(D1)} = C^{An(Dn)}$, the $C^{D1(A1)} C^{Dn(An)}$ and $C_v^{A1(D1)} C_v^{An(Dn)}$ are equal to the charge density of transport level and bridge orbital respectively, and thus the charge density at the linkage site plays an important role in SE coupling. The smaller the charge density at the linkage site is, the smaller the SE coupling will be.

RESULTS AND DISCUSSION

Geometry and Electronic Structures

The main chain of D-A copolymer can be approximately regarded as a 1D periodic structure. To simplify the question, we neglect the static disorders in D-A copolymers, such as relative orientation and torsional rotation between donor and acceptor moieties. Due to the computational amount restriction, we chose oligomer as theoretical model, and obtained the corresponding geometric and electronic structures (as shown in Fig. 1 and Fig. S1 in the electronic supplementary information, ESI).

Upon different chemical modifications to IID moiety, the geometric structure of oligomer presents obvious changes. The variations of bond length and dihedral angles are shown

in Table S1 (in ESI). From IID-BT, AzIID-BT to ThIID-BT and TzIID-BT, the bond length and the dihedral angle between bi-thiophene θ have no obvious change, but the dihedral angle β and Φ are obviously reduced, indicating that chemical modification can improve the coplanarity of copolymers. For IID-BT and AzIID-BT, the charge distributions of HOMO are mainly distributed on donor moiety BT, and a minor distribution on acceptor moiety IID/AzIID, while LUMO are mainly distributed on acceptor moiety IID/AzIID, there is a small distribution on BT donor moiety. However, with respect to ThIID-BT and TzIID-BT oligomer, the HOMO and LUMO of ThIID/TzIID and BT moieties both have large contribution to entire oligomer chain. And thus, the ThIID-BT and TzIID-BT oligomers reveal a more delocalized molecular orbital distribution for HOMO and LUMO, which promise excellent hole and electron transport.

Further, the band structures and partial charge densities at high symmetry points for the infinite copolymers have been calculated, shown in Fig. 2 and Table 1. The valence band (VB)/conduction band (CB) charge density distribution obtained from the band structure are similar to the electronic structure distribution calculated from the oligomer. For IID-BT and AzIID-BT, the donor moiety BT and the acceptor moiety IID/AzIID dominate the charge density distribution of VB and CB, respectively, while for ThIID-BT and TzIID-BT, the donor moiety BT and acceptor moiety ThIID/TzIID simultaneously play important roles in charge density distribution of the VB and CB, which is consistent with that of oligomer results.

From IID-BT, AzIID-BT, to ThIID-BT and TzIID-BT, the VBs dispersion has little variation, while the CBs reveal much larger dispersion, with the band gap (E_g) becoming smaller and

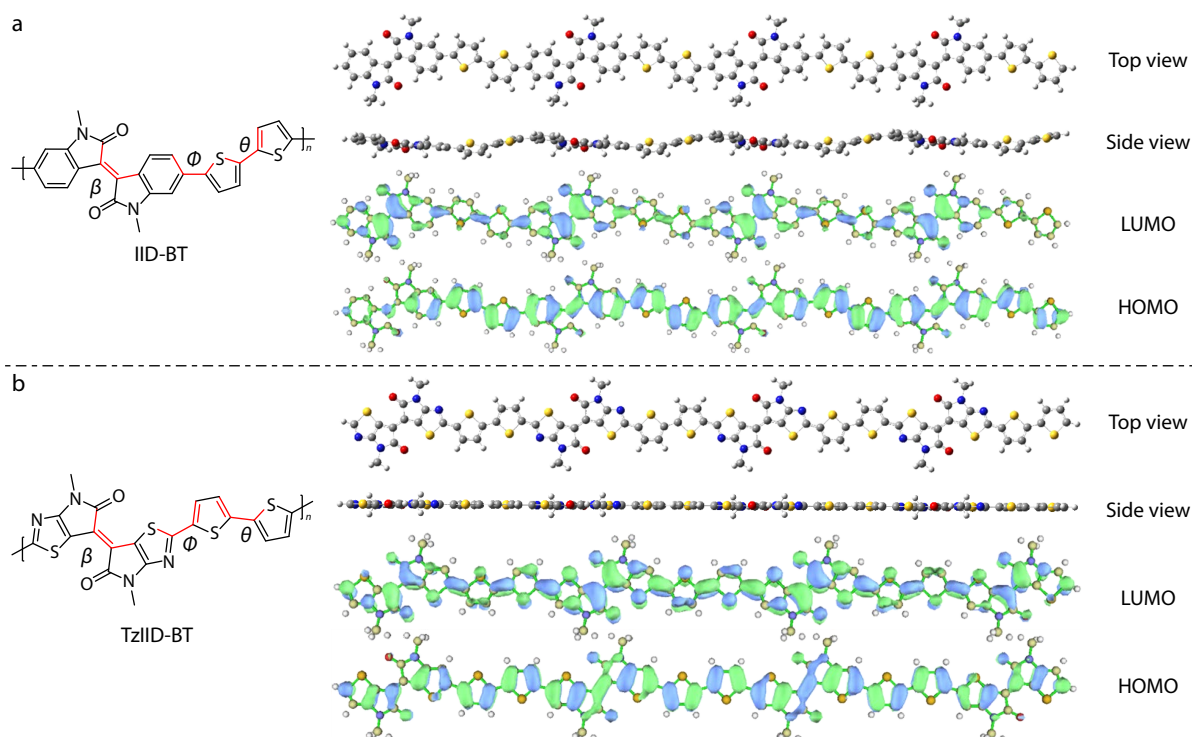


Fig. 1 The oligomer geometric structures, frontier molecular orbital (FMO) wave functions of (a) IID-BT and (b) TzIID-BT.

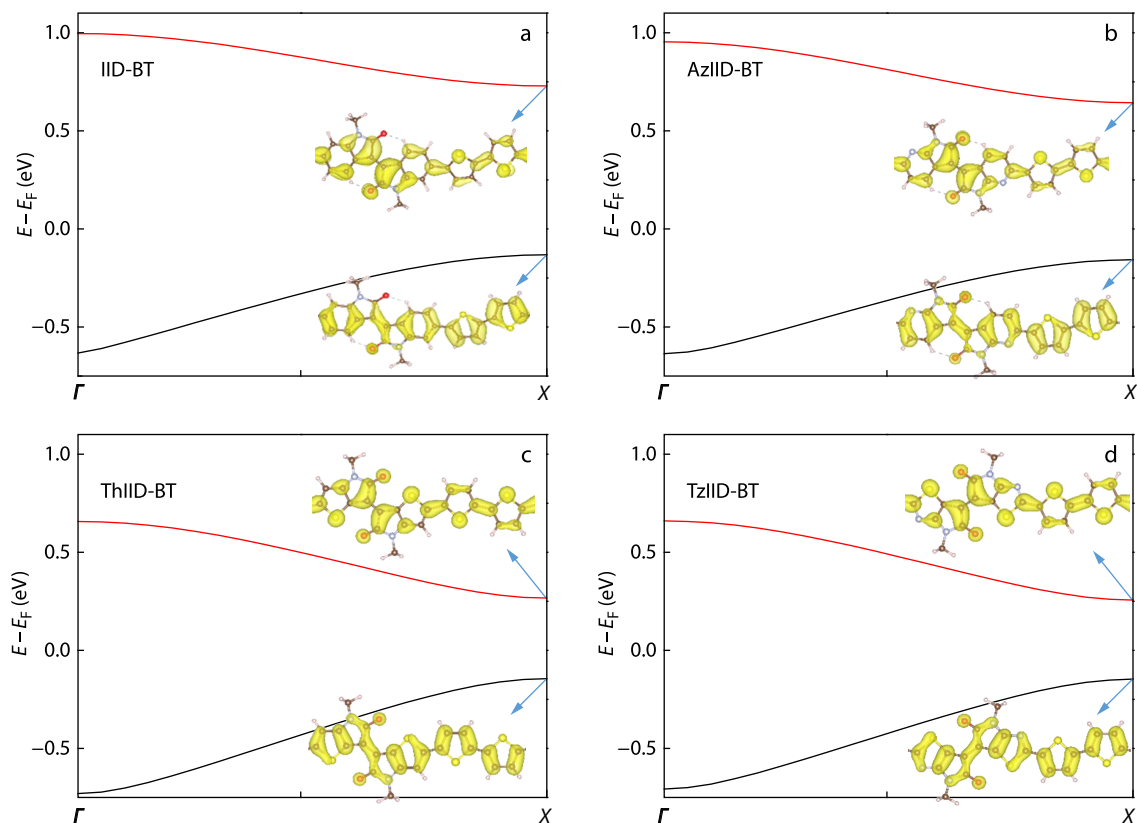


Fig. 2 The band structure and partial charge densities along backbone direction (Γ -X (1,0,0) π/a) for different systems.

Table 1 Band structure and effective mass of 1D periodic chain, the calculation level is PBE. Where m_e^* is the effective mass of electrons, and m_h^* is the effective mass of holes, in units of free electron mass m_0 .

System	VBW (eV)	CBW (eV)	E_g (eV)	m_h^*	m_e^*
IID-BT	0.501	0.267	0.861	0.161	0.346
AzIID-BT	0.479	0.310	0.801	0.169	0.291
ThIID-BT	0.586	0.391	0.410	0.177	0.287
TzIID-BT	0.560	0.403	0.403	0.186	0.265

smaller, and the valence band width (VBW) and conduction band width (CBW) of ThIID-BT and TzIID-BT turn to be more mirror symmetry. Moreover, the downshift of the CB reduces the injection barrier of electron from Au electrodes, while the VB remains little variation, maintaining the small injection barrier of hole. Thus, the reduction of the E_g is conducive to the injection of electrons and holes simultaneously.

In addition, the effective masses of hole and electron can be obtained from the second derivative of band structures (Table 1). The smaller the effective mass, the better the charge transport properties of the copolymer will be. For IID-BT and AzIID-BT, the hole effective mass is far smaller than that of electron. Thus, we can infer that these two polymers will present hole dominant transport, which is consistent with experimental measurement.^[57,58] For ThIID-BT and TzIID-BT, the electron effective mass become more and more close to hole effective mass. Although the LUMO of ThIID-BT is relatively high (about -3.06 eV, Table S2 in ESI), electron injection from electrode is difficult,^[59–61] and thus, ThIID-BT exhibits hole dominant transport polarity in experiment.^[57] Low-lying

LUMO energy and balanced electron and hole effective mass for TzIID-BT polymer, promise that ambipolar transport properties can be anticipated.

Intra-chain Super-exchange and Polarity

To understand the modulation of band structure from molecular insight along polymer backbone, we recall 1D band structure under tight-binding model:

$$W = \begin{cases} 4V_{DA} & \Delta\epsilon = 0 \\ \sqrt{(\Delta\epsilon/2)^2 + 4V_{DA}^2} - \Delta\epsilon/2 & 0 < \Delta\epsilon \ll V_{DA} \\ 4V_{DA}^{\text{eff}} & \Delta\epsilon \gg V_{DA} \end{cases} \quad (6)$$

$$m^* = \frac{\hbar^2}{a^2 V_{DA}^2} [(\Delta\epsilon/2)^2 + 4V_{DA}^2]^{1/2} = \begin{cases} \frac{\hbar^2}{2(a/2)^2 V_{DA}} \Delta\epsilon \ll V_{DA} \\ \frac{\hbar^2}{2a^2 V_{DA}^{\text{eff}}} \Delta\epsilon \gg V_{DA} \end{cases} \quad (7)$$

where W is the bandwidth, $\Delta\epsilon$ is the site energy difference between donor and acceptor moieties, a is the length of unit cell, V_{DA} is the nearest neighbor direct coupling between donor and acceptor moieties, and $V_{DA}^{\text{eff}} = V_{DA}^2/\Delta\epsilon$ is the bond-mediated SE coupling. From Eqs. (6) and (7), we found that the energy alignment between donor and acceptor moieties has large effect on band width and the effective mass. According to the electronic structure of oligomer and 1D periodic chain, the wave function of entire systems can be regarded as the combination of individual donor/acceptor moieties. And thus, we define donor and acceptor moieties according to the phase of molecular orbital, as shown in Fig. 3. The FMO energy levels

and wave functions of the acceptor moieties (IID, AzIID, ThIID and TzIID) and donor moieties, BT (2,2'-bithiophene) and TT (thieno[3,2-*b*]thiophene), FI (fluorene), T (thiophene) and Ph (benzene), were calculated at B3LYP/6-31G(d) level, the energy difference of donor and acceptor moieties correspond to $\Delta\epsilon = \epsilon_D - \epsilon_A$.

In contrast to IID moiety, the derivative AzIID, with the introduction of the pyridine group, reveal much lower HOMO and LUMO energy level; the ThIID derivative, with the introduction of thiophene group, presents much higher

HOMO/LUMO energy level. While TzIID derivative reveal narrower H-L gap. Based on the energy alignment between donor and acceptor moieties, as seen in Fig. 3, the HOMO and LUMO of IID (AzIID) are both lower than those of BT. ThIID and TzIID reveal higher HOMO those that of BT, while LUMO lower than that of BT. In view of the hole (electron) transport is mainly determined by HOMO (LUMO) orbital, the energy alignment between donor and acceptor moieties has large impact on charge distribution.

As shown in Fig. 4(a), when the HOMO and LUMO energy

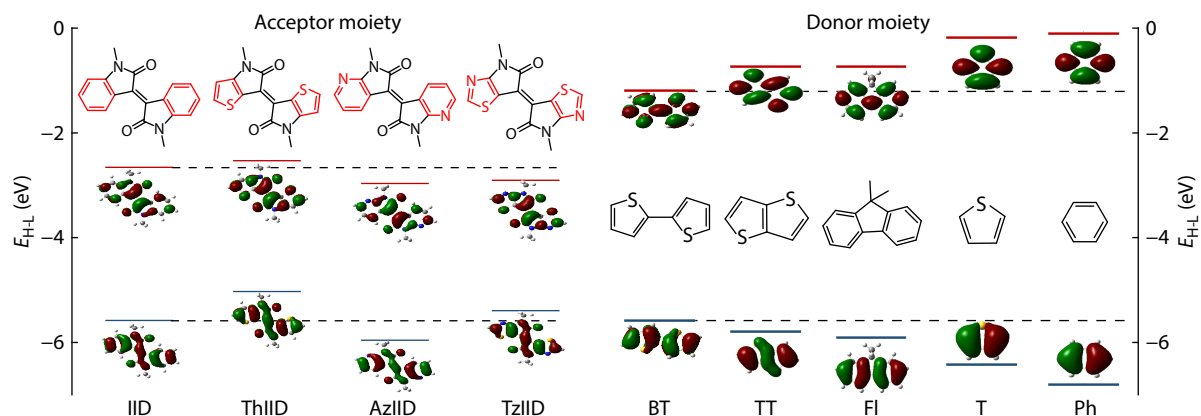


Fig. 3 Molecular orbitals and energy levels of the acceptor (IID, AzIID, ThIID and TzIID) and donor (BT, TT, FI, T and Ph) moieties.

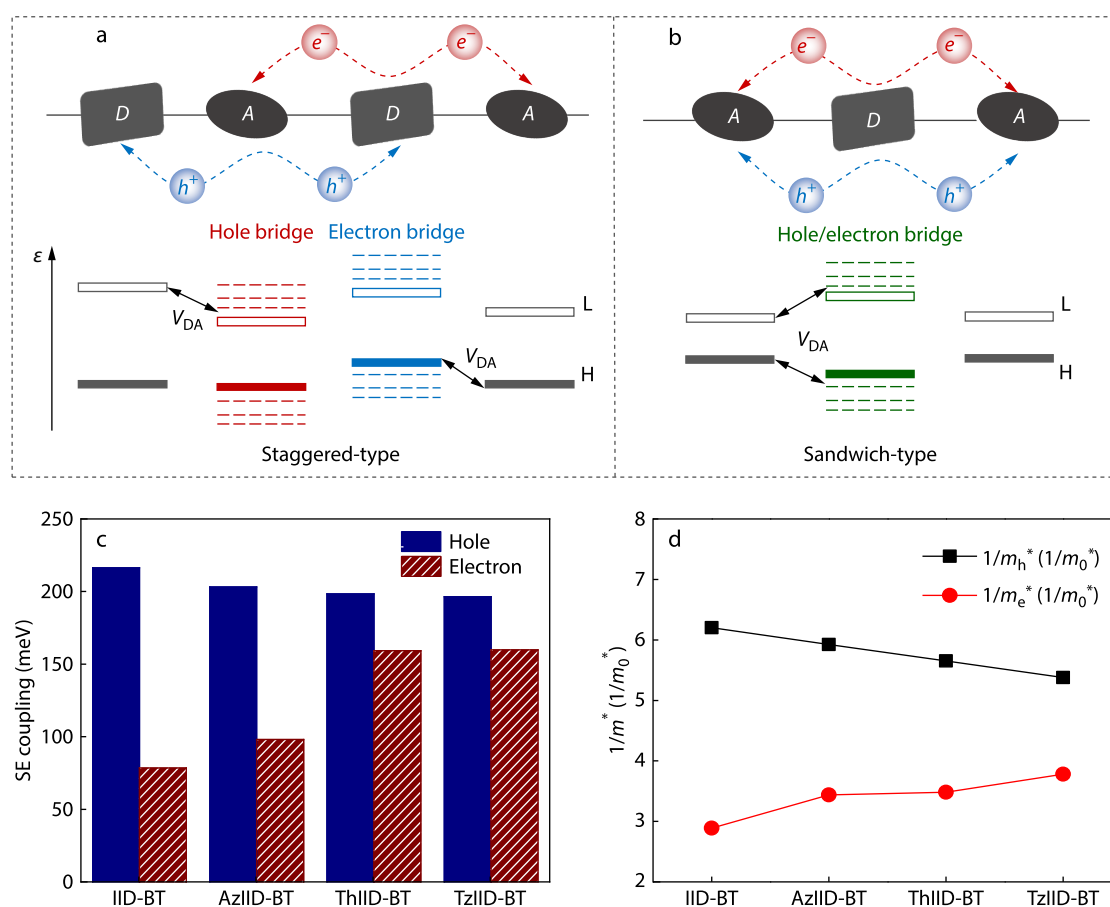


Fig. 4 The energy alignment and the SE coupling models: (a) Staggered-type and (b) Sandwich-type; (c) The SE coupling and (d) effective mass for investigated systems.

levels of the acceptor moiety are both lower than those of the donor moiety, the energy alignment presents staggered character. In this case, the hole (electron) is distributed on donor (acceptor) moiety, in-between acceptor (donor) moiety acts as the bridge for hole (electron) transport. In contrast, as shown in Fig. 4(b), when the acceptor moiety has narrow H-L gap, *i.e.*, the LUMO (HOMO) of the acceptor moiety is lower (higher) than that of the donor moiety, the energy alignment reveals sandwich character. The hole and electron are both distributed on acceptor moiety, in-between donor moiety acts as the bridge not only for hole but also for electron SE coupling. Therefore, according to the relative energy alignment between the donor and acceptor moieties, two kinds of SE models, staggered-type and sandwich-type, are proposed. From IID (AzIID)-BT to ThIID (TzIID)-BT, the SE model changed from staggered-type to sandwich-type.

Based on the SE models above-mentioned, the hole and electron SE coupling for four copolymers were calculated (Fig. 4c). From IID-BT, AzIID-BT, ThIID-BT to TzIID-BT, the hole SE coupling remains nearly constant (about 200 meV), while the electron SE coupling significantly increased, from 78 meV to 160 meV, gradually getting close to the hole SE coupling. In the case of electron transport, the SE coupling is lower than hole SE coupling, which is due to the smaller charge density at linkage sites of LUMO than that of HOMO (Table S3 in ESI and Eq. 5). According to Eq. (6), the larger the SE coupling, the wider the bandwidth, which is consistent with that of band structure for different copolymers, as shown in Fig. 2 and Table 1. Considering the hole SE coupling is large enough and thus wide band width for VB, the hole injection and transport is not a question in this case. While the increase of electron SE coupling for ThIID-BT and TzIID-BT is very important to realize ambipolar transport, since the CB turns much wider and downshift close to the Fermi level of Au electrode, which is convenient for electron injection. The reciprocal of the effective mass present similar tendency with SE coupling, which suggest that ultra-small effective mass originate from long range SE mechanism (Fig. S2 in ESI). The hole and electron coupling of ThIID-BT and TzIID-BT are more balanced than those of IID-BT and AzIID-BT, indicating the copolymer with donor-acceptor moieties energy alignment satisfying sandwich-type SE model will be more likely to exhibit ambipolar charge transport.

In order to understand the origin of the polarity change for different SE models, we took AzIID-BT and TzIID-BT as examples. For AzIID-BT, satisfying the staggered-type SE model, the hole SE coupling are calculated based on BT-AzIID-BT triad, while the electron SE coupling is computed based on AzIID-BT-AzIID triad. The transport level and corresponding bridge are completely different, on the condition that the H-L couplings plays a dominant role, the balance electron and hole coupling can be obtained.^[50] According to the contribution of the bridge orbitals to the SE coupling (Fig. S3 in ESI), many bridge orbitals have large contribution to SE coupling. There are seven main bridge orbitals (HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+3) involved in the contribution to hole SE coupling, while four main bridge orbitals (HOMO-3, HOMO, LUMO and LUMO+1) involved in the case of electron SE coupling. And thus, AzIID-BT presents

unbalanced hole and electron SE coupling.

As shown in Fig. 5, the energy alignment between donor and acceptor moieties of TzIID-BT satisfies the sandwich-type SE model, and the oligomer triad model is the same for hole and electron SE coupling (TzIID-BT-TzIID). The transport levels are HOMO of TzIID for hole, and LUMO of TzIID for electron. There are the same bridge contributions from the main orbitals of BT moieties (HOMO-3, HOMO, and LUMO, LUMO+1). Although the transport levels for hole and electron are different, the same bridge orbital contributions make it prone to achieve balanced hole and electron SE coupling. According to Eq. (5), the bridge contribution to SE coupling is related to two aspects: one is the symmetry of bridge orbital, the other is the energy alignment. Due to the symmetry of bridge orbital, there are constructive and destructive interference effects for different bridge orbitals, since the HOMO and LUMO+1 orbitals of BT moiety are antisymmetric, and the HOMO-3 and LUMO orbitals are symmetric. Considering the energy alignment of donor and acceptor moieties, the HOMO of BT is lower than that of TzIID, the LUMO of BT is higher than that of TzIID, the sign of the denominator is the same as that of the numerator, and then the bridge contribution of HOMO and LUMO are both constructive interference to the SE coupling,

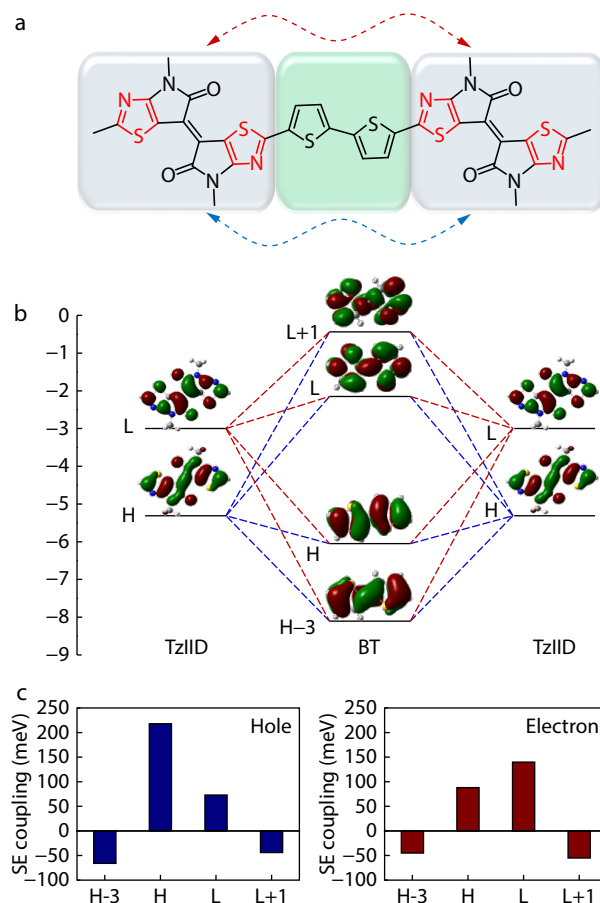


Fig. 5 (a) Oligomer triad model (ADA) for hole/electron SE coupling, (b) the polarized energy alignment and wavefunction for donor acceptor moieties. (c) Illustration of the contribution of the molecular orbital of the bridge to SE couplings for holes and electrons in TzIID-BT, calculated from a ADA oligomer triad at the B3LYP/6-31G(d) level.

while the HOMO-3 and LUMO+1 orbitals are destructive interference to the SE coupling due to the opposite signs of the denominator and numerator. In all, the sandwich-type energy alignment D-A composed copolymers are easier to achieve balanced electron and hole transport.

Prediction of High Performance Ambipolar Copolymer

Take the narrowest H-L gap acceptor moieties TzIID as example, combining with different donor moieties with wide H-L gap, (FI, Ph, BT, T and TT), we constructed a series of D-A copolymers satisfying the sandwich-type SE model, and the oligomer triad model are the same for hole and electron SE coupling (TzIID-

donor-TzIID).

All the copolymers show relatively balanced hole and electron SE coupling, as shown in Fig. 6(a), and main bridge orbitals contribution is the same for hole and electron (Table S4 in ESI). Although wide H-L gap are needed to satisfy sandwich model, the H-L gap cannot be so large as to reduce the magnitude of SE coupling. In addition, the large charge density for FMO at linkage site will be convenient to SE coupling, with the increase of the charge density; the hole and electron SE coupling both increase, as shown in Fig. 6(b) and Table S5 (in ESI).

Then we calculated the effective mass of hole (electron) of these TzIID-based D-A copolymers. As shown in Fig. 6(c), the hole (electron) effective mass of TzIID-TT is smaller than other copolymers. In D-A copolymers, the effective mass is related to both the SE coupling and the length of unit cell (Eq. 7). Although TzIID-T has large hole and electron SE coupling, it has larger hole (electron) effective mass than TzIID-TT due to its small unit cell length. And therefore, large charge density (Table S5) and narrow H-L gap for TT donor moiety enable TzIID-TT to have relatively large SE coupling and ultra-small effective mass, whose effective mass ($m_e^*=0.146$ and $m_h^*=0.128$) is one of the smallest effective masses in ambipolar materials. And thus, high-performance ambipolar copolymer TzIID-TT has been predicted through first-principle theoretical calculation.

CONCLUSIONS

In summary, through employing band structure and SE coupling calculation, we found that the energy alignment of donor and acceptor moieties has large impacts on charge transport polarity in D-A copolymers. The change of polarity has large difference with that of D-A co-crystal. Upon minor modification on acceptor IID moiety, the polarity of charge transport changes from hole dominant to ambipolar transport, which can be understood from the change of SE coupling models from staggered-type to sandwich-type.

When the energy alignment between donor and acceptor moieties satisfies the sandwich-type SE model, the D-A copolymers are more likely to present ambipolar charge transport properties. For sandwich-type SE model, the balanced hole and electron transport originates from almost the same bridge orbitals contribution. On the condition of sandwich-type SE model, different wide H-L gap donor moieties have been introduced, and polymerized with narrow H-L gap acceptor moiety TzIID, a series of D-A copolymers have been constructed and investigated. All these copolymers present ambipolar charge transport properties, and TzIID-TT reveals balance hole and electron SE coupling and the smallest effective mass, which suggest that it is an excellent ambipolar material. This finding can be used to design high performance ambipolar D-A copolymers. With respect to acceptor moiety, the H-L gap should be narrow enough, while the H-L gap of the donor moiety should be relatively wide, with its HOMO/LUMO lower/higher than that of acceptor moiety, which is prone to satisfy the sandwich-type energy alignment. It should be noted that we paid emphasis on intra-chain charge transport, completely ignoring the influence of inter-chain interaction, structural disorder, molecular weight,

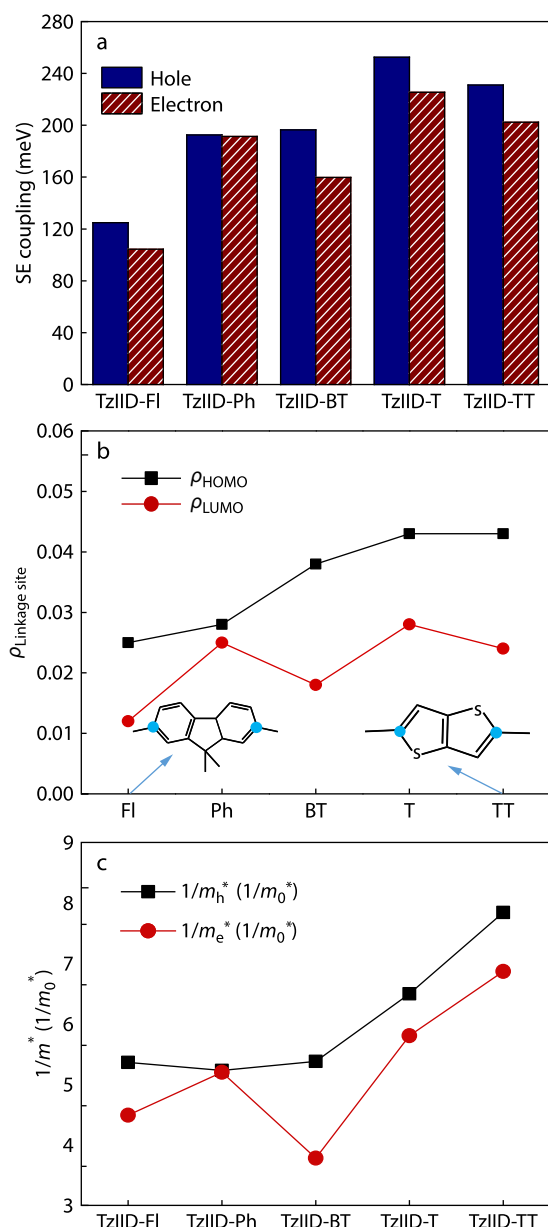


Fig. 6 Illustration of (a) the SE coupling, (b) the charge density at linkage sites, and (c) the effective mass for holes and electrons calculated from a TzIID-Donors-TzIID oligomer triad at the B3LYP/6-31G(d) level.

and so on. There is still a long way to go to understand charge transport properties for realistic polymer material.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2680-x>.

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