

Supporting Information

for

An Efficient Strategy for Designing n-Type Organic Semiconductor Materials -- Introducing Six-Membered Imide Ring into Aromatic Diimides

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Evaluating internal reorganization energy (λ) from the adiabatic potential-energy surfaces

λ for hole can be defined as follows

$$\lambda_h = \lambda_+ + \lambda_1 = [E^+(M) - E^+(M^+)] + [E(M^+) - E(M)] \quad (\text{S1})$$

As illustrated in Figure 3(b), $E^+(M^+)$ and $E(M)$ represent the energies of the cation and neutral species in their lowest energy geometries, respectively., while $E^+(M)$ and $E(M^+)$ represent the energies of cation and neutral species with the geometries of neutral and cation respectively. In this way, λ for electron can be expressed as follow

$$\lambda_e = \lambda_- + \lambda_2 = [E^-(M) - E^-(M^-)] + [E(M^-) - E(M)] \quad (\text{S2})$$

Evaluating transfer integral (V) values by employing two methods: Koopmans' theorem (KT) method and site-energy correction method

$$\text{KT method: } V = \frac{E_{\text{HOMO/LUMO}+1} - E_{\text{HOMO}-1/\text{LUMO}}}{2} \quad (\text{S3})$$

where $E_{\text{HOMO/LUMO}+1}$ and $E_{\text{HOMO}-1/\text{LUMO}}$ are the energies of the HOMO/LUMO+1 and HOMO-1/LUMO levels taken from the neutral dimer, respectively.

Site-energy correction method: transfer integral can be calculated from the spatial overlap (S_{RP}), charge transfer integrals (H_{RP}) and site energies (H_{RR} , H_{PP}). Transfer integral V is given by the following equation:

$$V = \frac{H_{RP} - 0.5S_{RP}(H_{RR} + H_{PP})}{1 - S_{RP}^2} \quad (\text{S4})$$

where $H_{RP} = \langle \psi_R | H | \psi_P \rangle$, $H_{RR} = \langle \psi_R | H | \psi_R \rangle$, $H_{PP} = \langle \psi_P | H | \psi_P \rangle$ and $S_{RP} = \langle \psi_R | \psi_P \rangle$; H is the system Kohn-Sham Hamiltonian of the dimer system, and $\psi_{R(P)}$ means the monomer's LUMO/HOMO (for electron/hole transport) with Löwdin's symmetric transformation, which can be used as the orthogonal basis set for calculation.

Fig. S1. The stereograph of the optimized molecules by B3LYP/6-31G(d,p).

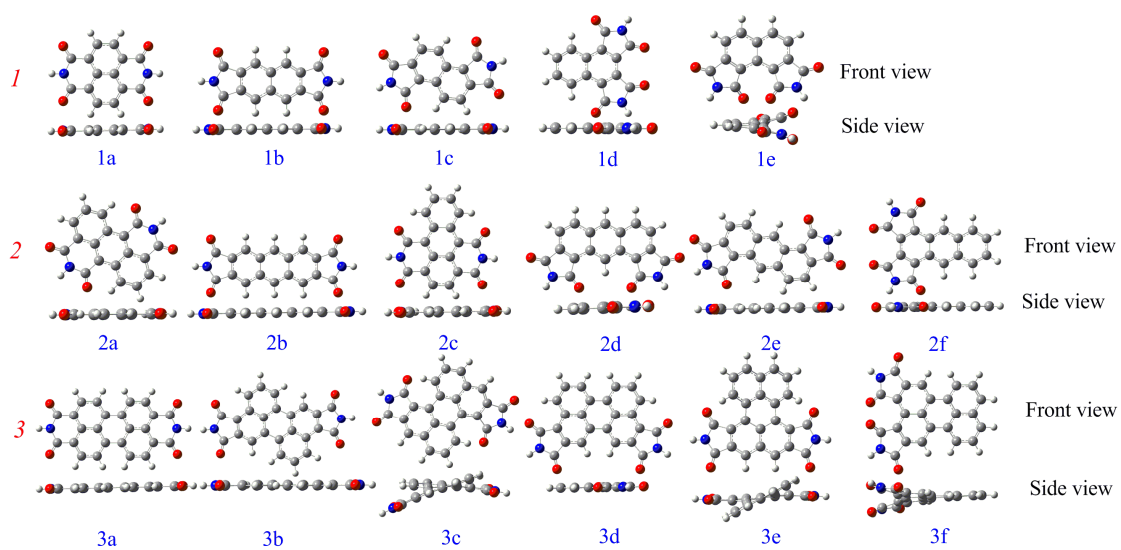


Fig. S2. Absolute values of bond lengths changes between the neutral and ionized geometries for these molecules: **1a/b**, **2a/b** and **3a/b**

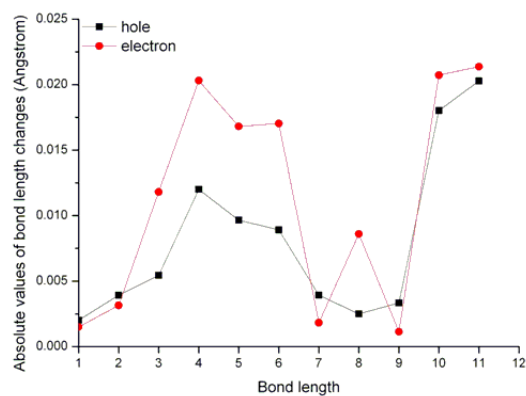
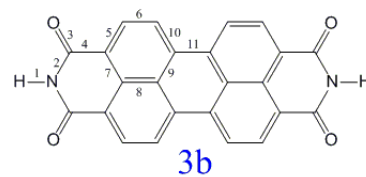
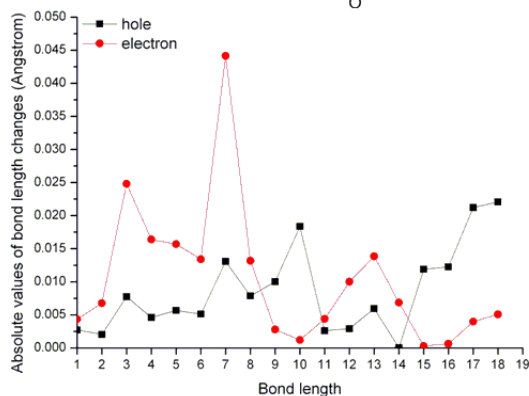
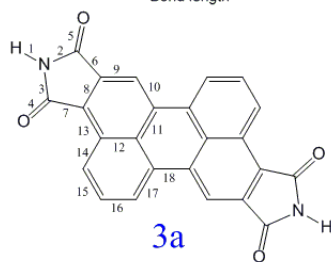
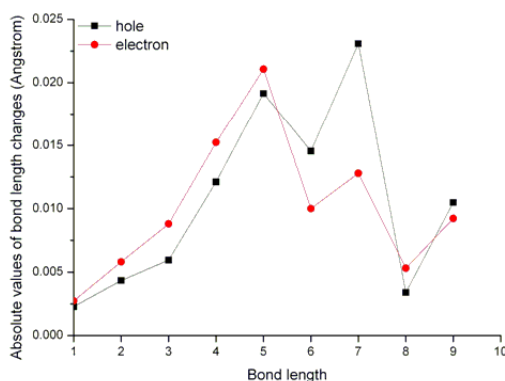
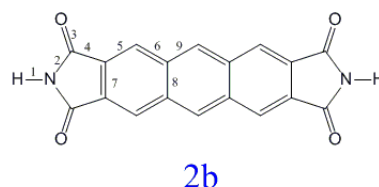
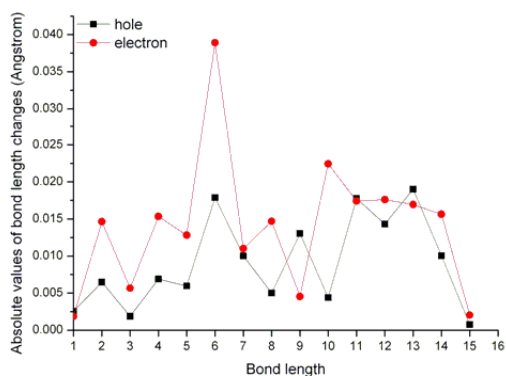
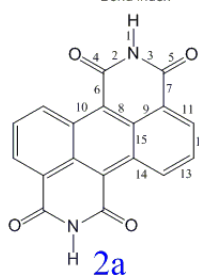
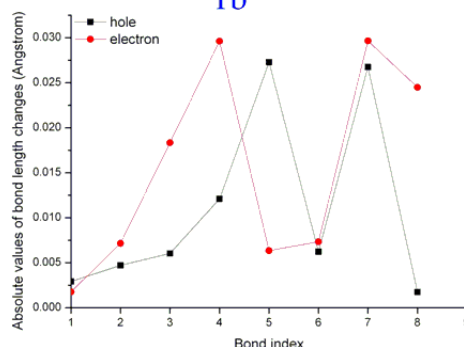
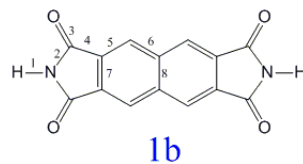
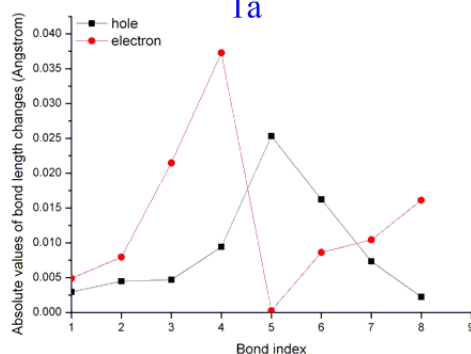
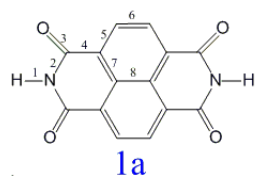
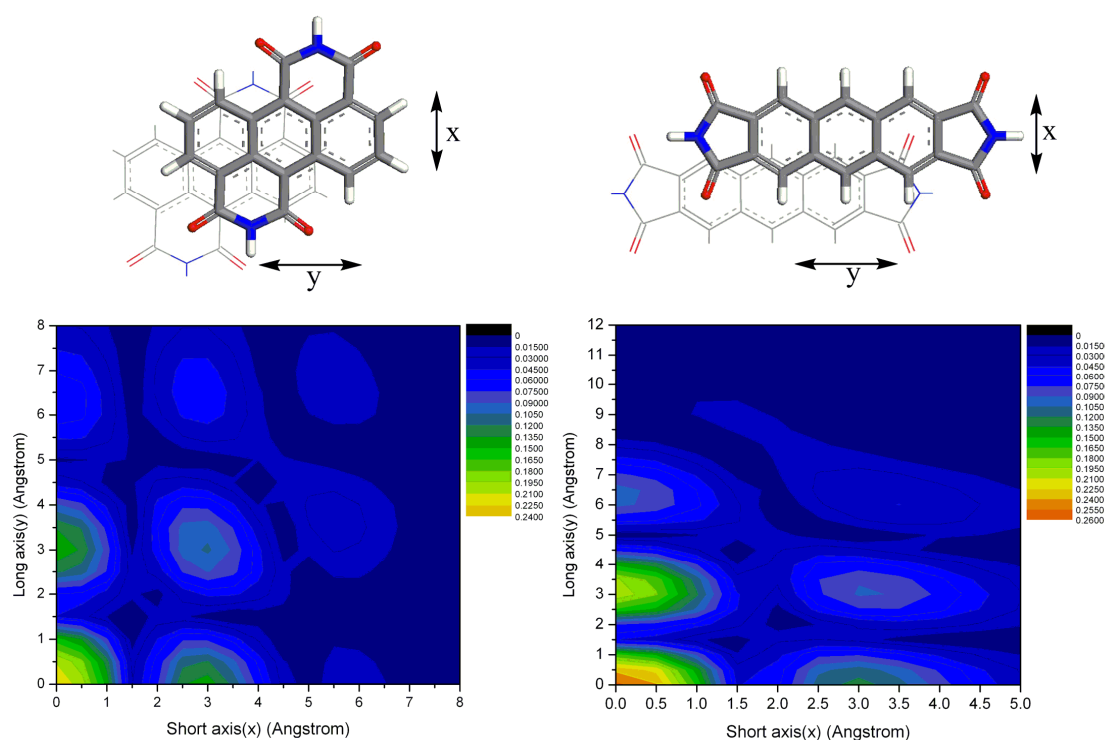


Fig. S3. Hole transfer integral values (in eV) are shown as a function of (x,y) displacement for molecule pairs **2a/b** and **3a/b**; here, transfer integral values are calculated by KT method at the PW91PW91/6-31G(d) level.



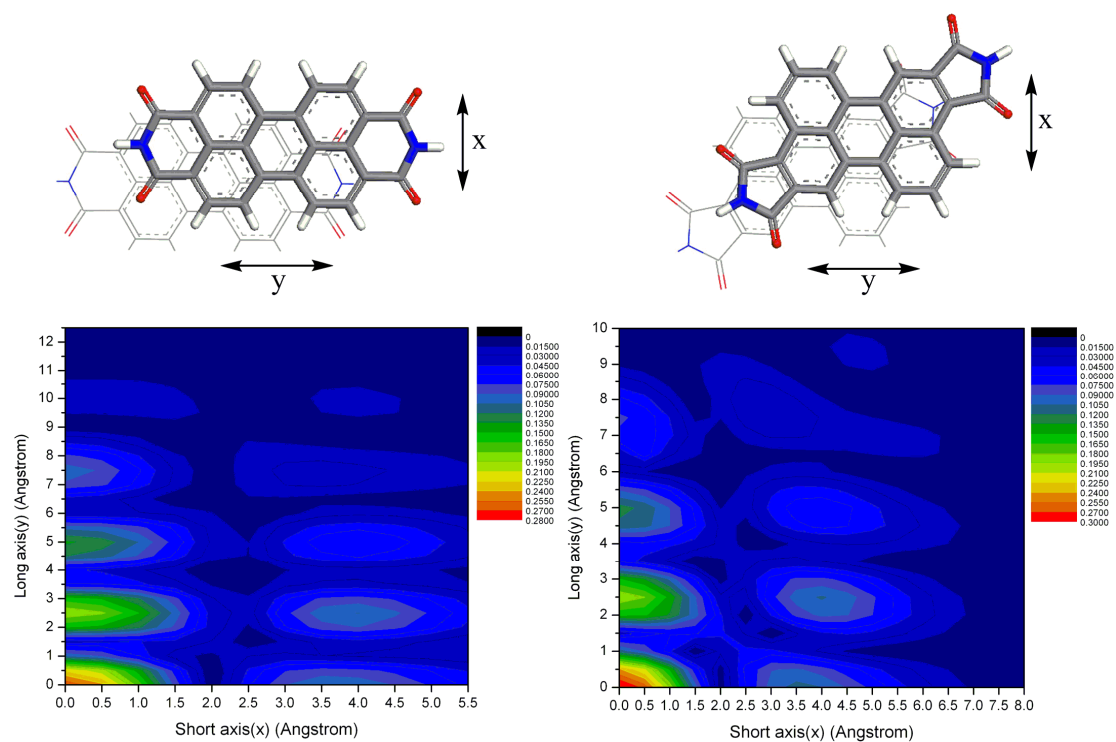


Fig. S4. Charge hopping pathways schemes for molecules **1A**, **2A** and **3A**;
Due to symmetry, the reverse pathways aren't labeled.

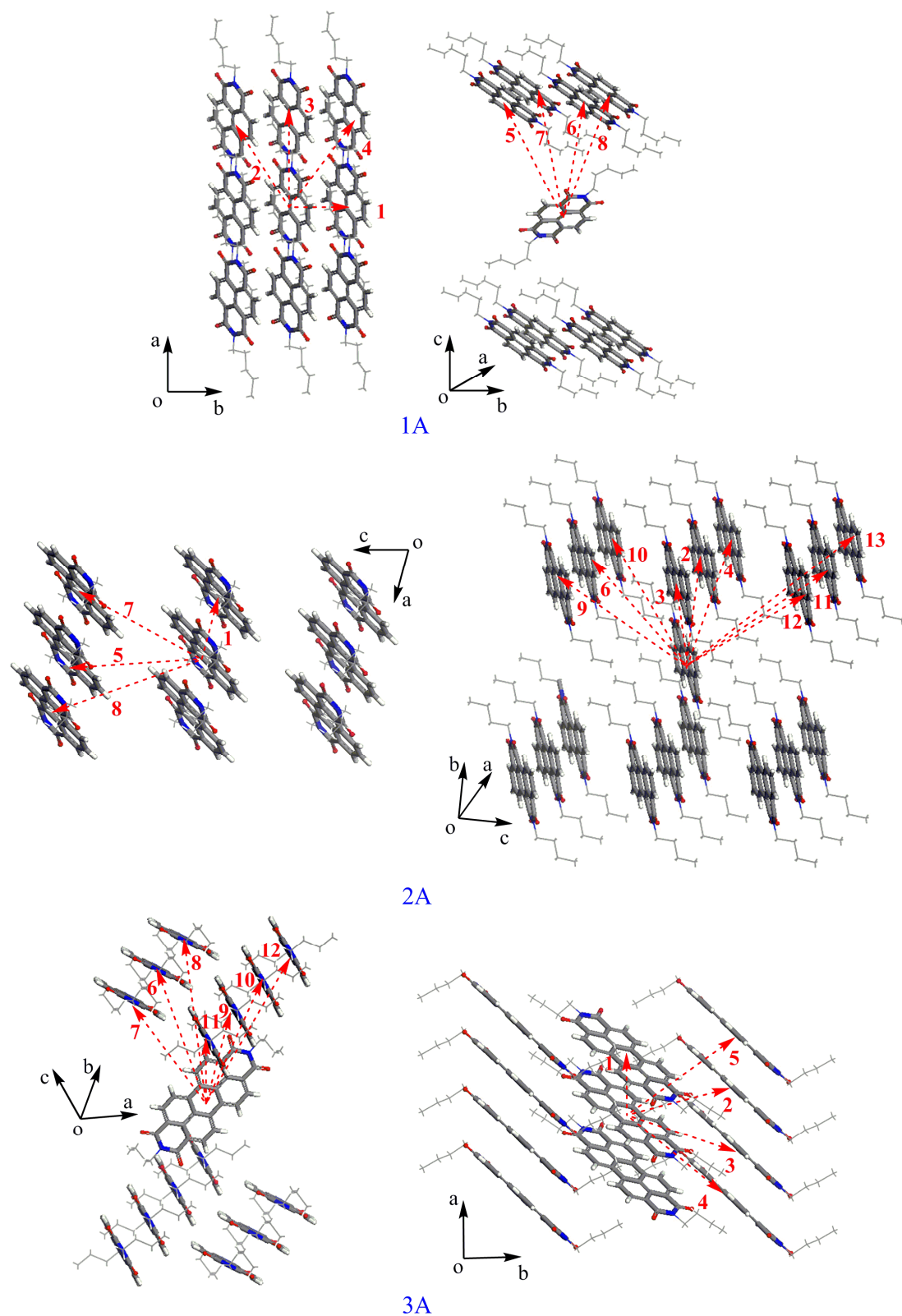


Fig. S5. The illustration of projecting different hopping pathways to a transistor channel in the a–b plane of the studied molecular crystals,

respectively. θ s are the angles of the dimers relative to the reference crystallographic axis a . Φ is the angle along a transistor channel relative to the reference crystallographic axis a .

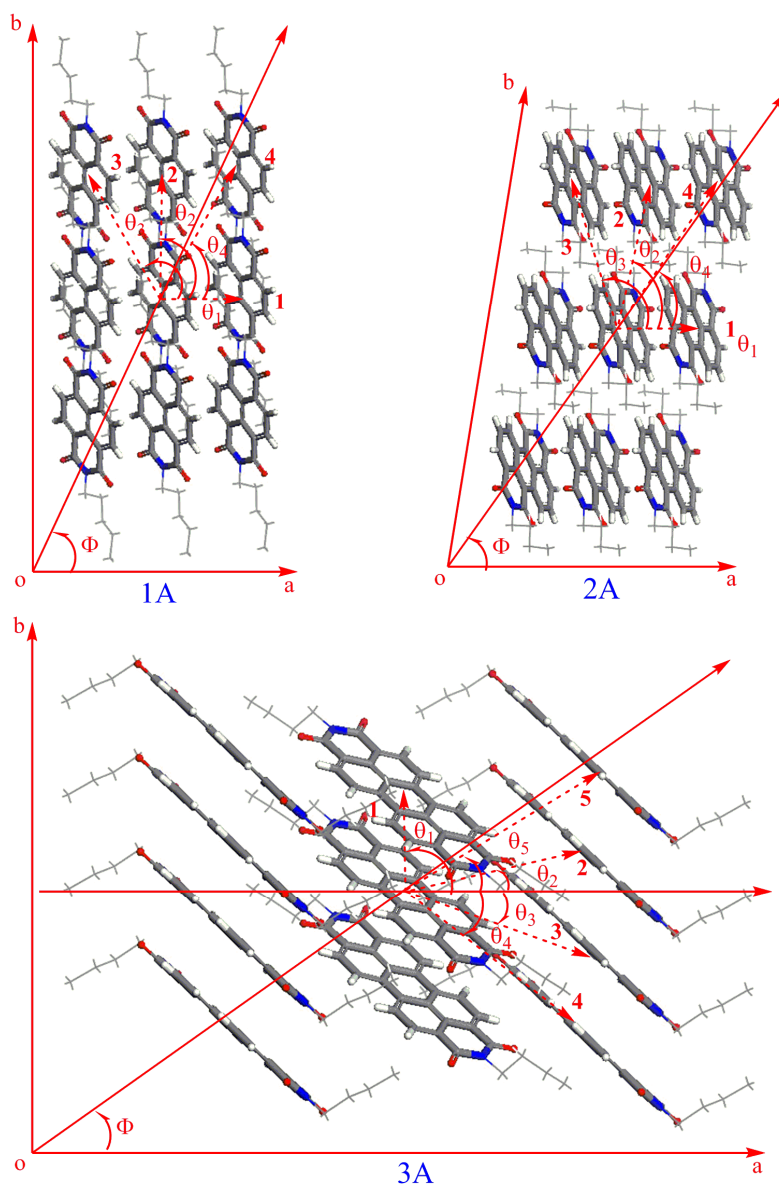


Table S1. HOMO and LUMO energies (E_{HOMO} and E_{LUMO}), ionization potentials (IP), electron affinities (EA) as well as hole and electron reorganization energies (λ_{h} and λ_{e}) for molecules 1A, 2A and 3A; IP and EA refer to the vertical values; all the values listed here are from

the single-point calculations at the B3LYP/6-31++G(d,p) level. (in eV)

Species	E _{HOMO}	E _{LUMO}	IP	EA	λ _h	λ _e
1A	-7.27	-3.70	8.74	2.29	0.20	0.34
2A	-6.58	-3.80	7.93	2.47	0.17	0.31
3A	-6.26	-3.78	7.48	2.58	0.16	0.27

Table S2. Hole transfer integrals ($V_h/V'_h \times 10^{-4}$ eV) for molecules 1A, 2A and 3A along different hopping pathways calculated (P: the hopping pathway; d/Å: the mass center distance). $\mu_h/\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ is the average hole mobility. V_{hs} and V'_{hs} denote the transfer integral values obtained by site-energy correction and KT methods, respectively.

P	1A		2A		3A	
	V_h	d	$V_h(V'_h)$	d	V_h	d
1	-6.93	5.03	-391.05(465.31)	4.85	1316.45	4.63
2	9.95	8.11	24.56(21.77)	9.3	3.53	9.49
3	-166.62	9.54	91.99(68.03)	9.52	-15.7	9.49
4	0	9.54	0.83(1.36)	11.37	-1.37	11.53
5	-1.55	12.98	0.01(0)	12.09	-0.1	11.53
6	-1.55	12.98	-18.56(17.69)	12.93	0	13.81
7	0	13.04	-0.91(0)	12.95	0	14.56
8	0	13.04	0(0)	13.09	-0.1	14.56
9			0.1(1.36)	13.16	1.98	14.55
10			-2.54(2.72)	14.43	1.98	14.55
11			0(0)	17.26	0.2	15.96
12			0(1.36)	17.33	0.2	15.96
13			0(2.72)	18.51		
μ_h	0.08		0.17(0.24)		2.11	