Supporting Information

Theoretical investigations of the substituent effect on the electronic and charge transport properties of the butterfly molecules

Lijuan Wang, Jianhong Dai* and Yan Song*

School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, 2West Wenhua Road, Weihai, 264209, China.

*E-mail: sy@hitwh.edu.cn; daijh@hit.edu.cn.

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green indicates Van der Waals interactions and red indicates strong repulsion.

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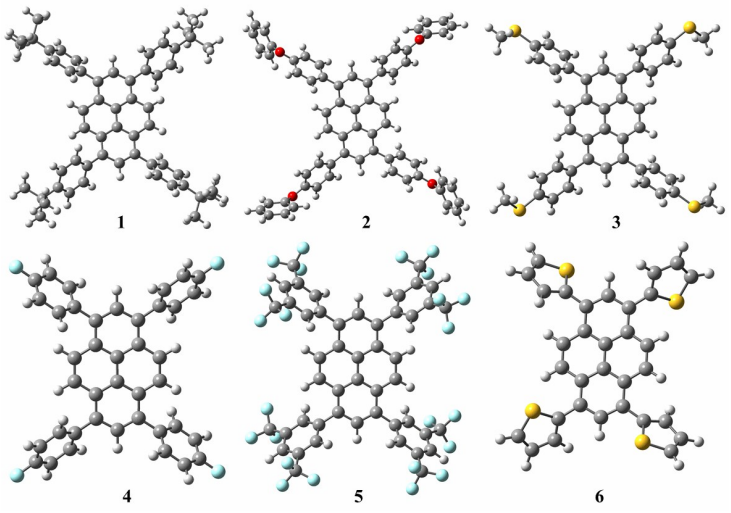


Figure S1. Optimized geometries of molecules 1 to 6.

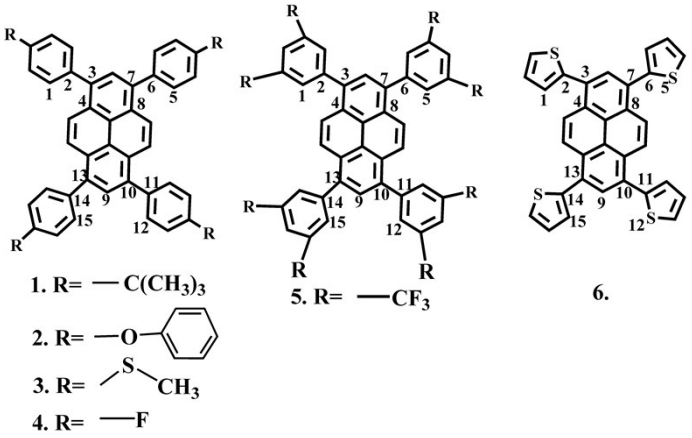


Figure S2. Chemical structures of molecules 1 to 6, with atom indices labeled on the structures.

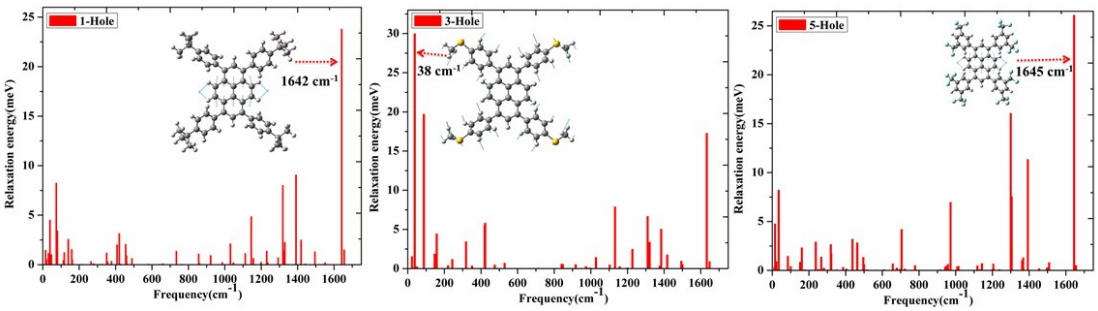
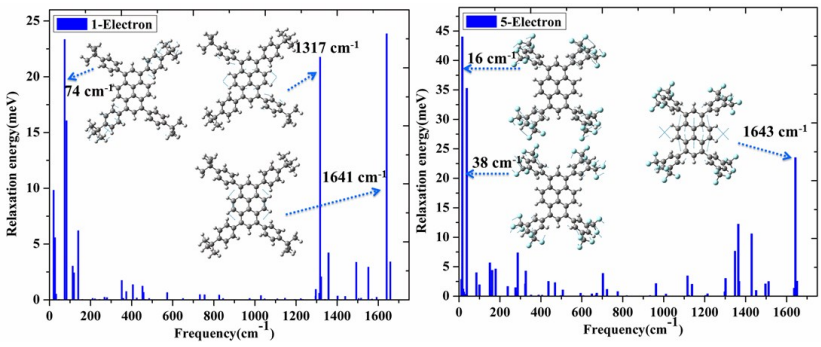


Figure S3. Contributions of the vibrational modes to the relaxation energies for molecules 1, 3 and 5, embedded with the normal modes contribute the most for the reorganization energies of holes.



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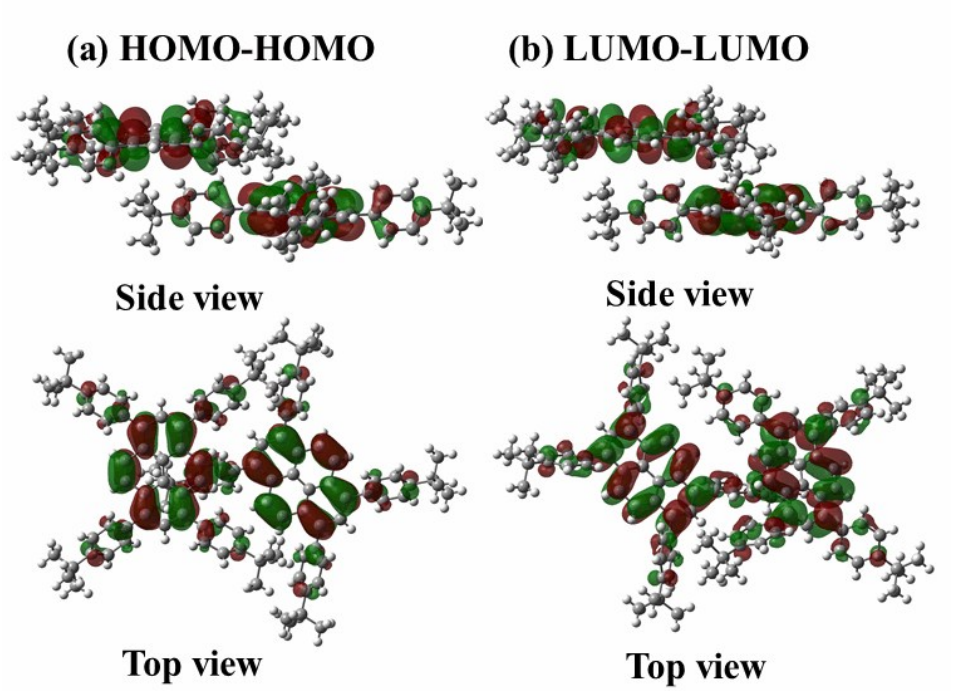


Figure S5. The pictorial HOMO-HOMO (a), and LUMO-LUMO (b) interactions of the most prominent pathway in molecule 1 from side view and top view.

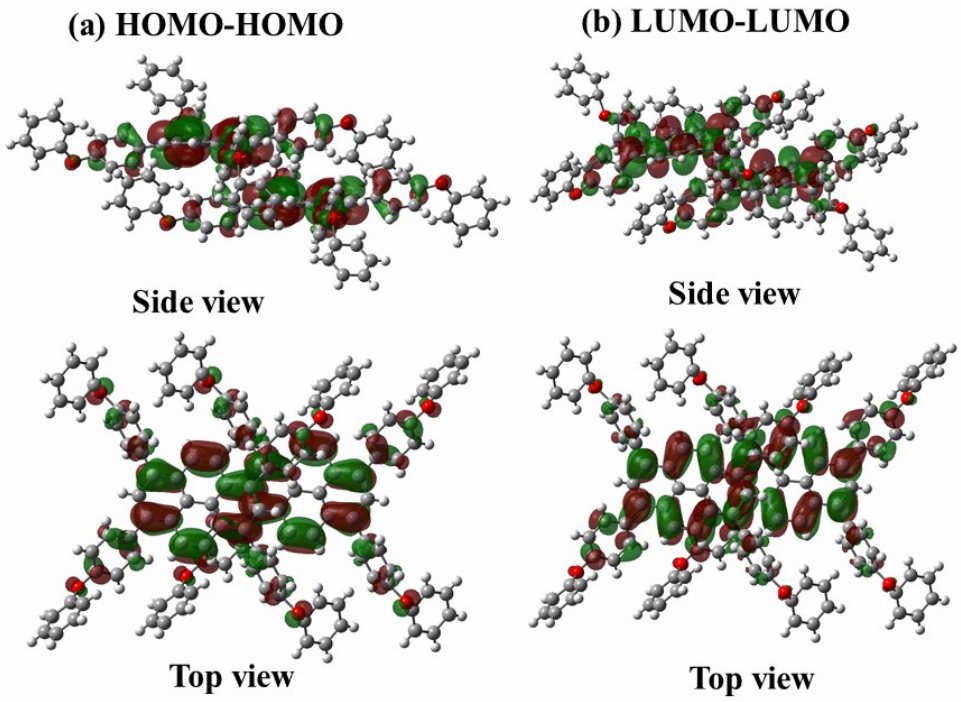
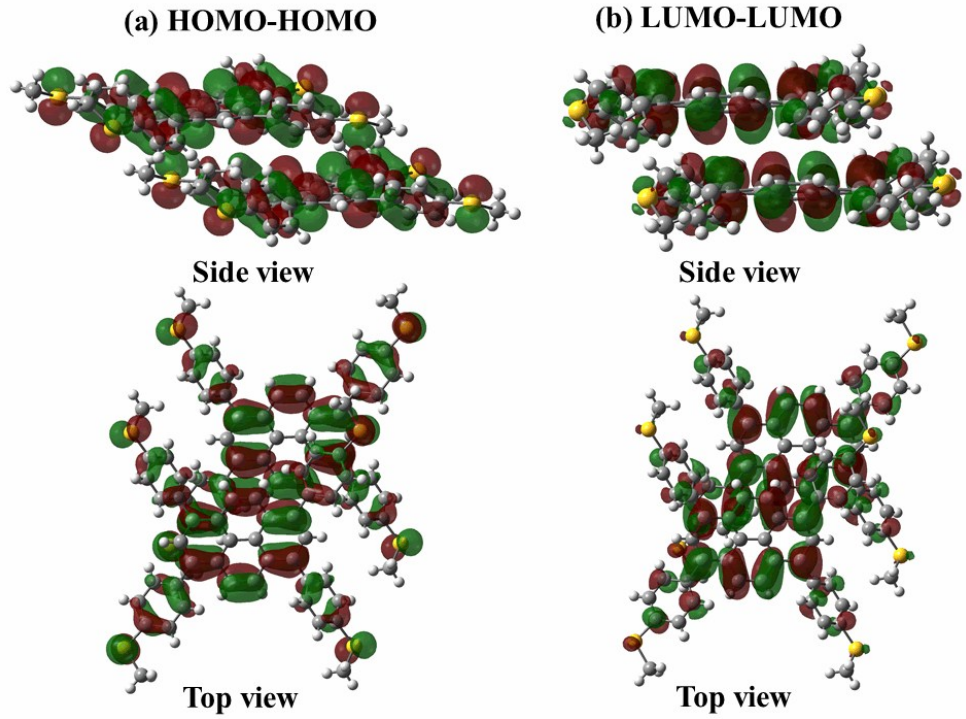


Figure S6. The pictorial HOMO-HOMO (a), and LUMO-LUMO (b) interactions of the most prominent pathway in molecule 2 from side view and top view.



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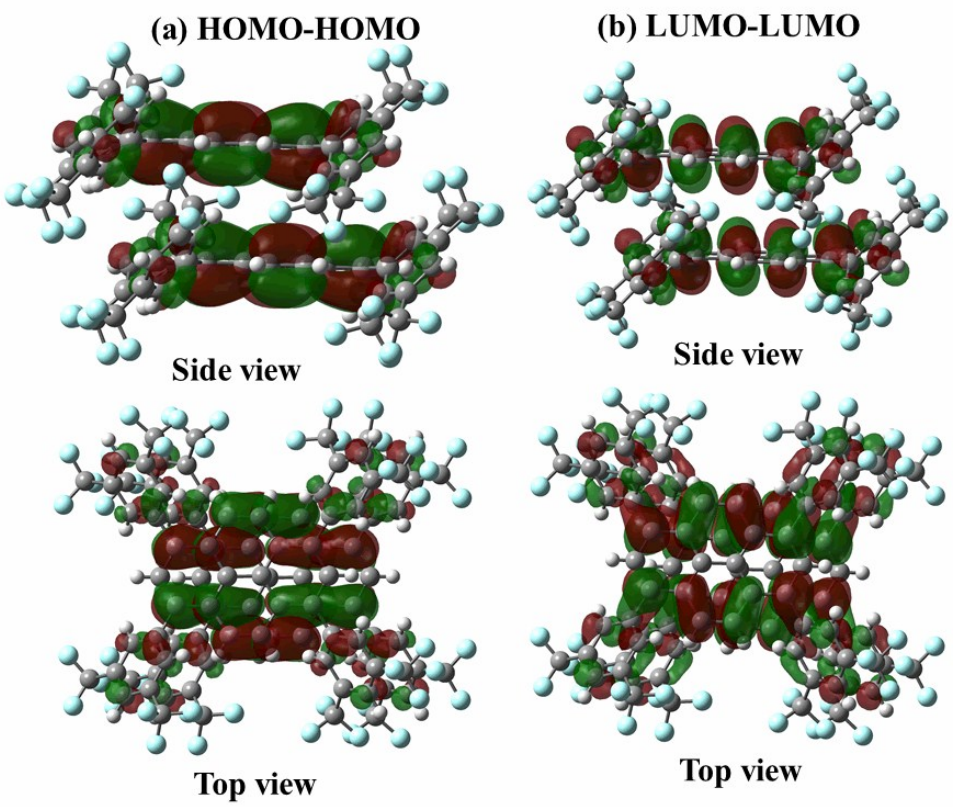

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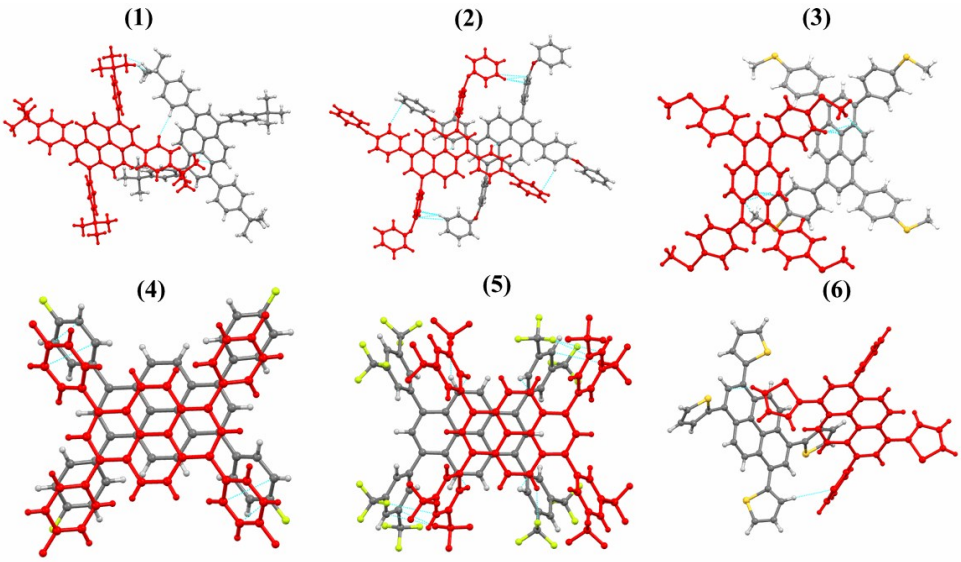

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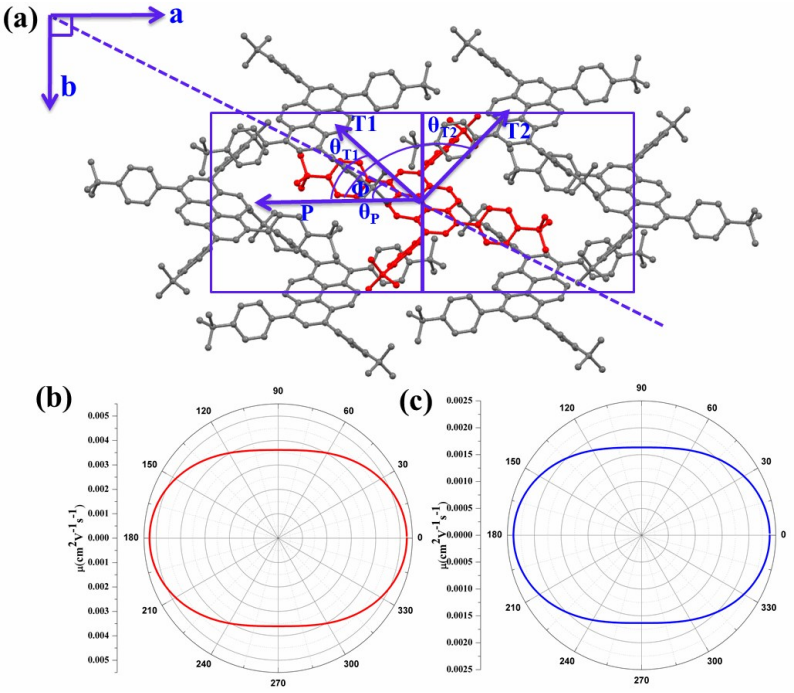


Figure S10. The projecting angle-dependent hopping paths to a transistor channel in the *ab* plane (a) and the calculated angle-resolved anisotropic hole (b) and electron (c) mobilities of molecule 1.

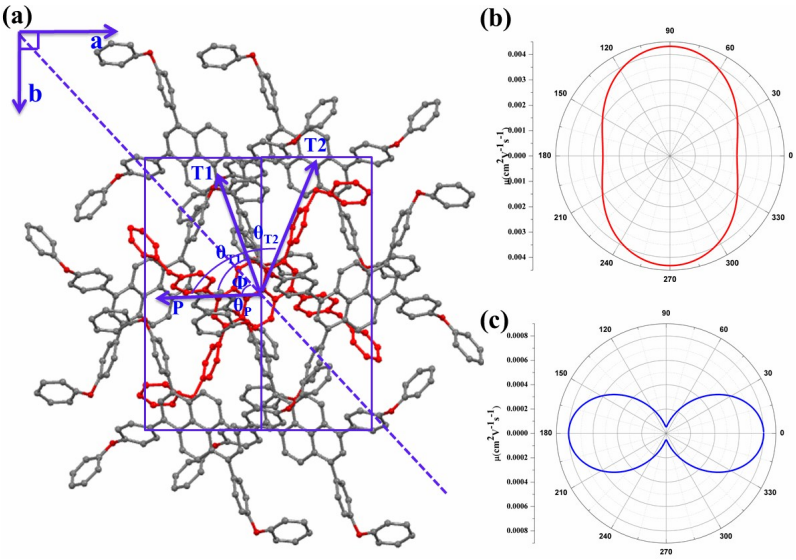
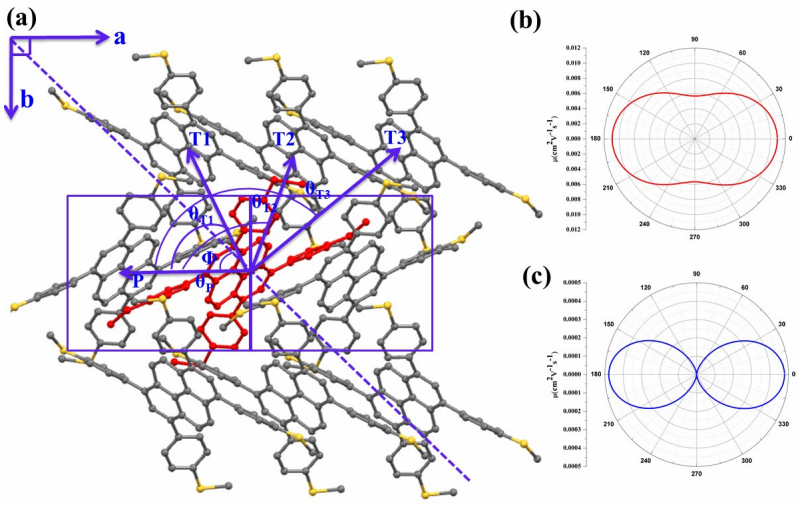


Figure S11. The projecting angle-dependent hopping paths to a transistor channel in the *ab* plane (a) and the calculated angle-resolved anisotropic hole (b) and electron (c) mobilities of molecule 2.



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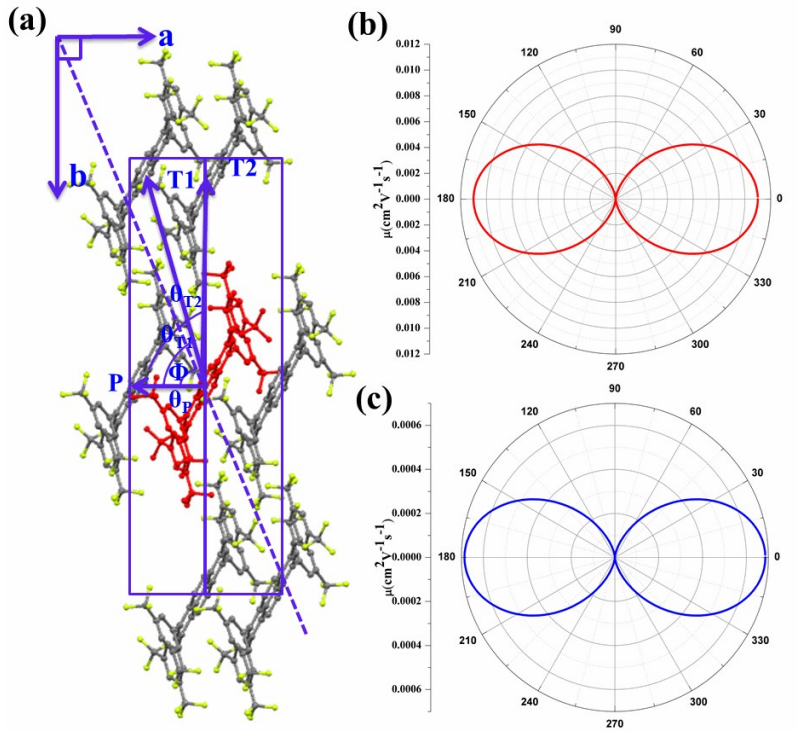
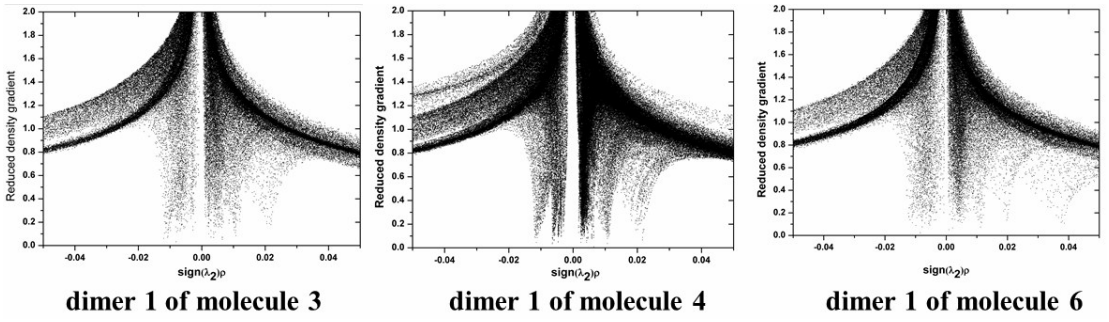


Figure S13. The projecting angle-dependent hopping paths to a transistor channel in the *ab* plane (a) and the calculated angle-resolved anisotropic hole (b) and electron (c) mobilities of molecule 5.



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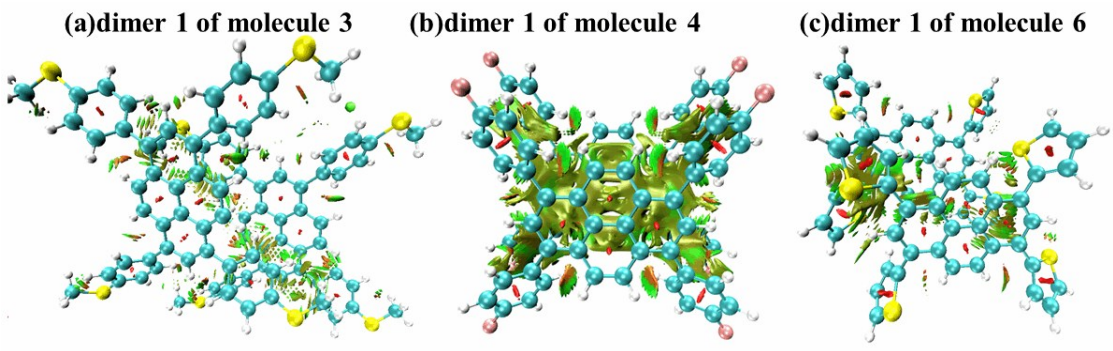

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Table S1. The selected optimized bond lengths, bond angles and dihedral angles of molecules 1 to 3 in the neutral and ionic states, together with experimental values[1] (the unit of bond lengths is in angstroms, and the bond angles and dihedral angles are in degrees).

Molecule	Bond Parameters	Neutral	Expt.[1]	Cationic	Anionic
1	R(C2-C3)	1.49	1.49	1.48	1.48
	R(C6-C7)	1.49	1.49	1.48	1.48
	R(C10-C11)	1.49	1.49	1.48	1.48
	R(C13-C14)	1.49	1.49	1.48	1.48
	θ(C2-C3-C4)	122.9	121.6	122.7	123.4
	θ(C6-C7-C8)	122.8	121.2	122.7	123.3
	θ(C9-C10-C11)	118.2	119.1	118.7	118.2
	θ(C9-C13-C14)	118.3	119.6	118.7	118.3
	θ(C1-C2-C3-C4)	53.5	53.6	48.5	45.1
	θ(C5-C6-C7-C8)	54.5	57.5	48.7	45.2
	θ(C9-C10-C11-C12)	50.2	51.5	44.7	41.9
	θ(C9-C13-C14-C15)	51.1	55.5	44.9	42.1
2	R(C2-C3)	1.49	1.48	1.47	1.48
	R(C6-C7)	1.49	1.48	1.47	1.48
	R(C10-C11)	1.49	1.48	1.47	1.48
	R(C13-C14)	1.49	1.48	1.47	1.48
	θ(C2-C3-C4)	122.8	123.5	122.7	123.2
	θ(C6-C7-C8)	122.8	122.4	122.8	123.3
	θ(C9-C10-C11)	118.3	118.0	118.8	118.3
	θ(C9-C13-C14)	118.3	118.4	118.7	118.2
	θ(C1-C2-C3-C4)	55.1	45.8	47.0	46.3
	θ(C5-C6-C7-C8)	55.8	65.9	47.0	45.8
	θ(C9-C10-C11-C12)	51.6	39.3	43.1	43.1
	θ(C9-C13-C14-C15)	52.4	64.8	42.8	42.8
3	R(C2-C3)	1.49	1.49	1.47	1.48
	R(C6-C7)	1.49	1.50	1.47	1.48
	R(C10-C11)	1.49	1.49	1.47	1.48
	R(C13-C14)	1.49	1.50	1.47	1.48
	θ(C2-C3-C4)	122.9	122.1	122.9	123.5
	θ(C6-C7-C8)	122.9	123.9	122.9	123.5
	θ(C9-C10-C11)	118.2	118.8	118.6	118.1
	θ(C9-C13-C14)	118.2	117.7	118.6	118.1
	θ(C1-C2-C3-C4)	54.9	52.2	47.1	44.4
	θ(C5-C6-C7-C8)	54.9	43.3	47.1	44.4
	θ(C9-C10-C11-C12)	51.3	49.9	42.9	41.7
	θ(C9-C13-C14-C15)	51.3	38.2	42.9	41.7

Table S2. The selected optimized bond lengths, bond angles and dihedral angles of molecules 4 to 6 in the neutral and ionic states, together with experimental values[1] (the unit of bond lengths is in angstroms, and the bond angles and dihedral angles are in degrees).

Molecule	Bond Parameters	Neutral	Expt.[1]	Cationic	Anionic
4	R(C2-C3)	1.49	1.49	1.48	1.48
	R(C6-C7)	1.49	1.50	1.48	1.48
	R(C10-C11)	1.49	1.49	1.48	1.48
	R(C13-C14)	1.49	1.50	1.48	1.48
	θ(C2-C3-C4)	122.8	122.6	122.7	123.2
	θ(C6-C7-C8)	122.8	123.3	122.7	123.2
	θ(C9-C10-C11)	118.3	119.0	118.7	118.3
	θ(C9-C13-C14)	118.3	118.0	118.7	118.3
	θ(C1-C2-C3-C4)	55.7	45.6	48.8	46.5
	θ(C5-C6-C7-C8)	55.8	45.2	49.0	46.5
	θ(C9-C10-C11-C12)	52.3	39.4	45.0	43.1
	θ(C9-C13-C14-C15)	52.4	41.7	45.1	43.2
5	R(C2-C3)	1.49	1.49	1.48	1.48
	R(C6-C7)	1.49	1.49	1.48	1.48
	R(C10-C11)	1.49	1.49	1.48	1.48
	R(C13-C14)	1.49	1.50	1.48	1.48
	θ(C2-C3-C4)	122.7	120.8	122.7	123.5
	θ(C6-C7-C8)	122.8	120.6	122.8	123.6
	θ(C9-C10-C11)	118.0	119.6	118.2	117.7
	θ(C9-C13-C14)	117.9	119.5	118.2	117.6
	θ(C1-C2-C3-C4)	59.0	51.8	52.6	46.5
	θ(C5-C6-C7-C8)	57.2	54.7	51.5	45.9
	θ(C9-C10-C11-C12)	57.2	54.1	51.2	46.2
	θ(C9-C13-C14-C15)	55.3	51.4	50.2	45.6
6	R(C2-C3)	1.47	1.48	1.46	1.46
	R(C6-C7)	1.48	1.49	1.46	1.46
	R(C10-C11)	1.47	1.48	1.46	1.46
	R(C13-C14)	1.48	1.49	1.46	1.46
	θ(C2-C3-C4)	122.3	121.3	122.1	122.7
	θ(C6-C7-C8)	123.7	122.7	124.0	124.4
	θ(C9-C10-C11)	118.8	119.1	119.4	118.8
	θ(C9-C13-C14)	117.3	117.6	117.4	117.0
	θ(C1-C2-C3-C4)	48.3	55.4	40.2	39.0
	θ(S5-C6-C7-C8)	55.3	60.5	42.6	45.5
	θ(C9-C10-C11-S12)	44.9	53.6	34.7	36.3
	θ(C9-C13-C14-C15)	47.5	55.9	35.0	36.9

Table S3. The transfer integrals of hole (V_{hole}) and electron ($V_{electron}$) (absolute value) for different hopping pathways of molecules 1 to 6 based on B3LYP/6-31G(d, p) level.

Molecule	Pathway	Distance (Å)	V_{hole} (meV)	$V_{electron}$ (meV)
1	1, 2, 3, 4	9.64	3.3	3.7
	5, 6, 7, 8	13.76	1.2	0.7
	9, 10, 11, 12	13.13	0.1	1.3
2	1, 2	7.20	18.6	9.4
	3, 4	14.61	9.2×10^{-4}	3.6×10^{-4}
	5, 6, 7, 8	10.47	8.2	3.0
	9, 10	19.36	0.04	0.04
	11, 12, 13, 14	16.46	0.09	0.02
3	1, 2	6.99	3.9	9.7
	3, 4, 5, 6	8.89	4.7	0.2
	7, 8	13.30	1.2	2.0
	9, 10, 11, 12	15.34	4.7	0.7
	13, 14	17.63	0.2	0.6
	15, 16	18.97	2.6	0.7
4	1, 2	3.91	18.7	27.9
	3, 4	12.56	0.2	0.3
	5, 6	12.56	1.7×10^{-3}	0.01
	7, 8	11.93	1.3	0.1
	9, 10, 11, 12	15.31	0.3	0.2
	13, 14, 15, 16	15.26	0.2	0.06
5	1, 2	4.80	9.9	6.3
	3, 4	15.13	0.05	0.2
	5, 6	14.35	0.03	3.9×10^{-4}
	7, 8, 9, 10	16.38	0.05	0.07
	11, 12, 13, 14	16.22	0.02	0.04
6	1, 2, 3, 4	6.93	18.2	3.0
	5, 6	10.99	5.9	3.5
	7, 8, 9, 10	13.38	0.3	2.0
	11, 12, 13, 14	17.08	1.3×10^{-3}	6.8×10^{-4}
	15, 16	13.98	2.2	2.8
	17, 18	13.69	5.8	4.1

Table S4. The calculated average mobilities of hole ($\mu_{h,ave.}$) and electron ($\mu_{e,ave.}$) of molecules 1 to 6 based on B3LYP/6-31G (d, p) level.

Molecule	**$\mu_{h,ave.}$ ($cm^2V^{-1}s^{-1}$)**	**$\mu_{e,ave.}$ ($cm^2V^{-1}s^{-1}$)**
1	2.8×10^{-3}	1.4×10^{-3}
2	3.9×10^{-3}	3.6×10^{-4}
3	0.01	1.2×10^{-4}
4	0.01	0.01
5	4.6×10^{-3}	3.2×10^{-4}
6	0.02	2.9×10^{-3}

Table S5 Intermolecular interaction energies for the most prominent dimers of molecules 3, 4 and 6.

Dimers	**Interaction energies (kcal/mol)**
Dimer 1 of molecule 3	-31.75
Dimer 1 of molecule 4	-36.81
Dimer 1 of molecule 6	-24.74

Table S6. The reorganization energies of hole (λ^+) and electron (λ^-) using adiabatic potential energy surfaces (APES) approach, the HOMO, LUMO energies, as well as the vertical and adiabatic ionization potentials (IP_V, IP_A) and electron affinities (EA_V, EA_A) of molecule 6 at B3LYP-D3/6-31G (d, p) level: All the data are in unit of eV.

λ^+	λ^-	**HOMO**	**LUMO**	**IP_V**	**IP_A**	**EA_V**	**EA_A**
0.285	0.266	-5.05	-2.02	6.14	6.00	-0.89	-1.02

Table S7 The transfer integrals of hole (V_{hole}) and electron ($V_{electron}$) (absolute value) for different hopping pathways and charge mobilities of hole and electron for molecule 6 based on B3LYP-D3/6-31G(d, p) level.

Molecule	Pathway	Distance (Å)	V_{hole} (meV)	$V_{electron}$ (meV)
6	1, 2, 3, 4	6.93	18.4	3.0
	5, 6	10.99	6.0	3.5
	7, 8, 9, 10	13.38	0.3	2.0
	11, 12, 13, 14	17.08	1.3×10^{-3}	6.9×10^{-4}
	15, 16	13.98	2.2	2.9
	17, 18	13.69	5.9	4.2
μ ($cm^2V^{-1}s^{-1}$)			0.02	3.2×10^{-3}

References

1. T. H. El-Assaad, M. Auer, R. Castañeda, K. M. Hallal, F. M. Jradi, L. Mosca, R. S. Khnayzer, D. Patra, T. V. Timofeeva, J.-L. Brédas, E. J. W. List-Kratochvil, B. Wex, and B. R. Kaafarani, *J. Mater. Chem. C*, 2016, **4**, 3041−3058.