

Support Information:

First Principles Investigation of Anisotropic Hole Mobilities in Organic Semiconductor

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Documentary statement

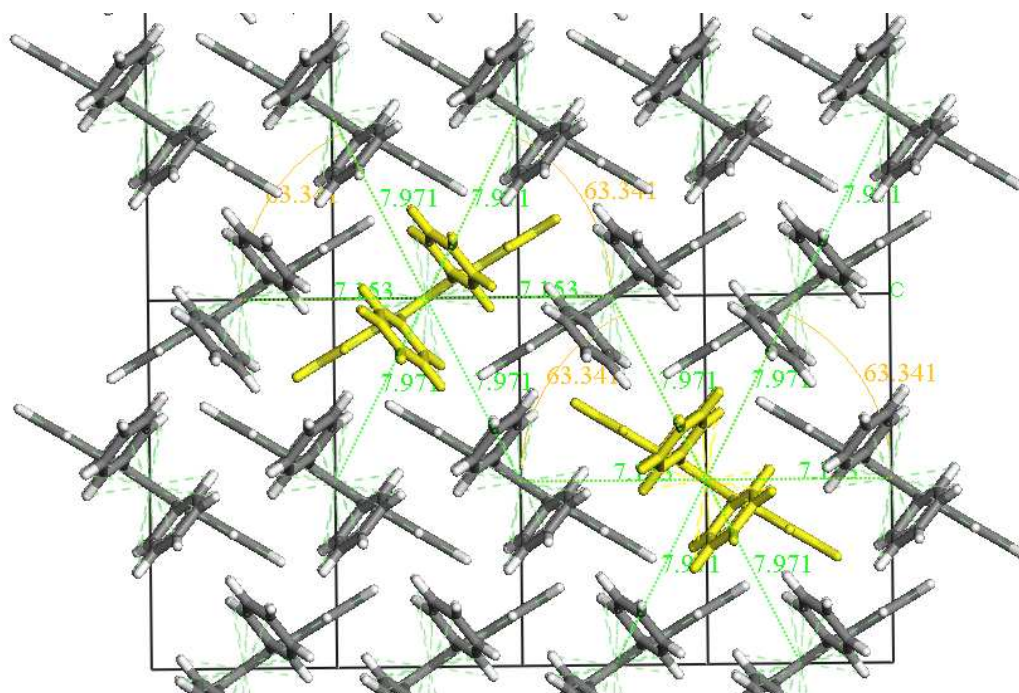
Figure S1 Illustrations of the identical surrounding of random selected molecules in the rubrene crystals.

The derivation of eq. 8

Table S1 Computation details of internal reorganization energy (λ). E (neutral in neutral geometry), E^* (neutral in ion geometry), E_+ (ion in ion geometry) and E_+^* (ion in neutral geometry) are in Hartree, and the VIP(vertical ionization potential) and λ are in eV.

Table S2 Calculated electronic coupling elements for different dimer types in tetracene, pentacene, rubrene, DCT, HTP, and Bracelet-14 organic semiconductor. (values from reference⁵ are shown in parentheses)

Figure S1. Illustrations of the identical surrounding of random selected molecules in the rubrene crystals.



The derivation of eq. 8

$$\begin{aligned}
\mu'(\Phi) &= \left(\frac{e}{2k_B T} \sum_i \rho_i W_i r_i^2 \cos^2 \gamma_i \cos^2(\theta_i - \Phi) \right)' \\
&= \frac{e}{2k_B T} \sum_i \rho_i W_i r_i^2 \cos^2 \gamma_i (2 \cos(\theta_i - \Phi) (\sin(\theta_i - \Phi))) \\
&= \frac{e}{2k_B T} \sum_i \rho_i W_i r_i^2 \cos^2 \gamma_i \sin 2(\theta_i - \Phi) \\
&= \frac{e}{2k_B T} \sum_i (\rho_i W_i r_i^2 \cos^2 \gamma_i (\sin(2\theta_i) \cos(2\Phi) - \cos(2\theta_i) \sin(2\Phi))) \\
\mu'(\Phi) = 0 &\Rightarrow \\
\left(\frac{e}{2k_B T} \sum_i \rho_i W_i r_i^2 \cos^2 \gamma_i \sin(2\theta_i) \right) \cos(2\Phi) &= \left(\frac{e}{2k_B T} \sum_i \rho_i W_i r_i^2 \cos^2 \gamma_i \cos(2\theta_i) \right) \sin(2\Phi) \\
\Rightarrow \tan(2\Phi) &= \frac{\sum_i \rho_i W_i r_i^2 \cos^2 \gamma_i \sin(2\theta_i)}{\sum_i \rho_i W_i r_i^2 \cos^2 \gamma_i \cos(2\theta_i)} \\
\because W_i &= \frac{V_i^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} \exp\left(-\frac{\lambda}{4k_B T} \right) \\
\Rightarrow \Phi_{\text{extrema}} &= \frac{n\pi}{2} + \frac{1}{2} \arctan \left(\frac{\sum_i P_i V_i^2 r_i^2 \cos^2 \gamma_i \sin 2\theta_i}{\sum_i P_i V_i^2 r_i^2 \cos^2 \gamma_i \cos 2\theta_i} \right), n = 0, \pm 1, \pm 2, \pm 3, \dots
\end{aligned}$$

Table S2. Computation details of internal reorganization energy (λ). E (neutral in neutral geometry), E^* (neutral in ion geometry), E_+ (ion in ion geometry) and E_+^* (ion in neutral geometry) are in Hartree, and the VIP(vertical ionization potential) and λ are in eV.

	TETR	PENT	RUBR	DCT	HTP	1CT	2CT	Bracelet-14
E	-693.32185	-846.98821	-1617.69581	-1612.55784	-3232.68949	-785.58749	-877.85116	-2150.77471
E^*	-693.31982	-846.98649	-1617.69301	-1612.55516	-3232.68692	-785.58570	-877.84955	-2150.77451
E_+	-693.08279	-846.76312	-1617.47425	-1612.31024	-3232.44351	-785.33387	-877.58360	-2150.59643
E_+^*	-693.08056	-846.76125	-1617.47148	1612.30751	-3232.44088	-785.33193	-877.58197	-2150.59533
VIP	6.5658	6.1758	6.1032	6.8117	6.7649	6.9542	7.3249	4.8849
	6.97 ^a	6.63 ^a	6.41 ^a	6.505 ^d				
λ	0.1157	0.0976	0.1521	0.1472	0.1428	0.1017	0.0881	0.0357
	0.1176 ^b	0.0992 ^b	0.1590 ^c	0.1410 ^d				

^a NIST database. ^b Reference 2 ^c Reference 3 ^d Reference 4

- 2 (a) Podzorov, V., Sysoev, S.E., Loginova, E., Pudalov, V.M. & Gershenson, M.E. *Appl. Phys. Lett.* **2003**, *83*, 3504-3506. (b) Podzorov, V., Pudalov, V.M. & Gershenson, M.E. *Appl. Phys. Lett.* **2003**, *82*, 1739-1741.
- 3 da Silva, D. A.; Kim, E. G.; Bredas, J. L. *Advanced Materials* **2005**, *17*, 1071-1076.
- 4 Kuo, M. Y.; Chen, H. Y.; Chao, I. *Chemistry-a European Journal* **2007**, *13*, 4750-4758.

Table S3 Calculated electronic coupling elements for different dimer types in tetracene, pentacene, rubrene, DCT, HTP, 1CT, 2CT and bracelet-14 organic semiconductor. (values from reference⁵ are shown in parentheses)

	TETR	PENT	RUBR	Bracelet-14
V_{T1} (eV)	-0.017 (-0.023)	0.085 (0.085)	0.019 (0.015)	0.054
R_{T1} (Å)	5.11	4.73	7.97	14.3
V_{T2} (eV)	0.070 (0.070)	-0.048 (-0.051)	0.019 (0.015)	0.053
R_{T2} (Å)	4.82	5.19	7.97	14.3
V_P (eV)	-0.001 (-0.004/16)	0.036 (0.037/34)	0.089 (0.083)	0.052
R_P (Å)	6.08	6.26	7.15	14.3
V_L (eV)	0.0000 (0.0000)	0.001 (0.0000)	0.0023 (0.0000)	-0.005
R_L (Å)	13.38	14.12	13.73	7.131

DCT

V_{T1} (eV)	-0.006
R_{T1} (Å)	9.822
V_{T2} (eV)	-0.0055
R_{T1} (Å)	10.435
V_P (eV)	-0.0863
R_P (Å)	3.848
V_{L1} (eV)	-0.0017
R_L (Å)	8.652
V_{L2} (eV)	0.00049
R_L (Å)	12.717

HTP

V_{T1} (eV)	0.0035
R_L (Å)	12.477
V_{T2} (eV)	0.0031
R_L (Å)	12.749
V_{T3} (eV)	0.0026
R_L (Å)	9.323
V_{T4} (eV)	0.003
R_L (Å)	9.567
V_P (eV)	0.0225
R_L (Å)	3.934
V_L (eV)	-0.00066
R_L (Å)	14.311

⁵ Coropceanu, V., Cornil, J., da Silva, D.A., Olivier, Y., Silbey, R. & Bredas, J.L. Charge transport in organic semiconductors. *Chem. Rev.* **107**, 2165-2165 (2007).

