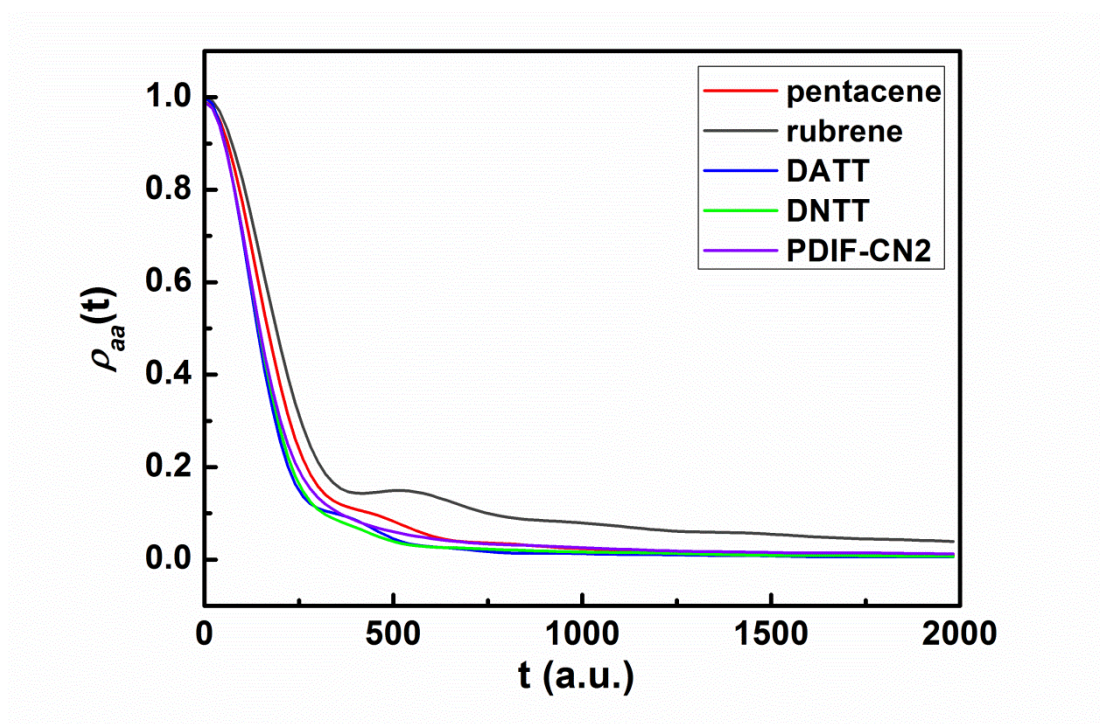


## Supporting information

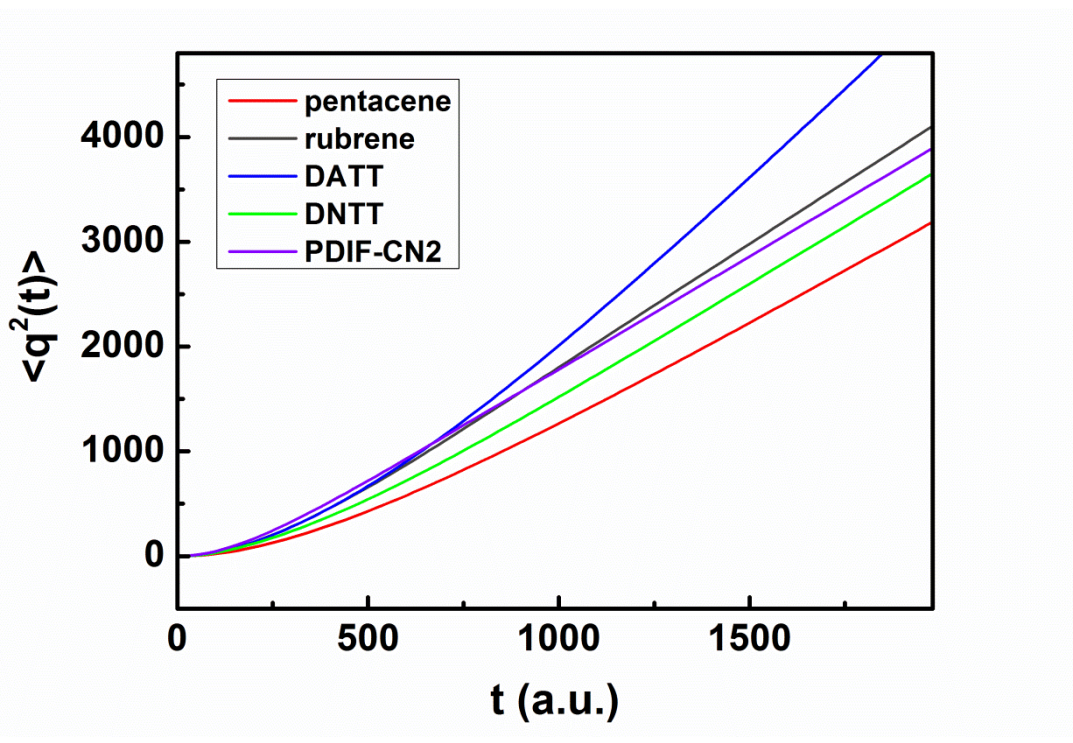
### Nuclear tunnelling and carrier delocalization to bridge the gap between hopping and bandlike behaviors in organic semiconductors

*Yuqian Jiang, Xinxin Zhong, Wen Shi, Qian Peng, Hua Geng, Yi Zhao\*, and Zhigang Shuai\**

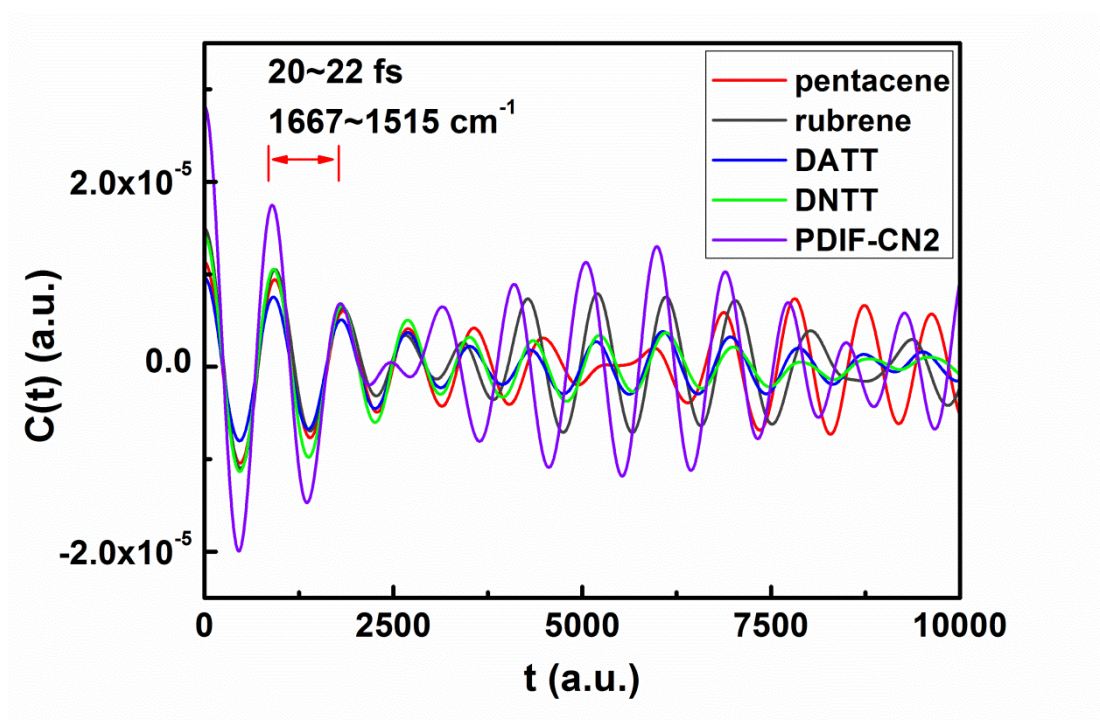
#### 1. TDPWD calculation results for all systems.



**Figure S1.** The time-dependent charge population on initial site  $a$  ( $\rho_{aa}(t)$ ) for all systems.



**Figure S2.** the time-dependent mean-square displacement ( $\langle q^2(t) \rangle$ ) of charge for all systems.



**Figure S3.** The quantum correlation functions  $C(t)$  of site energy fluctuation for all systems.

## 2. The calculation details of band mobility for rubrene and PDIF-CN2 resulted from Boltzmann transport theory and deformation potential theory.

Geometry optimizations and the band structure calculations are performed by the projector augmented wave (PAW) method with the Perdew-Burke-Ernzerhof including dispersion (PBE-D) exchange correlation functional in the Vienna ab initio simulation package (VASP 5.3.2).<sup>S1-S3</sup> The cut-off energy for the plane-wave basis was set to be 600 eV. The convergence criterion of the total energy was set to be  $10^{-5}$  eV in the self-consistent field iteration. The spin-orbit coupling was not considered. The Monkhorst-Pack  $\mathbf{k}$ -mesh of  $4 \times 4 \times 1$  was used for the ionic and lattice constant relaxations and that of  $8 \times 8 \times 2$  was used for the single-point energy and charge density calculations. The tetrahedron method with Blöch corrections was used for smearing. The cut-off radius for pair interactions was set to be 50 Å.

We then apply the Boltzmann transport equation in the relaxation time approximation to model the microscopic electrical transport process.<sup>S4-S5</sup> In the Boltzmann transport theory, the electrical conductivity  $\sigma$  is related to a transport distribution function<sup>4</sup>  $\sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \tau_{\mathbf{k}}$ , where  $\tau_{\mathbf{k}}$  is the relaxation time,  $\mathbf{v}_{\mathbf{k}} = \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}} / \hbar$  is the group velocity of an electron in a specified band,  $\varepsilon_{\mathbf{k}}$  is the band energy at a given  $\mathbf{k}$ -point. We can obtain the group velocity from the first-principles band structure calculations. The band energies on a fine  $\mathbf{k}$ -mesh of  $41 \times 41 \times 9$  are calculated for systems. After achieving the electrical conductivity  $\sigma$ , mobility can be obtain with  $\sigma = Ne\mu$ .

The relaxation times measure how quickly the electrons are restored to their equilibrium distribution via various scattering mechanisms. Here, we consider the longitudinal acoustic phonon scatterings in the long wavelength limit. Assuming that the scattering matrix element is independent of the direction of the lattice wave propagation, the relaxation time has the form  $\frac{1}{\tau_{\mathbf{k}}} = \frac{2\pi}{\hbar} \frac{k_B T E_f^2}{C_{ii}} \sum_{\mathbf{k}'} \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) [1 - \cos \theta]$ , where  $\delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})$  is the Dirac delta function,  $\theta$  is the angle between  $\mathbf{k}$  and  $\mathbf{k}'$ .

$|M(\mathbf{k}, \mathbf{k}')|^2 = k_B T E_1^2 / C_{ii}$  is the matrix element for electrons to be scattered from the Bloch state  $\mathbf{k}$  to  $\mathbf{k}'$ , where  $E_1$  is the DP constant and  $C_{ii}$  is the elastic constant in the direction of the lattice wave propagation.<sup>S6</sup> For simplicity, we stretch the unit cell along the crystal directions  $a$ ,  $b$ , and  $c$ , respectively.  $E_1$  is obtained by the linear fit of the band edge energy shift with respect to the lattice dilation, and  $C_{ii}$  is obtained by the parabolic fit of the total energy with respect to the lattice dilation.

**Table S1.** Band dispersions of rubrene and PDIF-CN2 along the high-symmetry directions.

		$\Gamma X$ (eV)	$\Gamma Y$ (eV)	$\Gamma Z$ (eV)
<b>Rubrene</b>	<b>VB</b>	0	0.378	0.064
	<b>CB</b>	0	0.156	0.025
	<b>Band gap</b>		1.153	
<b>PDIF-CN2</b>	<b>VB</b>	0.260	0.034	0
	<b>CB</b>	0.092	0.316	0
	<b>Band gap</b>		0.941	

**Table S2.** Deformation potential constants ( $E_1$ ), elastic constants ( $C_{ii}$ ) for electrons and holes in rubrene and PDIF-CN2 along the  $a$ ,  $b$ , and  $c$  directions.

	<b>Directions</b>	$E_1$ (eV)		$C_{ii}$ ( $10^9$ J m <sup>-3</sup> )
		<b>Holes</b>	<b>Electrons</b>	
<b>Rubrene</b>	<b>a</b>	0.195	0.133	9.326
	<b>b</b>	0.634	1.374	5.133
	<b>c</b>	1.453	0.336	6.334
<b>PDIF-CN2</b>	<b>a</b>	0.397	0.237	21.113
	<b>b</b>	1.854	0.584	13.621

<b>c</b>	2.965	2.877	18.244
----------	-------	-------	--------

**Table S3.** The calculated electrons or holes relaxation times  $\tau$  for rubrene and PDIF-CN2 at room temperature.

	<b>rubrene</b>	<b>PDIF-CN2</b>
<b>Electrons</b>	-	101.09
<b>Holes</b>	157.74	-

**Table S4.** Calculated electron and hole mobility ( $\mu$ ) for rubrene and PDIF-CN2 at room temperature along  $a$ ,  $b$  or  $c$  directions.

	<b>Carrier types</b>	$\mu_a$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_b$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_c$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
<b>rubrene</b>	<b>Holes</b>	-	242.6	72.7
	<b>Electrons</b>	-	-	-
<b>PDIF-CN2</b>	<b>Holes</b>	-	-	-
	<b>Electrons</b>	132.8	91.2	-

## References

- (S1) P. E. Blöchl, Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953.
- (S2) S. Grimme, Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787.
- (S3) G. Kresse, J. Furthmüller, Efficient Iterative Schemes for *ab initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169.

- (S4) T. J. Scheidemantel, C. Ambrosch-Draxl, T. Thonhauser, J. V. Badding, J. O. Sofo, Transport Coefficients from First-Principles Calculations. *Phys. Rev. B* **2003**, *68*, 125210.
- (S5) J. Yang, H. Li, T. Wu, W. Zhang, L. Chen, J. Yang, Evaluation of Half-Heusler Compounds as Thermoelectric Materials Based on the Calculated Electrical Transport Properties. *Adv. Funct. Mater.* **2008**, *18*, 2880.
- (S6) L. Tang, M. Long, D. Wang, Z. Shuai, The Role of Acoustic Phonon Scattering in Charge Transport in Organic Semiconductors: A First-Principles Deformation-Potential Study. *Sci. China Ser. B: Chem.* **2009**, *52*, 1646.