Supporting information for

Insights into the vibration coupling effects on reorganization

energy in π -isoelectronic frameworks

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1. The methodology of computational details.

All the calculations were performed with the DFT program Gaussian 09 and DUSHIN¹ as well as MOMAP². For the data processing of the studied molecules, computational work is finished by Multiwfn³ and the figures drawing is assisted by VMD⁴. The reorganization energies have been calculated by the four-point method of adiabatic potential surface and the normal mode (NM) approach simultaneously, which are in excellent agreement (Figure S1). Other computational details are listed below.

(1) Reorganization energy

According to Marcus' theory, reorganization energy is a crucial parameter for calculating carrier transfer rates, and it can be divided into internal and external reorganization energy components. The internal reorganization energy represents the energy change within the system due to geometric structural relaxation during the electronic state transition. On the other hand, the external reorganization energy corresponds to the polarization effects caused by the surrounding environment. Previous studies have extensively discussed how to calculate the reorganization energy of molecules and its dependence on different solvents ^{5,6}.

In this study, our focus is specifically on the inner reorganization energy (λ), which directly depends on the molecular structure as an inherent property. Typically, there are two methods for computing reorganization energy: the 4-point method, as introduced by Nelsen, and the normal mode analysis strategy.

Nelsen's 4-poi method shows that λ can be evaluated by theadiabatic potential energy

surface method: $\lambda_h = (E_+^* - E_+) + (E_-^* - E)\lambda_e = (E_-^* - E_-) + (E_-^* - E)\lambda_e$

where λ_h and λ_e stand for the hole and electron reorganization energies, respectively; E_+^* and E_-^* denote energies of the cationic and anionic species, respectively, with geometries fixed at neutral states before carrier inction. E, E_+, E_- are the energies of the neutral/cation/anion adiabatic potential energy surface at optimized geometries with the lowest energy, respectively, and E^* is the energy of neutral potential energy surface with the geometry of cation and anion. The alternative approach involves using normal mode (NM) analysis to compute λ by summing the potential energy of harmonic oscillators ^{7,8}. This method allows for the assessment of vibronic coupling contributions from modes during geometric relaxation. In this study, we utilize the NM method to perform a decomposition of the reorganization energy. After calculating the frequencies for each molecule in both the neutral and charged states, we can decompose the displacement between two minima points on the two potential energy surfaces into contributions from the normal coordinates of the molecules. According to the definition of a harmonic potential, the reorganization energy λ can be partitioned into contributions from normal modes as follows:

 $\lambda_i = \frac{1}{2} k_i (\Delta Q_i)^2$

where ΔQ_i represent the contribution of the ith mode, k_i is the force constant of the related vibronic normal mode. The harmonic potential model is an approximation of the actual potential surface, after all, the $\sum_{i=1}^{\lambda_i} \lambda_i$ is not exactly equal to λ but as qualitative analysis.

It can be seen in Table S1 that the ratio of λ_e/λ_h is greater than 1 for all the molecules, indicating higher hole transport mobility in these materials. Specifically, as sulfur is added to anthracene, tetracene, and pentacene, the ratios for BDT, NDT, and ADT increase. In contrast, when adding a heteroatom to phenanthrene, chrysene, and picene, the ratio of λ_e/λ_h (DBT, BTBT and DBTBT) does not follow a simple trend. This strongly suggests that both the topology of the molecules and the position of the heteroatom play crucial roles in determining the polar/bipolar properties of the molecules.

To assess the reliability of the decomposition using the harmonic approximation, we present the results calculated using both harmonic analysis and Nelsen's 4-point

method (Figure S1). The consistency between these results validates the credibility of reorganization energy decomposition using the harmonic approximation.



Figure S1 The comparison of results calculated by 4-points method and NM method.

(2) Natural population analysis (NPA) charge

Natural population analysis (NPA) is one computational method to calculate the atomic charge to describe the charge distribution in chemical systems.⁹ The key of NPA is to transform the wave function described by the random original basis set (usually extended basis) into the description under the orthogonal minimal basis with clear physical meaning, so that there is a clear correspondence between the basis function and the atomic orbital. It greatly avoids the impact of the imbalance of the basis set on the results and also avoids the difficulty of dividing the cross-term. Since NPA is a component within the framework of the natural bond orbit (NBO) method¹⁰, and it is usually calculated by the NBO program¹¹, the NPA charge is often referred to as the NBO charge in literature.

Molecule		Energy l	evels/eV	Reorga Energ	inization gy/meV	Ratio(λ_e/λ_h)	$\Delta\lambda_{h}^{a}$	
		НОМО	LUMO	λ_h	λ_{e}			
Group Zigzag	3-Ant	-5.49	-1.91	141.7	205.7	1.45	16.9%	
	3-BDT	-5.67	-1.33	165.6	303.6	1.83		
	4-Tetra	-5.12	-2.35	115.8	164.7	1.42	-8.0%	
	4-NDT	-5.30	-1.84	106.5	215.8	2.03		

Tal	ble	2 S1	The	cald	culatec	pro	perties	of r	mol	ecul	les	in	Figure	1
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	5-Penta	-4.86	-2.66	96.5	135.2	1.40	1.2%		
	5-ADT	-5.02	-2.27	97.7	165.0	1.69			
Group Armcha	3-DBT	-6.03	-1.25	140.9	314.7	2.23	-36.8%		
	3-Phe	-5.99	-1.28	222.8	322.7	1.45			
	4-BTBT	-5.80	-1.52	231.9	303.5	1.31	38.2%		
	^{ir} 4-Chry	-5.78	-1.54	167.9	219.6	1.31			
	5-DBTBT	-5.77	-1.73	104.3	282.9	2.71	-45.1%		
	5-Pice	vice -5.76		190.0	278.6	1.47			
$\Delta \lambda_h = \frac{\lambda_h^{surfur} - \lambda_h^{acene}}{$									

 $\lambda^{acene}_{\ h}$, this parameter can be used to quantify the difference in hole reorganization energy levels between acenes and thienoacenes systems.



Figure S2 The HOMO distribution of studied π -isoelectronic molecules.



Figure S3 The LUMO distribution of studied π -isoelectronic molecules.



Figure S4 The vibrational regimes at different frequency of hole reorganization energy for tetracene and NDT.



Figure S5 The summary of hole reorganization energy decomposition for the studied molecules.



Fig S6 213cm⁻¹ vibration mode of DBT



Figure S7 Hole reorganization energy of interposition-fused furan molecules of the armchair group.



Figure S8 Components analysis of HOMO and natural population atomic (NPA) charge of studied molecules. (a) Components analysis with NAO method for the HOMO of studied molecules, the squares in orange color represent sulfur atom in materials, the gray, green, blue and red refers to carbons in different sites as displayed in molecular formulas in the X-axis. (b) NPA charge for sulfur atom and every kind of carbons according to specific sites (the same as above).



Figure S9 HOMO and HOMO-1 distribution of sulfur-fused isoelectronic molecules of zigzag group.

References

(1) Peng, Q.; Yi, Y.; Shuai, Z.; Shao, J. Excited state radiationless decay process with Duschinsky rotation effect: formalism and implementation. *The Journal of chemical physics* **2007**, *126*, 114302.

(2) Nan, G.; Yang, X.; Wang, L.; Shuai, Z.; Zhao, Y. Nuclear tunneling effects of charge transport in rubrene, tetracene, and pentacene. *Physical Review B* **2009**, *79*.

(3) Lu, T.; Chen, F. Multiwfn: a multifunctional wavefunction analyzer. *J Comput Chem* **2012**, *33*, 580-592.

(4) Humphrey, W.; Dalke, A.; Schulten, K. VMD: visual molecular dynamics. *Journal of molecular graphics* **1996**, *14*, 33-38.

(5) McMahon, D. P.; Troisi, A. Evaluation of the External Reorganization Energy of Polyacenes. *The Journal of Physical Chemistry Letters* **2010**, *1*, 941-946.

(6) Huang, W.; Shi, H.; Liu, H.; Corminboeuf, C. The influence of external electric fields on charge reorganization energy in organic semiconductors. *Chem. Commun.* **2019**, *55*, 2384-2387.

(7) Kwon, O.; Coropceanu, V.; Gruhn, N. E.; Durivage, J. C.; Laquindanum, J. G.; Katz, H. E.; Cornil, J.; Bredas, J. L. Characterization of the molecular parameters determining charge transport in anthradithiophene. *The Journal of chemical physics* **2004**, *120*, 8186-8194.

(8) Coropceanu, V.; Malagoli, M.; da Silva Filho, D. A.; Gruhn, N. E.; Bill, T. G.; Brédas, J. L. Hole- and Electron-Vibrational Couplings in Oligoacene Crystals: Intramolecular Contributions. *Physical Review Letters* **2002**, *89*, 275503.

(9) Tian, L. U.; Fei-Wu, C. Comparison of Computational Methods for Atomic Charges. *Acta Physico-Chimica Sinica* **2012**, *28*, 1-18.

(10) Weinhold, F.: Natural Bond Orbital Methods. . In *In Encyclopedia of Computational Chemistry*; P. v. R. ed.; Schleyer, Ed.; John Wiley & Sons:West Sussex, 1998; Vol. 2; pp 1792-1811.

(11) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. NBO. 5.0 ed., 2001.