

Supplemental Material to the article

“Method for rapid estimation of lattice distortion energy in organic semiconductors”

1. Details for method formulation

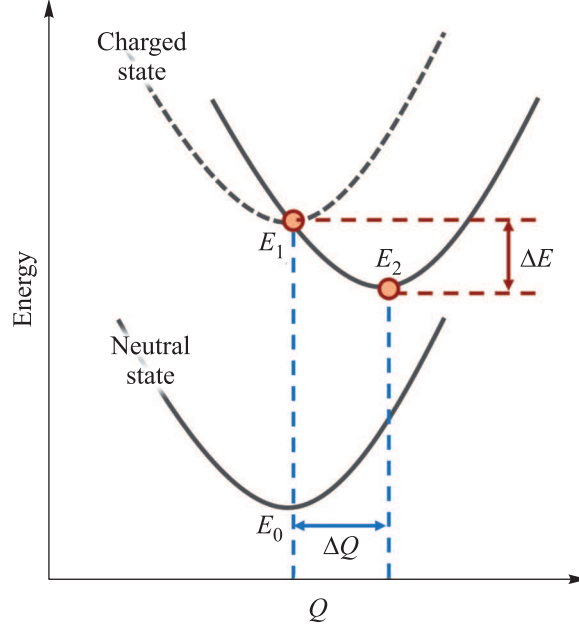


Fig. S1. Reorganization of molecular dimer after charging

In this section, justification of the suggested approach for assessment of the lattice distortion energy, L , is provided. Assume a dimer consisting of two identical molecules (monomers). Let the energy of the charge carrier (electron or hole) at each of these molecules equal ε . If emergence of the charge carrier at the dimer does not alter neither ε nor the charge transfer integral between the molecules, J , the potential energy of this charge carrier (delocalized within the dimer) reads [1]:

$$E(\mathbf{Q}) = \varepsilon - J + \frac{1}{2} \sum_i \hbar \omega_i Q_i^2, \quad (\text{S1})$$

where ω_i are the vibrational frequencies, and Q_i are the corresponding vibrational displacements. According to Eq. (S1), potential energy curve with respect to any particular vibrational coordinate Q is a parabola, which is sketched in Fig. S1 with a dashed line. However, in reality, both ε and J depend on Q_i due to the electron-phonon coupling:

$$\varepsilon = \varepsilon_0 + \sum_i \frac{\partial \varepsilon}{\partial Q_i} Q_i, \quad (\text{S2})$$

$$J = J_0 + \sum_i \frac{\partial J}{\partial Q_i} Q_i. \quad (\text{S3})$$

In this case, the potential energy curve for the charge carrier delocalized within the dimer is described by the following equation:

$$E(\mathbf{Q}) = \varepsilon_0 + \sum_i \frac{\partial \varepsilon}{\partial Q_i} Q_i - J_0 - \sum_i \frac{\partial J}{\partial Q_i} Q_i + \frac{1}{2} \sum_i \hbar \omega_i Q_i^2. \quad (\text{S4})$$

Again, the potential energy curve is a parabola, which is depicted in Fig.S1 with the upper solid line. However, as follows from Eq. (S4), the minimum point of this parabola is shifted by $\Delta Q = \frac{\frac{\partial J}{\partial Q_i} - \frac{\partial \varepsilon}{\partial Q_i}}{\hbar \omega_i}$ along the vibrational coordinates and by $\Delta E = \sum_i \frac{\left(\frac{\partial J}{\partial Q_i} - \frac{\partial \varepsilon}{\partial Q_i}\right)^2}{2\hbar \omega_i}$ in energy with respect to that described by Eq. (S1). Since considerable $\frac{\partial J}{\partial Q_i}$ are observed mainly for low-frequency vibrations, and considerable $\frac{\partial \varepsilon}{\partial Q_i}$ are observed for high-frequency vibrations [2], the quantity $\frac{\partial J}{\partial Q_i} \cdot \frac{\partial \varepsilon}{\partial Q_i}$ is generally low and can be neglected. In this case, the energy relaxation for the charge delocalized at the dimer is:

$$\Delta E = \sum_i \frac{\left(\frac{\partial J}{\partial Q_i}\right)^2 + \left(\frac{\partial \varepsilon}{\partial Q_i}\right)^2}{2\hbar \omega_i} = \frac{\lambda_2}{2 + L}, \quad (\text{S5})$$

where $\lambda_2 = \sum_i \frac{\left(\frac{\partial \varepsilon}{\partial Q_i}\right)^2}{\hbar \omega_i}$ is the charge transfer reorganization energy of the two non-interacting molecules (monomers), and $L = \sum_i \frac{\left(\frac{\partial J}{\partial Q_i}\right)^2}{2\hbar \omega_i}$ is the lattice distortion energy [1]. At the same time, considering the dimer as a single molecular system, one reads:

$$\Delta E = \frac{\lambda_d}{2}, \quad (\text{S6})$$

where λ_d is the dimer reorganization energy. Combining Eqs. (S5) and (S6), we obtain Eq. (3) of the main text, which constitutes the basis for the suggested approach of L estimation.

2. Dimer types and studied compounds.

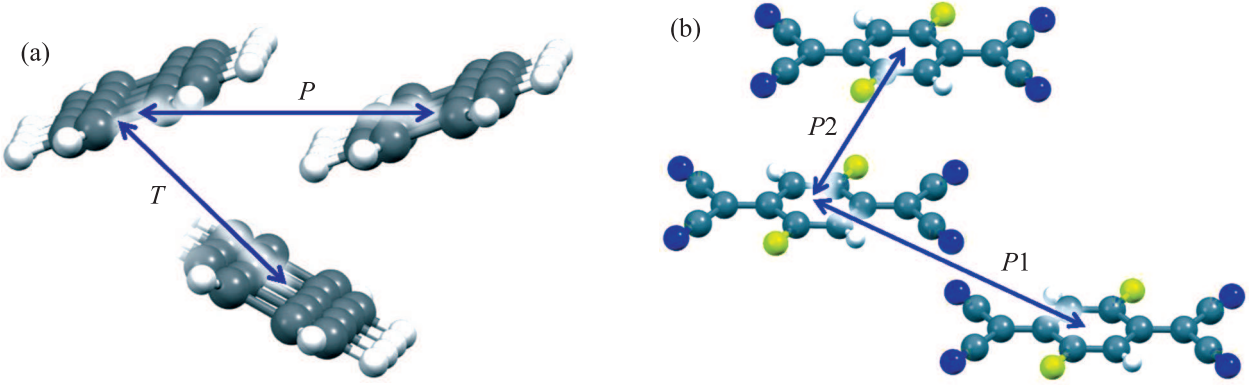


Fig. S2. Types (configurations) of the considered molecular dimers for crystalline tetracene (a) and F₂-TCNQ (b)

3. Reorganization energies for single molecules, dimers and trimers.

Table S1. Reorganization energies for single molecules (monomers), molecular dimers and trimers of the organic semiconductors studied. The molecular structures of these organic semiconductors are shown in Fig. S3. The data for TCNQ and F₂-TCNQ are from [3]

Organic semiconductor	Reorganization energy λ , meV		Trimer (P type)
	Single molecule	Dimer (type)	
Naphthalene	186	108 (P), 108 (T)	86
Anthracene	141	81 (P), 95 (T)	–
Tetracene	111	68 (P), 80 (T)	–
HM-TTF	265	138 (P)	95
TTF	292	173 (P)	130
F ₂ -TCNQ	240	164 ($P1$), 130 ($P2$)	95
TCNQ	237	145 (P), 147 (T)	100

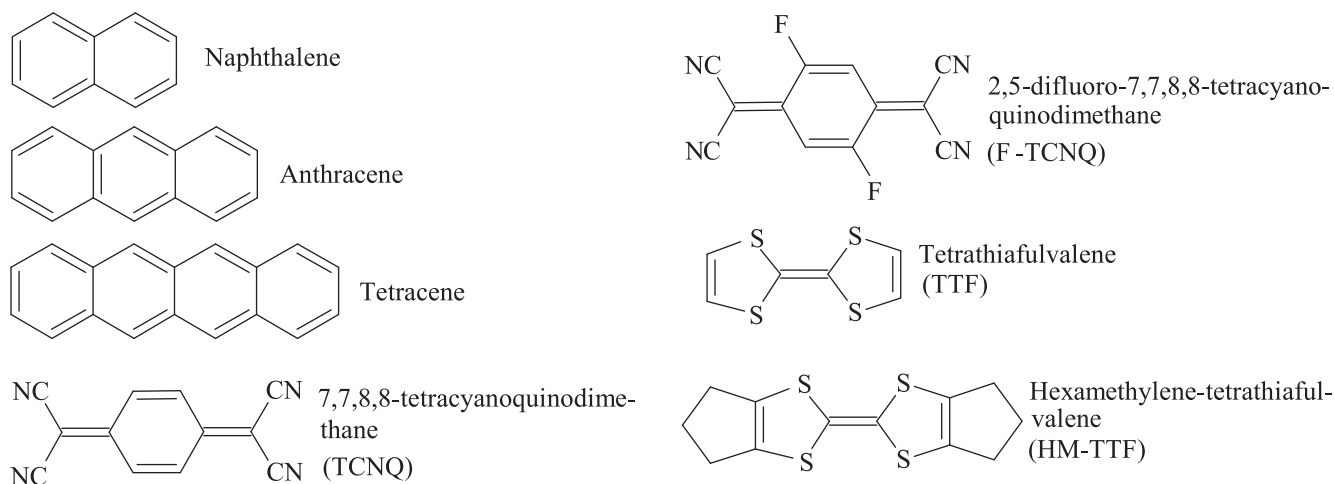


Fig. S3. Molecular structures of the organic semiconductors studied

References

- [1] Y. Li, V. Coropceanu, and J.-L. Bredas, *Charge Transport in Crystalline Organic Semiconductors*, in *Wspc Reference On Organic Electronics, The Organic Semiconductors (In 2 Volumes)*, ed. by S.R. Marder and J.-L. Bredas, World Scientific Publishing Company, Singapore (2016), ch. 7, p. 193.
- [2] A. Girlando, L. Grisanti, M. Masino, I. Bilotti, A. Brillante, R. G. Della Valle, and E. Venuti, *Phys. Rev. B* **82**, 035208 (2010).
- [3] A. Y. Sosorev, *Phys. Chem. Chem. Phys.* **19**, 25478 (2017).