Electronic Supplementary Information

Vibronic Coupling Density Analysis for Chain-Length Dependence of Reorganization Energies in Oligofluorenes: A Comparative Study with Oligothiophenes

Motoyuki Uejima[a], Tohru Sato [*a,b], Kazuyoshi Tanaka[a], and Hironori Kaji[c]

[a] Department of Molecular Engineering, Graduate School of Engineering,
Kyoto University, Kyoto 615-8510, Japan.

[b] Unit of Elements Strategy Initiative for Catalysts & Batteries,
Kyoto University, Kyoto 615-8510, Japan.

[c] Institute for Chemical Research,
Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

Submitted May 27, 2013

---

[*] To whom correspondence should be addressed.

Fax: +81-75-383-2555; Tel: +81-75-383-2803; E-mail: tsato@moleng.kyoto-u.ac.jp

1 Calculation of Hole Mobility

1.1 Method of Calculation for Hole-Mobility

To confirm the validity of the present calculation, we estimated the hole mobilities for fluorene and thiophene and compared them with the experimental data. The method of calculation is based on the Monte Carlo approach[1]. In the Marcus-Levich-Jortner formalism[2], the transfer rate k is given by

$$k = \frac{2\pi t^2}{\hbar}\sqrt{\frac{1}{4\pi\lambda_{\mathrm{ex}}T}}\sum_{n_\alpha=0}^{\infty}\exp(-S_\alpha)\frac{S_\alpha^n}{n_\alpha!}\exp\left[-\frac{(\Delta G^\circ+\lambda_{\mathrm{ex}}+n_\alpha\hbar\omega_\alpha)}{4\lambda_{\mathrm{ex}}k_BT}\right], \tag{1}$$

where t, λ_{ex},k_B, T, ΔG°, and S_α denote transfer integral between molecules, intermolecular reorganization energy, the Boltzmann constant, temperature, the difference of Gibbs free energy, and the Huang-Rhys factor, respectively. The summation is done from zero phonon level to n_α phonon level. The Huang-Rhys factor S_α is defined by

$$S_\alpha = \frac{\lambda_\alpha}{\hbar\omega_\alpha} = \frac{V_\alpha^2}{2\hbar\omega_\alpha^3}, \tag{2}$$

where λ_α and V_α denote the intramolecular reorganization energy and the VCC for mode α.

Now, we consider the oligomers are aligned in parallel to the long axes with distance d, and the external electric field F is applied in the alignment direction. Then, the energy difference between HOMOs of adjacent molecules is equal to $\Delta G^\circ = eFd$. The energy levels for the frontier orbitals is not so sensitive to the external electric filed with the range $F = 0-11\times 10^6\mathrm{V\cdot cm^{-1}}$, that the transfer integral t is obtained from a half of the energy split of the HOMOs in the non-biased system, where the two molecules are aligned in parallel with distance d[1].

The hole mobilities were obtained by evaluating the propagation of a single hole using the Monte Carlo simulations. The probability of transferring the charge to the left and right directions are defined by transfer rates:

$$p_{\rightarrow} = \frac{k_{\rightarrow}}{k_{\leftarrow}+k_{\rightarrow}}, \tag{3}$$

where the transfer rates $k_{\leftarrow}$ and $k_{\rightarrow}$ are based on Eq. (1). If the randomly generated number r is greater than $p_{\rightarrow}$, the hole transfers to the right molecule; else the hole reverses to the left molecules. The hopping time $\tau_{\leftarrow}$ and $\tau_{\rightarrow}$ are given by $1/k_{\leftarrow}$ and $1/k_{\rightarrow}$, respectively. The hole mobility μ is estimated from the total distance that charge traveled L, total time τ, and electronic field F:

$$\mu = \frac{L}{\tau F}. \tag{4}$$

The Monte Carlo simulation is continued until the standard deviation σ for the each calculation of μ becomes less than 0.01%.

1.2 Hole Mobilities for Fluorene and Thiophene

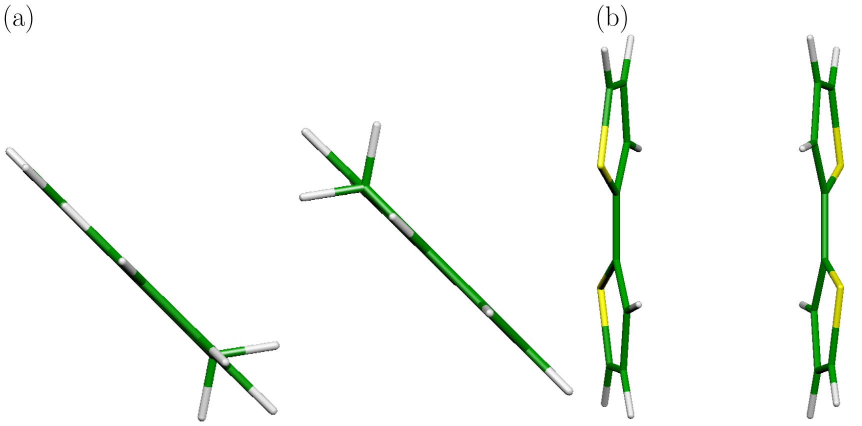

Figure S1: Optimized structures: (a) dimer **OF**(1) and (b) dimer **OT**(2). The optimization is performed at the B3LYP/6-3G(d,p) level of theory.

The intermolecular distance d is obtained from the optimized structures of the face-to-face dimers. The dimer optimization is carried out using the B3LYP/6-31G(d,p) calculation. The optimized dimer structures are shown in Fig. S1. While the **OF**(1) dimers are obliquely aligned to the molecular plane with 4.24 Å, the **OT**(2) dimers are aligned in parallel with 4.41 Å. The transfer integrals are estimated as a half value of the HOMO splitting in the monomers.

Table S1: Parameters for the hole mobility calculation.

	ω_α (cm^{-1})	S_α	t (eV)	d (Å)
Fluorene	1663.55	0.1366	0.0227	4.24
Thiophene	1502.23	0.4207	0.0412	4.41

The hole mobility as a function of the external electric field F $1.0 \times 10^4 - 1.0 \times 10^7$ V·cm^{-1} is calculated with the external reorganization energy $\lambda_{\text{ex}} = 0.4$ eV and with temperature $T = 300K$. In this calculation, the maximum-coupling mode α is taken into account. The parameters for the hole mobility simulation are summarized in Table S1.

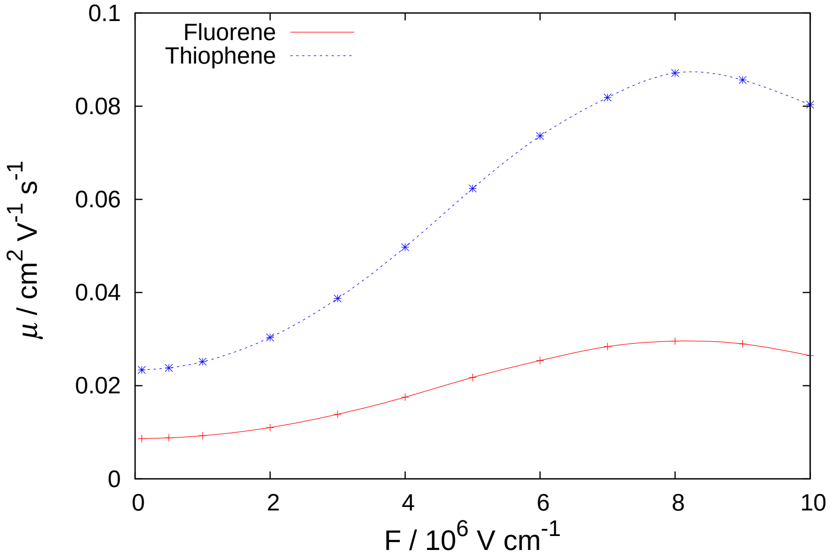

Figure S2: Simulated hole mobilities μ as a function of electric field F in the fluorene and thiophene one-dimensional crystalline structures. The red solid line with crosses indicates fluorene and the dashed blue line with asterisks indicates thiophene.

The hole mobilities for fluorene and thiophene are shown in Fig. S2. It is found that the hole mobility for the fluorene is lower than that for thiophene, although the Huang-Rhys parameter S_α for fluorene is smaller than that for thiophene. This is because of the small transfer integral t for the fluorene. The calculated hole mobilities qualitatively agree with the experimental values: parallel direction for poly(9,9'-dioctylfluorene) $\mu = 0.7 \times 10^{-3}$ cm^2 / V · s[3] and poly(3-hexylthiophenes) 0.1 cm^2 / V · s[4,5]. Therefore, we can conclude that the present calculation provides the qualified results in accordance with the experiments.

References

[1] Y. Oliber, V. Lemaur, J. L. Brédas and J. Cornil, *J. Phys. Chem. A*, 2006, **110**, 6356–6364.

[2] J. Jortner, *J. Chem. Phys.*, 1976, **64**, 4860.

[3] H. Kajii, K. Koiwai, Y. Hirose and Y. Ohmori, *Organic Electronics*, 2010, **11**, 509–513.

[4] Z. Bao, A. Dodabalapur and A. J. Lovinger, *Appl. Phys. Lett.*, 1996, **69**, 4108–4110.

[5] H. Sirringhaus, P. J. Brown, R. H. Friend, M. N. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig and D. M. de Leeuw, *Nature*, 1999, **401**, 685–688.