Supporting Information

Influences of crystal structures and molecular sizes on the charge mobility of organic semiconductors: oligothiophenes

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Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.;

Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Revision D. 01; Gaussian, Inc.: Wallingford, CT, **2003**.

Random walk simulation from Marcus electron tranfer rates to charge mobility

Random walk is a statistical method to predict the properties of a random process on average by means of simulation. In this work, we start from the molecular crystal structures determined by experiment and perform random walk simulations of hole diffusion constant with the Marcus inter-molecular charge transfer rates. Here we give a description of simulation process below.

Step 1: All the independent nearest neighbor pairs of molecules are identified in the single crystal. In the layered structure of an organic crystal, both the intra-layer neighbors and inter-layer neighbors are considered in the random walk simulation. Detailed Information can be found in the main text.

Step 2: Calculate the Marcus hopping rates $\{k^{\alpha}\}$ between all these nearest neighbor pairs, called pathway. The charge is only allowed to transport between these pathways and the probability for a specific pathway α is calculated as $p_{\alpha} = \frac{k^{\alpha}}{\sum_{\alpha} k^{\alpha}}$. The time cost in the transfer between α *-th* neighbor is $1/k^{\alpha}$.

Step 3: Perform the random walk simulation. We choose an arbitrary molecule as the starting point. The hole is only allowed to transfer between the chosen neighbors with the probability p_{α}. At each step, a random number r uniform distributed between 0 and 1 is generated. If $\sum_{\alpha}^{j-1} p_{\alpha} < r \le \sum_{\alpha}^{j} p_{\alpha}$, the *j-th* neighbor is chosen as the next position. We save the positions every 100 ns, and then the function between the squared displacement and time can be obtained. The snapshot time is much longer

than the time spent in the transfer between the neighbors and the total simulation time (10 μs) is again much longer than the snapshot time.

Step 4: Repeat Step 3 by many times in order to obtain an average diffusion constant $D = \lim_{t\to\infty} \frac{< l(t)^2 >}{6t}$, and then the mobility by the Einstein formula $\mu = \frac{eD}{k_B T}$. Two thousand simulations (Step 3) have been done, see Figure S1 for the example of 6T/LT , where we depict result for 10 simulations and the average over 2000 simulations.

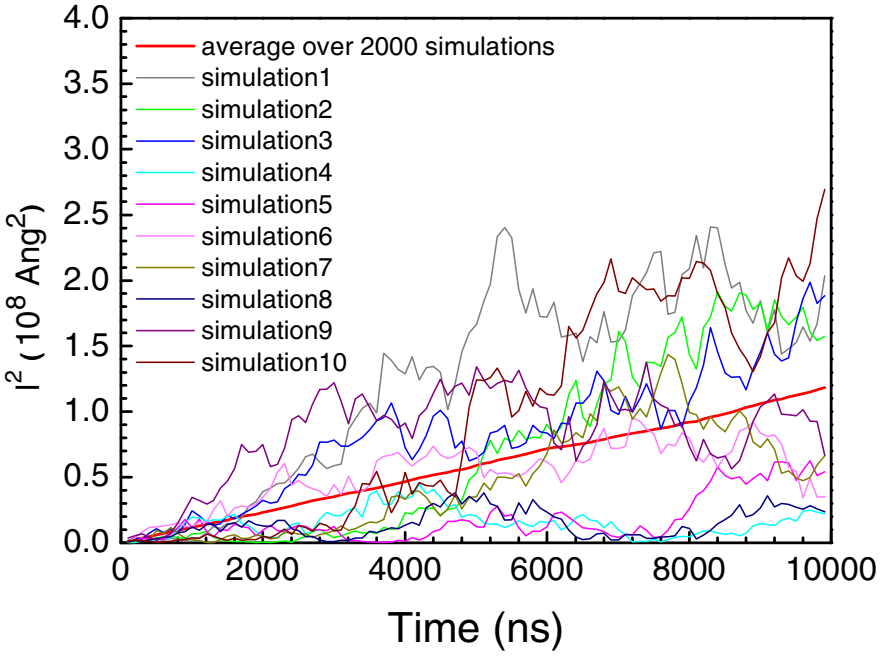

Figure S1. Squared displacement vs simulation time for 6T/LT.

Step5: Determine the error of the calculated charge mobility. We repeat Step4 for twenty times, namely, totally 40000 simulations have been done. Then the error of the mobility is evaluated as $\frac{\max\{\mu_i\} - \min\{\mu_i\}}{2}$, and the average mobility is $\frac{1}{20}\sum_i^{20} \mu_i$. For 6T/LT, the mobility is calculated to be 0.0075 cm^2/Vs with an error of 0.00025 cm^2/Vs. According to this method, a huge amount of simulations are needed to get an accurate result and evaluate the error.

We propose the following simple scheme to estimate the error. In principle, all the simulations should be chosen randomly from an infinite set of simulations which contains all the possible charge transport tracks (See the schematic diagram below). In practice, we can use a large number of simulations (two thousands here) to express this set approximately. One hundred choices with two thousands of simulations each are used to evaluate the error. For 6T/LT, according to this scheme, the averaged mobility is obtained as 0.0075 cm^2/Vs, and the error is 0.00028 cm^2/Vs, which are very close the results of the brute average from 40000 simulations. Therefore, we adopt this simple process in the article work.

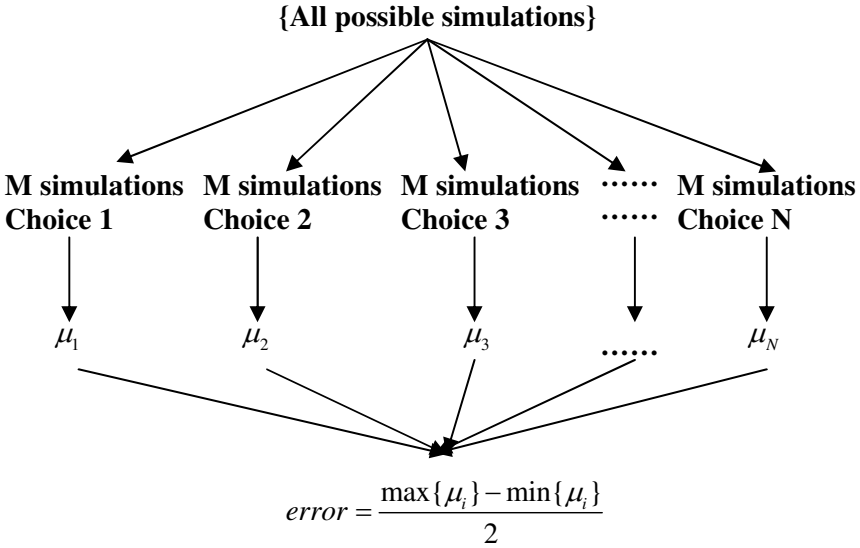

Diagram S1. Schematic diagram of evaluating the error of mobility

We give in Figure S2 and Figure S3 the simulated mobility and the estimated statistcal error versus the number of samplings (N in Diagram S1), respectively. The converged behavior further confirms the reliability of our proposed simulation and anaysis scheme.

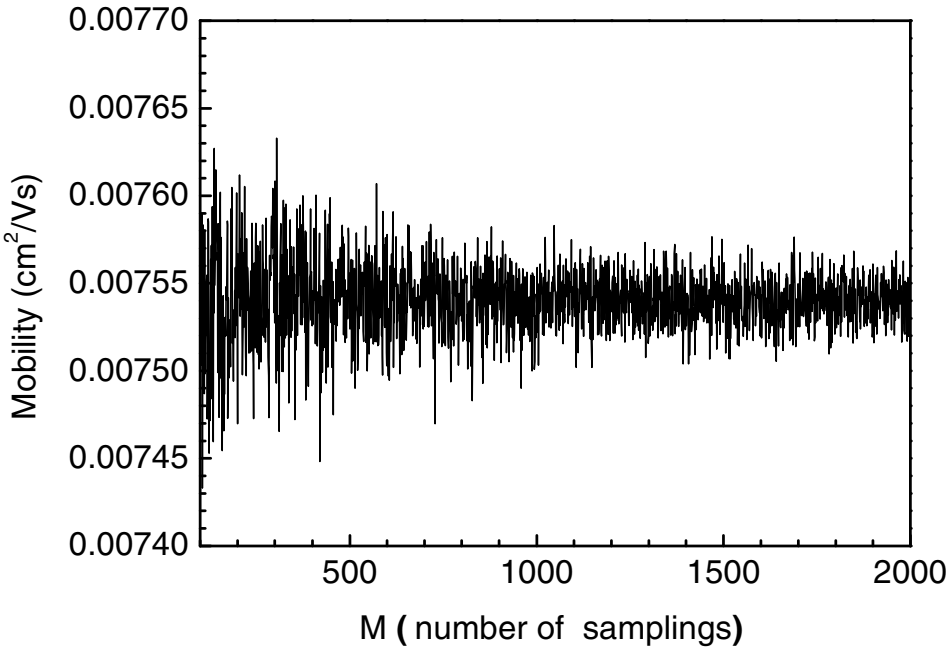

Figure S2. Mobility vs number of simulations for 6T/LT (N=100)

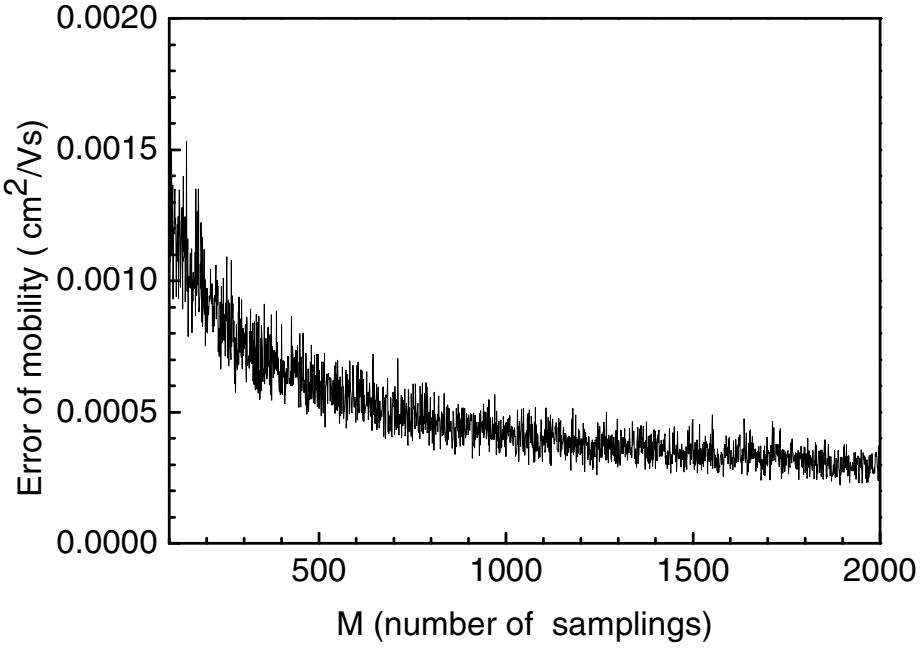

Figure S3. The error of mobility vs number of simulations for 6T/LT (N=100)