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Charge transport in amorphous and smectic mesophases of dicyanovinyl-substituted oligothiophenes

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I. ATOMISTIC SIMULATIONS

Atomistic simulations are performed as described in sec. II of the main text. While equilibrating the systems of 4096 DCVnT molecules at high temperatures, inter-thiophene and DCV-thiophene torsion angles can change their configurations from the cis to the trans state. The barrier between these states is 0.15 eV (14.5 $k_{\mathrm{B}}T$ at 300 K) for the thiophene-thiophene dihedral and 0.45 eV (43.4 $k_{\mathrm{B}}T$ at 300 K) for the thiophene-DCV dihedral [1]. Analysis of the molecular dynamics snapshots shows that all possible rotamers are present in the systems. For the DCV4T system, the distribution of rotamers is shown in fig. S1 (P), together with their respective energy (ΔE) and dipole moment (D).

II. CHARGE TRANSPORT

Intermolecular charge tranfer (hopping) rates are evaluated according to eq. 1 in the main text. Transfer integrals and site energy differences are calculated explicitly for each pair of molecules using the semi-empirical ZINDO method [2]. Corresponding distributions are shown in fig. S2 and fig. S3, while average values are tabulated in tab. S1.

Site energies are calculated self-consistently based on the Thole model [3] using the atomic partial charges and atomic polarizabilities (fitted to reproduce molecular polarizabilities), which can be found in tab. S2. The polarization contribution is refined iteratively. After evaluating the electric field at atom a in molecule i, $\vec{F}_{a_i}^{(0)}$, created by all atomic partial charges (nearest image convention), the induced dipole moments, $\vec{\mu}_{a_i}^{(0)}$, are computed. During this first step, intramolecular interactions are excluded. Induced dipole moments are then iteratively refined as $\vec{\mu}_{a_i}^{(k+1)} = \omega\vec{F}_{a_i}^{(k)}\alpha_{a_i} + (1-\omega)\vec{\mu}_{a_i}^{(k)}$, where α_{a_i} is the isotropic atomic polarizability and $\omega = 0.5$ is a damping constant for successive overrelaxation. The new electric fields are computed using the induced dipole moments, which now interact with each other also within molecules, allowing for anisotropic molecular polarizabilities. The procedure is repeated until $\sum_{a_i} |\vec{\mu}_{a_i}^{(k+1)} - \vec{\mu}_{a_i}^{(k)}| < 10^{-6}$ Debye.

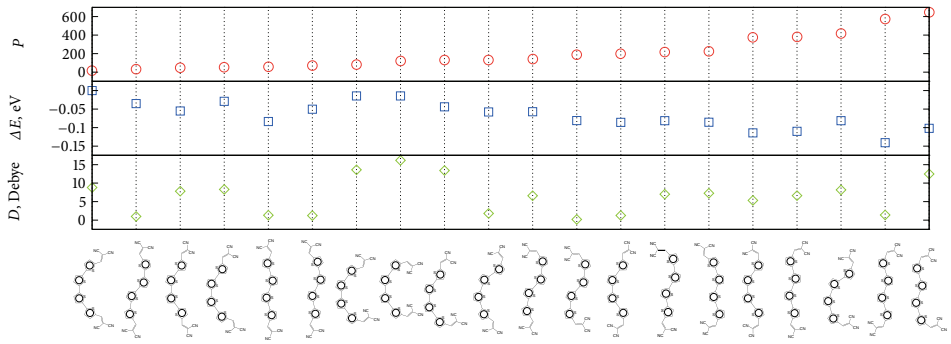

FIG. S1: Molecular structure with atom types, total count of all rotamers (P), relative energy of a rotamer (ΔE), and its dipole moment (D) in an amorphous system of 4096 DCV4T molecules.

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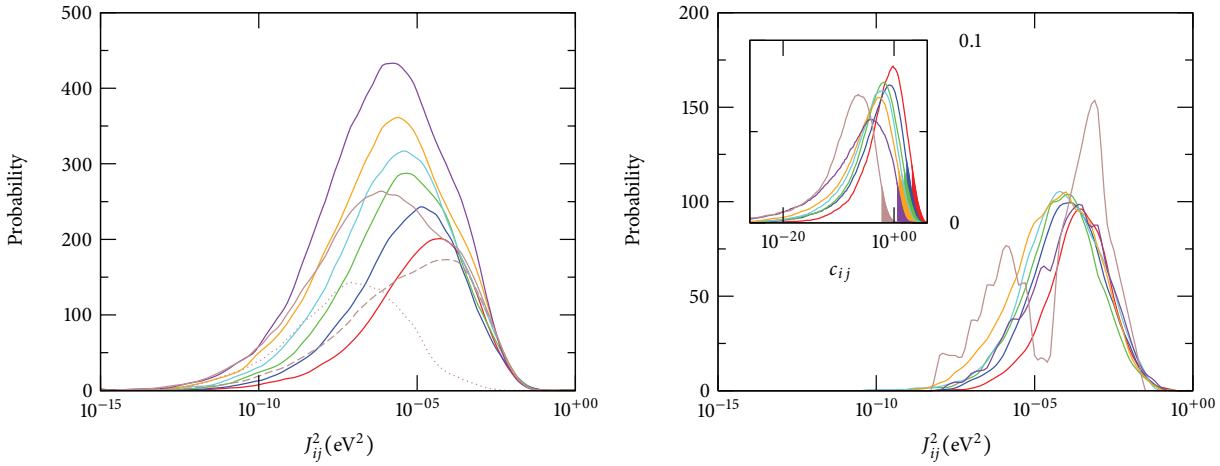

FIG. S2: Left: Distribution of transfer integrals for the entire neighbor list. Coloring according to the main text. Right: Distribution of transfer integrals based on the edges with high currents.

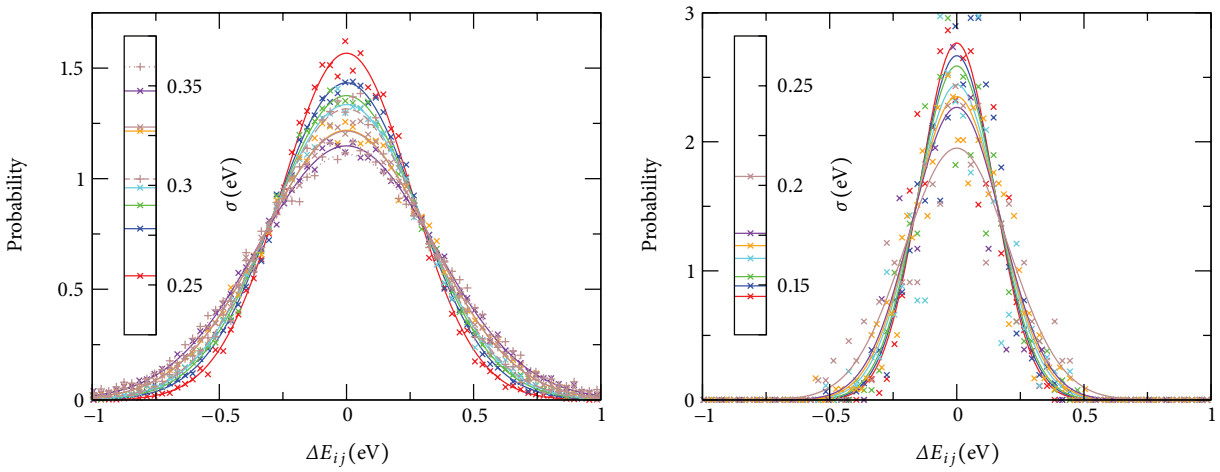

FIG. S3: Left: Polarized site energy difference distributions and width of gaussian fit (inset). Right: Effective distributions.

The molecular polarizabilities of neutral DCV4T rotamers have a standard deviation of 2.73 Å^3, hence negligibly small compared to the absolute values. The contribution to the site energy difference due to internal energy differences is neglected since its standard deviation is 0.04 eV, thus small compared to electrostatic energetic disorder.

The reorganization energies of DCV4T rotamers is calculated using B3LYP hybrid functional and 6-311g(d,p) basis set and have standard deviation (0.01 eV), thus the value corresponding to the ground state of the molecule is used.

Charge transport is simulated by solving the master equation for a charge carrier drift-diffusing in an applied electric field by averaging over 14 different field directions (axis and main diagonals forward and backward). Kinetic Monte Carlo runs are performed for 10^{-1} s for DCV1T and DCV2T, 1 s for DCV3T and DCV4T, 10 s for DCV5T and DCV6T and 10^5 s for DCV6T smectic. The last snapshot of the 300 K trajectory is used and the mobility is averaged over three randomly chosen injection points.

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[2] J. Kirkpatrick, Int. J. Quant. Chem. **108**, 51 (2007).
[3] B. Thole, Chem. Phys. **59**, 341 (1981).

	DCV1T	DCV2T	DCV3T	DCV4T	DCV5T	DCV6T	DCV6T smectic (x / yz)	
$\langle J_{ij}^2 \rangle$	$4.9 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$(1.4 \cdot 10^{-5}/4.4 \cdot 10^{-4})$
$\langle r_{ij} \rangle$	0.88	1.02	1.15	1.29	1.42	1.54	1.60	(2.54 / 0.90)
σ	0.25	0.28	0.29	0.30	0.33	0.35	0.33	(0.36 / 0.30)
$\langle J_{ij}^2 \rangle_{\text{eff}}$	$1.4 \cdot 10^{-3}$	$9.9 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$	$8.5 \cdot 10^{-4}$	$7.1 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$7.3 \cdot 10^{-4}$	
$\langle r_{ij} \rangle_{\text{eff}}$	0.81	0.91	1.02	1.10	1.11	1.17	1.13	
σ_{eff}	0.144	0.150	0.154	0.163	0.170	0.176	0.205	

TABLE S1: Average transfer integrals, $\langle J_{ij}^2 \rangle$ (eV^2), separations, $\langle r_{ij} \rangle$ (nm), and energetic disorder σ for all compounds.

	DCV1T	DCV2T	DCV3T	DCV4T	DCV5T	DCV6T
α_H^n	0.89	0.99	1.09	1.19	1.24	1.29
α_N^n	1.93	2.15	2.36	2.58	2.68	2.79
α_C^n	2.40	2.67	2.93	3.20	3.33	3.47
α_S^n	5.94	6.60	7.62	7.92	8.25	8.58
α^c/α^n	1.16	1.35	1.5	1.75	2.12	2.54
α_{Thole}^n	33.9	52.6	74.3	99.1	123.0	148.5
α_{DFT}^n	33.5	53.3	75.2	98.6	123.7	148.3
α_{Thole}^c	38.1	65.7	99.6	146.8	205.7	277.4
α_{DFT}^c	37.7	65.2	100.3	147.5	205.2	277.5

TABLE S2: Atomic polarizabilities (in Å^3) of a neutral molecule and the scaling factor for the cation, α^c/α^n. The bottom of the table lists traces of molecular polarizability tensors calculated using either the Thole model or B3LYP/6-311G(d,p).