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Strategies to reduce the dynamic disorder in molecular semiconductors

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1. Effective Hamiltonian

A tight-binding Hamiltonian for the study of charge transport in molecular semiconductors can be recast as,¹

$$\begin{aligned} \hat{H} = & \sum_i \varepsilon_i \hat{c}_i^+ \hat{c}_i + \sum_{\langle ij \rangle} J_{ij}^0 \hat{c}_i^+ \hat{c}_j + \sum_M \hbar \omega_M (\hat{a}_M^+ \hat{a}_M + \frac{1}{2}) \\ & + \sum_{i,M} g_{i,M} \frac{1}{\sqrt{2}} (\hat{a}_M^+ + \hat{a}_M) \hat{c}_i^+ \hat{c}_i + \sum_{i \neq j, M} g_{ij,M} \frac{1}{\sqrt{2}} (\hat{a}_M^+ + \hat{a}_M) \hat{c}_i^+ \hat{c}_j \end{aligned} \quad (S1)$$

where the first two terms are indicative of the electronic part of the Hamiltonian, the third term represents the lattice phonons, and the last two terms denote the local and nonlocal electron-phonon couplings; where the first two terms are indicative of the electronic part of the Hamiltonian, the third term represents the lattice phonons, and the last two terms denote the local and nonlocal electron-phonon couplings; ε_i stands for the on-site electronic energy of the hole; J_{ij}^0 are the transfer integral elements between adjacent molecules at the equilibrium geometry; \hat{c}_i^+ (\hat{c}_i) are the creation (annihilation) operator for a hole at site i (there is one state per site); $\langle ij \rangle$ nearest-neighbor pairs of occupied sites; \hbar is the reduced Planck constant; ω_M is the phonon frequency of mode M ; $g_{i,M}$ and $g_{ij,M}$ are the local and nonlocal electron-phonon couplings measuring the strength of interaction between charge carriers and

intra-molecular and inter-molecular vibrations; \hat{a}_M^+ (\hat{a}_M) are the phonon creation (annihilation) operators. In the presence of thermal fluctuations, the transfer integral between two electronic states denoted by i and j can be evaluated as,

$$J_{ij} = J_{ij}^0 + \sum_M g_{ij,M} Q_M$$

with J_{ij} being the modulated transfer integral and Q_M the dimensionless coordinate of the associated normal mode.² The nonlocal electron-phonon coupling for a given molecular pair ij due to mode M is, therefore, can be recast as,

$$g_{ij,M} = \frac{\partial J_{ij}}{\partial Q_M} \quad (\text{S3})$$

Representing the modes as Cartesian displacements $Q_M^C = \{x_k^M\}$ leads to the following formula for computing the nonlocal electron-phonon couplings,

$$g_{ij,M} = \nabla J_{ij} \cdot Q_M^C \quad (\text{S4})$$

with $\nabla J_{ij} = \frac{\partial J_{ij}}{\{\partial x_k\}}$ being the Cartesian gradients of the transfer integrals. Ultimately, the nonlocal electron-phonon couplings gives access to the dynamic disorder σ_{ij} ,

$$\sigma_{ij}^2 = \langle (J_{ij} - \langle J_{ij} \rangle)^2 \rangle = \sum_M \frac{|g_{ij,M}|^2}{2} \coth\left(\frac{\hbar\omega_M}{2k_B T}\right) \quad (\text{S5})$$

with $\hbar\omega_M$ and $k_B T$ being respectively the phonon and the thermal energies.²

2. Computational Details

In this study, the data computed in ref.³ have been utilized. The considered structures are semiconductors extracted from the Cambridge Structural Database (CSD),⁴ as identified in ref.⁵. The calculations of the transfer integrals (J_{ij}) were carried out based on *ab initio* methods⁶ at the B3LYP/3-21G* level of the theory calibrated against large basis set calculations. For the phonons calculations, it was assumed that each molecule oscillates independently from the others. All phonons including those deriving from translation and rotation of the isolated molecules (acoustic and libration modes) are assumed to be localized on a single molecule (Einstein dispersion-less phonons). The phonons are then calculated as the

vibrational modes of a molecule embedded in an environment defined by the surrounding (rigid) molecules in a Quantum Mechanics/Molecular Mechanics (QM/MM) calculation.⁷ The calculations were performed using the ONIOM scheme (B3LYP/3-21g*:UFF) with embedded charges,⁸ as implemented in Gaussian16.⁹ Non-local electron-phonon coupling parameters and consequently the dynamic disorders (σ_{ij}) are computed via numerical differentiation. The gradient of the overlap integral (neglecting the contribution from hydrogen atoms) were used instead of transfer integrals' gradient. For more details, the interested reader is referred to ref.³ and its supplementary information file.

3. The Correlation Map

We have evaluated the correlation between the computed dynamic disorder for the molecular pair exhibiting the largest transfer integral and a list of characteristics that could potentially be linked with the degree of dynamic disorder. The considered parameters cover the molecular topology, the stoichiometry, the frontier orbital energy levels, and descriptors of the HOMO orbitals. In more detail, the considered parameters are: the number of atoms, number of bonds, number of cyclic bonds, number of rotatable bonds, number of conjugated bonds, number of rings, number of fully conjugated rings, number of aromatic rings, number of fused rings, molecular weight and volume (all extracted using the CSD Python API interface⁴), the degree of unsaturation, averaged principal moment of inertia ($|P|$), the inverse participation ratio (IPR) of the HOMO orbital (computed as in ref.¹⁰), the frontier orbitals energies and the gap (computed at B3LYP/3-21G* level of the theory⁹), the number of atoms contributing (R_C) and not contributing (R_{NC}) to the HOMO orbital and also number of sp^2 - hybridized atoms in van der Waals contact (R_{sp^2}), number of sp^3 - hybridized carbon atoms (R_{sp^3}) and the ratio between molecular mass and number of atoms (R_{Mass}). In addition, the effects of number of molecules in the crystal's unit cell and crystal's space-group (centrosymmetric or Sohncke) on the dynamic disorder are also investigated which did not show a remarkable impact on the dynamic disorder and, therefore, are not reported.

To show the results in an intuitive way, a correlation matrix representation is used (Figure S1), where, each cell represents the correlation between two variables. To avoid looking at quantities bearing essentially the same information, we have removed any descriptor showing large correlation with other descriptors. The impact of parameters highly correlated to the dynamic disorder (i.e. ∇J , R_{sp^2} , R_{sp^3} , J and R_{Mass}) is discussed in the main manuscript. Apart from those, a relatively important correlation is also

observed between the dynamic disorder and the HOMO energy, the molecular volume and the number of atoms contributing and not contributing to the HOMO orbital.

Volume	1	0.25	0.15	0.41	-0.45	-0.45	0.41	-0.62	0.62	-0.11	-0.12	-0.31	-0.23
HOMO	0.25	1	0.33	0.016	-0.33	-0.2	0.16	-0.27	0.27	-0.075	-0.27	-0.34	-0.27
Gap	0.15	0.33	1	0.13	0.013	-0.028	0.076	-0.061	0.061	0.00023	-0.17	-0.16	-0.14
IPR	0.41	0.016	0.13	1	-0.17	0.3	-0.031	0.26	-0.26	-0.055	-0.07	-0.15	-0.11
R_{Mass}	-0.45	-0.33	0.013	-0.17	1	0.18	-0.33	0.31	-0.31	0.1	0.11	0.4	0.3
R_{sp^2}	-0.45	-0.2	-0.028	0.3	0.18	1	-0.36	0.75	-0.75	0.21	0.44	0.65	0.46
R_{sp^3}	0.41	0.16	0.076	-0.031	-0.33	-0.36	1	-0.43	0.43	-0.12	-0.36	-0.52	-0.41
R_C	-0.62	-0.27	-0.061	0.26	0.31	0.75	-0.43	1	-1	0.025	0.12	0.25	0.26
R_{NC}	0.62	0.27	0.061	-0.26	-0.31	-0.75	0.43	-1	1	-0.025	-0.12	-0.25	-0.26
J	-0.11	-0.075	0.00023	-0.055	0.1	0.21	-0.12	0.025	-0.025	1	0.25	0.44	-0.31
∇J	-0.12	-0.27	-0.17	-0.07	0.11	0.44	-0.36	0.12	-0.12	0.25	1	0.93	0.63
σ	-0.31	-0.34	-0.16	-0.15	0.4	0.65	-0.52	0.25	-0.25	0.44	0.93	1	0.65
Δ	-0.23	-0.27	-0.14	-0.11	0.3	0.46	-0.41	0.26	-0.26	-0.31	0.63	0.65	1
	Volume	HOMO	Gap	IPR	R_{Mass}	R_{sp^2}	R_{sp^3}	R_C	R_{NC}	J	∇J	σ	Δ

Figure S1. Correlation matrix reflecting the rank correlation between the various parameters and the strength of dynamic disorder.

The correlation between the HOMO orbital energy and the computed dynamic disorder can be interpreted based on the fact that in molecules with high HOMO energy, acquiring or losing a charge after the charge transfer induces weaker changes in the molecular geometry because of the lower excess charge density and therefore leads to smaller fluctuations in the values of transfer integrals.

The molecular volume which is strongly correlated in a positive manner with the number of atoms, bonds and molecular weight (i.e. the molecular size) shows a relatively large negative correlation of strength with the dynamic disorder. This is perceivable as one would expect larger accumulated forces between large molecules which in return reduces the thermal fluctuations. As a matter of fact, enthalpy of sublimation that can be considered as a quantitative estimate of the intermolecular interaction is shown to increase gradually with the molecular size of oligoacene: it varies from ~ 73 kJ/mol to ~ 155 kJ/mol in going from naphthalene¹¹ to pentacene.¹² This analysis is in agreement with ref.¹³.

The number of atoms contributing (not contributing) to the HOMO normalized to the number of atoms R_C (R_{NC}) shows a positive (negative) correlation with the dynamic disorder. The sum of these two

quantities, i.e. R_C and R_{NC} , for each material is equal to the total number of atoms and the correlation between them is equal to -1, meaning that, obviously, by increasing one of them the other one would decrease. As can be seen, for growing values of R_C , the dynamic disorder increases while by increasing R_{NC} the dynamic disorder shows descending behavior. R_C can be considered as a measure of the orbital size and accordingly we can conclude that materials with smaller HOMO orbital fluctuate less. R_{NC} is related to the number of sp^3 Carbon atoms implying that alkylated structures are expected to suppress the thermal fluctuations.

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