

Electronic Structure of Self-assembled Amorphous Polyfluorenes.

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Computational Approach to Electron Localization

To study the localization (delocalization) of molecular orbitals of amorphous PFO aggregates, we employed the following computational strategy. First, we calculated the percentage of the partial charge density (PCD), $\rho_i = |\psi_i|^2$, for a specific Kohn-Sham orbital, ψ_i , which is localized on one of the eight PFO molecules in the aggregate (see Fig. 3 in the paper). To determine this percentage, we initially found a total charge density, $\bar{\rho}_n(r)$, of the n -th isolated PFO molecule: for each of the eight PFO configurations in the amorphous sample, the $\bar{\rho}_n(r)$ was calculated in a simulation cell of an aggregate where all but the n -th molecule were removed. Assuming that charge density has significantly large values in the space regions associated with a polymer and exponentially decreases at regions away from the molecule, a mask function $M_n(r)$ can be constructed by comparing the magnitude of the total electronic density to a specific tolerance parameter ε at each grid point r of the simulation cell:

$$M_n(r) = \begin{cases} 0, & \bar{\rho}_n(r) < \varepsilon \\ 1, & \bar{\rho}_n(r) \geq \varepsilon. \end{cases} \quad (1)$$

The tolerance parameter ε characterizes the radius of the isosurface for a PFO molecule and is chosen to be much smaller than the maximal value of charge density for a given PFO configuration. On the other hand, the ε has to be large enough to prevent the overlap between charge density distributions of different PFO molecules in the amorphous sample. Since the averaged distance between PFO chains in the aggregates is about is large enough (around 3-4 Å), $\varepsilon \approx 10^{-7} \text{ e}/\text{\AA}$ (versus $\rho_n^{max} \approx 10^{-3} \text{ e}/\text{\AA}$) is suitable to satisfy both of the above mentioned conditions. The right choice of the ε provides the normalization of the mask function, so that $\sum_{n=1}^N M_n = 1$, where $N = 8$ is the total number of PFO molecules in the aggregate.

As a next step, the mask functions were used to identify the portion, P_{in} , of the PCD of i -th orbital in an aggregate that is localized on the molecule n , as follows:

$$P_{in} = \frac{\int_V M_n(r) \rho_i(r) dv}{\int_V \rho_i(r) dv}, \quad (2)$$

where integration is done over the volume V of the simulation cell. Here the numerator defines the portion of the charge density on the n -th molecule, while the denominator represents the total PCD of the aggregate. Since we avoided cross-overlaps between charge densities

of different PFO chains (e. g., the mask function is normalized), the P_{in} also satisfies the normalization condition $\sum_{n=1}^{N=8} P_{in} = 1 \pm o(\varepsilon)$.

The values of P_{in} for one equilibrium configuration of amorphous PFO aggregates are shown in Fig. 3 in the paper. To illustrate the relationship between P_{in} values and localized (delocalized) molecular orbitals, Fig. 1 represents charge density distribution corresponding to partially delocalized HOMO-2 and the mostly delocalized LUMO+58. As discussed in the paper, HOMO-2 is spread over three molecules (see P_{in} values corresponding to the length of intervals between vertical lines in the left panel of Fig. 3 in the paper). Fig. 1 (a) confirms the delocalization of the partial charge density of this state over three molecules. The LUMO+58 is very deep inside the conduction band and is the most delocalized orbital in the amorphous configuration considered. This orbital is spread over seven PFO molecules, each roughly contributing 10% - 20% to the charge density.

For further understanding of the delocalization of electronic states in amorphous PFO aggregates, the participation ratio (PR) and inverse participation ratio (IPR) were calculated. The IPR and PR are commonly used in solid state physics to characterize disorder and localization in a bulk crystal of a volume V , as follows:¹ $IPR = \int_V \rho_i^2(r)dv / (\int_V \rho_i(r)dv)^2$. However, usually it is more convenient to use a discrete space, such as a total number of atoms (N), rather than a volume.² Then, in atomic basis, $IPR = \sum_{n=1}^N q_n^2(E_i)$, where $q_n(E_i)$ is the Mulliken charge residing at an atomic site n for an electronic state with energy E_i that satisfies $\sum_n q_n(E_i) = 1$. For an ideally localized state, only one atom contributes all the charge and $PR = 1/IPR = 1$. For uniformly distributed charge over all N atoms, each of the atoms equally contributes with Mulliken charge $1/N$ and so $PR = N$. Using an analogous approach but in a molecular basis instead of the atomic one, we define PR as

$$IPR(i) = \frac{\sum_n P_{in}^2}{(\sum_n P_{in})^2} = \sum_n P_{in}^2, \quad (3)$$

where P_{in} is a portion of the PCD ρ_i on the n -th molecule, previously defined in Eq.2. The P_{in} is normalized and is a direct analog of the Mulliken charge $q_n(E_i)$, but for a molecule. Consequently, $PR = 1/IPR = 1/\sum_n P_{in}^2$ provides $PR = 1$ for an electronic state of a PFO aggregate that is completely localized on a single PFO chain, and $PR = N = 8$ for a state that is delocalized over all of the eight PFO molecules in an aggregate. For HOMO-2, shown in Fig. 1, $PR = 2.6 \sim 3$. For the most delocalized LUMO+58, $PR \sim 7$, indicating delocalization of the charge density nearly over the entire system. However, states similar

to LUMO+58 (see Fig. 1) are very rare. In all 20 amorphous samples, most of states have $PR \leq 4$, showing significant localization not only near the energy gap, but deep inside the valence and conduction bands.

References

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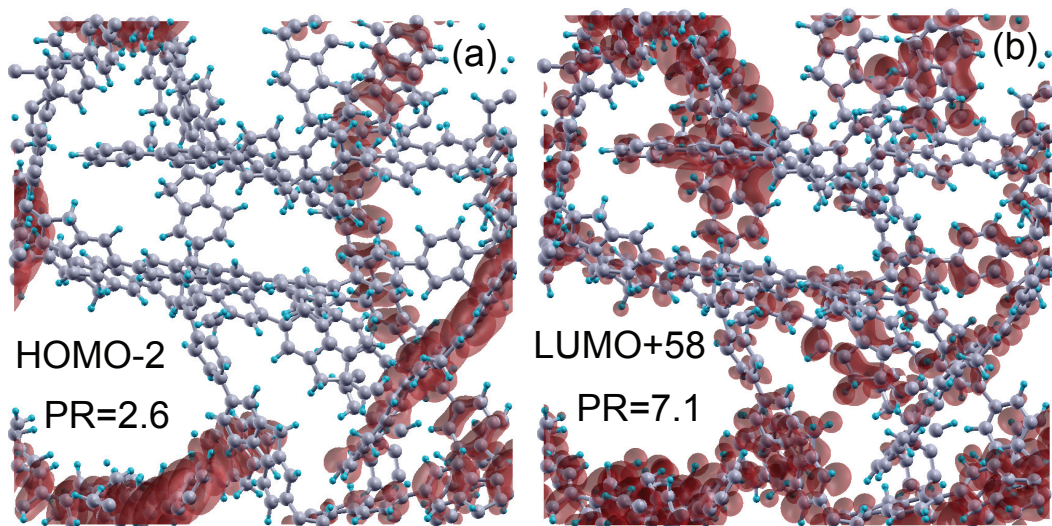


Figure 1: Delocalized orbitals of amorphous PFO aggregates. 3-dimensional distribution of the PCD for HOMO-2 (a) and LUMO+58 (b). HOMO-2 is delocalized over three PFO molecules, which is also reflected in its participation ratio $PR \sim 3$. LUMO+58 is the most delocalized state for this amorphous sample. Its $PR \sim 7$ indicates a delocalization over seven PFO chains from the eight molecules in the system.