

Are Organic Framework Materials the Better “Organic Semiconductors”?

Christian Winkler and Egbert Zojer

*Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16,
8010 Graz, Austria (Egbert.zojer@tugraz.at)*

Two factors primarily determine through-space charge transport in organic semiconducting materials: The electronic coupling between neighboring conjugated entities and the nature of the vibrational modes that strongly couple to the electronic degrees of freedom and, thus, lead to dynamic localization effects. The electronic coupling is crucially influenced by the relative alignment of π -conjugated molecules and can vary by orders of magnitude depending on lateral displacements or rotations. Unfortunately, when relying on the self-assembly of π -conjugated molecules alone, they will typically arrange in a way that tends to minimize parameters like transfer integrals or band widths, concomitantly maximizing the effective mass of the charge carrier [1]. The reason for that are repulsive exchange interactions that largely scale with the magnitude of the electronic coupling. A successful strategy for avoiding non-ideal structures is exploiting “extrinsic” factors such as steric constraints due to substituent groups, as it is done, for example, in high-mobility materials like rubrene or TIPS-pentacene.

In MOFs the situation is fundamentally different: There, the structure is typically not determined by the free assembly of p -conjugated entities, but by the topology and the dimensions of the surrounding network. Considering, for example, $Zn_2(TTFTB)$ [2], which comprises helical stacks of tetrathiafulvalene (TTF) units, the relative rotation of the conjugated elements is determined by the periodicity of the helix, which is, in turn, dictated by the details of the surrounding MOF framework. This, rotation, however, determines parameters, like the band widths and effective masses of the charge carriers [3]. Similar considerations apply to covalent organic frameworks[4] and SURMOF-2 type structures built from oligo-acene containing linkers [5]. In the latter, the relative displacements of neighboring acene entities and, concomitantly their electronic coupling and the ensuing transport-relevant [6] as well as optical properties [7] are controlled by the distance between the metal paddlewheels. Here, based on quantum-mechanical simulations, we suggest a straightforward to implement strategy to increase carrier mobilities by at least an order of magnitude.[7]

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The work has been financially supported by the TU Graz Lead Project “Porous Materials at Work” (LP-03). The computational results have been achieved using the (VSC3).