

Supporting Information

Interfacial and Bulk Properties of Hole Transporting Materials in Perovskite Solar Cells: Spiro-MeTAD versus Spiro-OMeTAD

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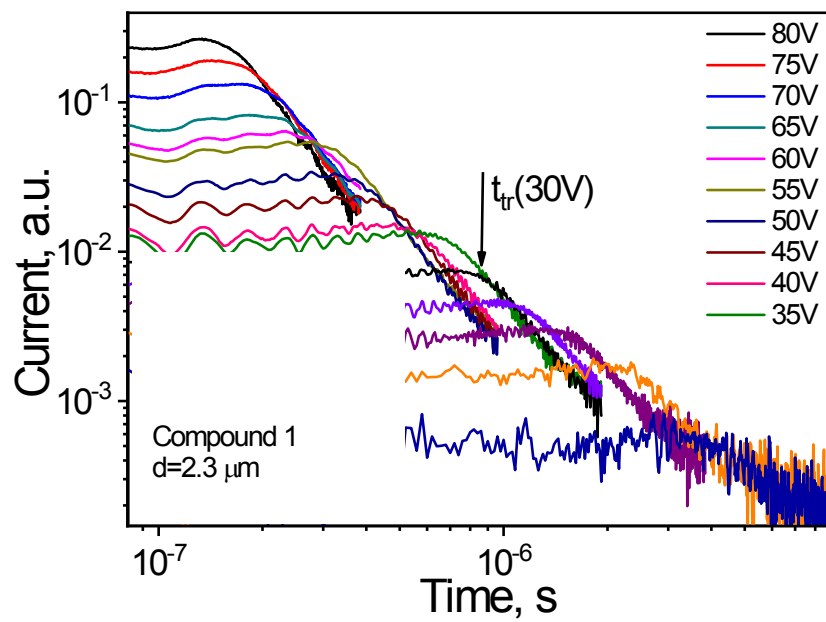
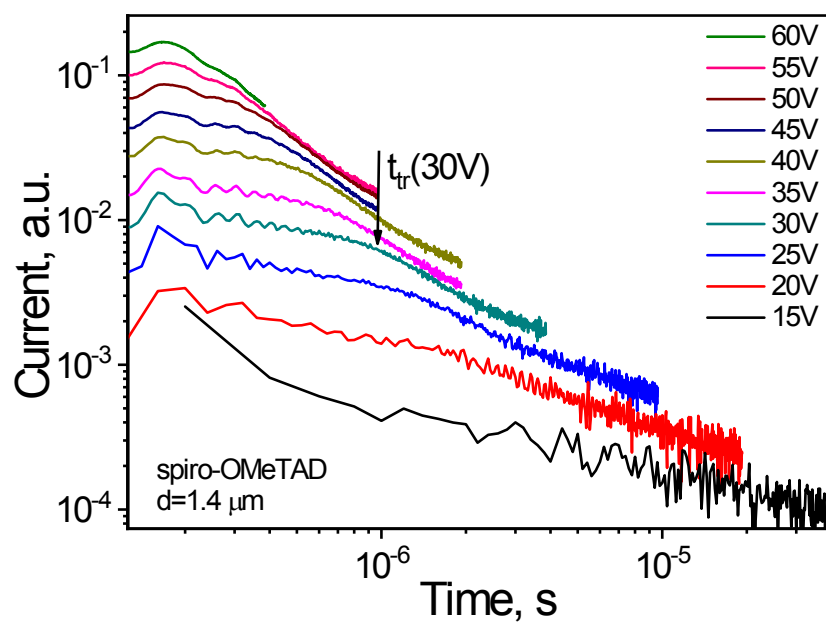
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I- Figures



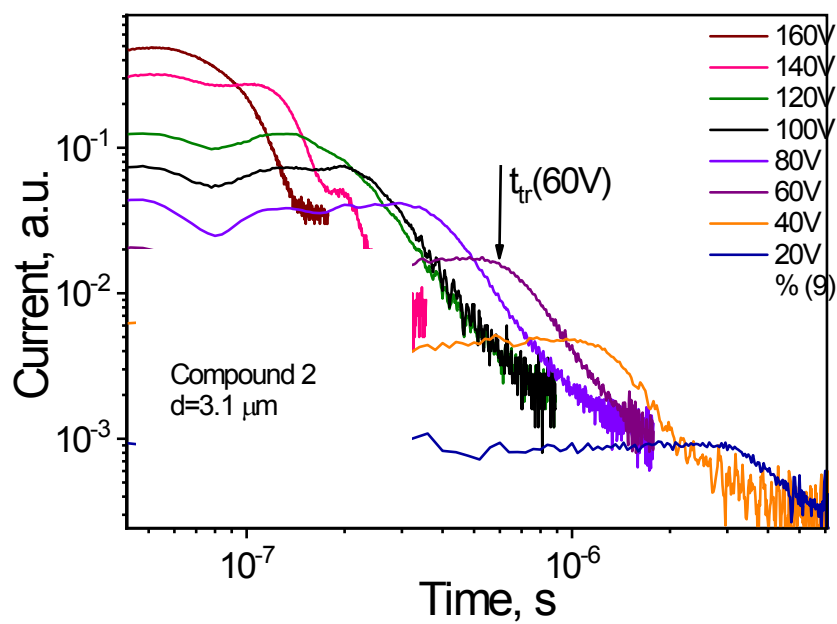


Figure S1. Current transient pulses at different electric fields and room temperature.

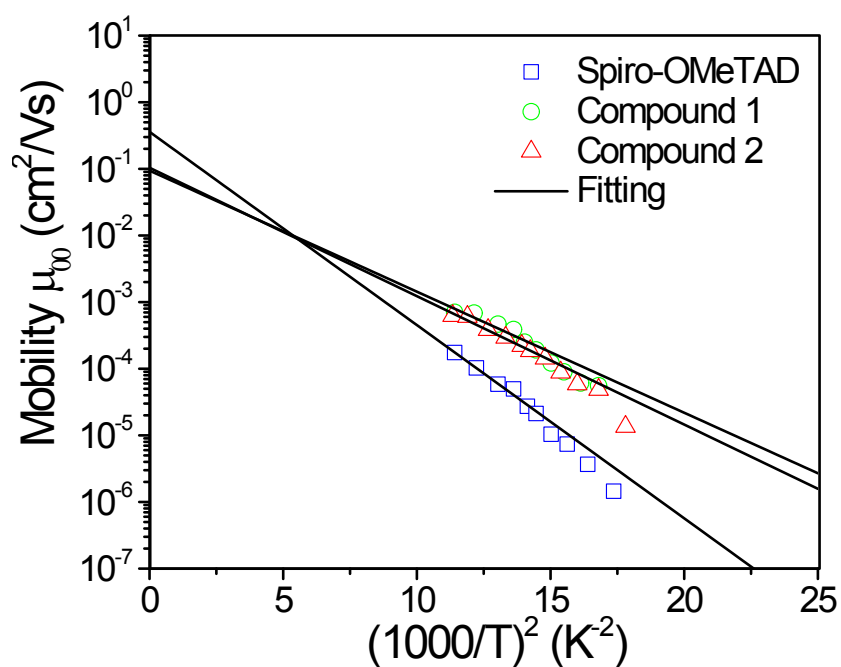


Figure S2. The logarithm of the zero-field mobility vs $(1/T)^2$. The zero-field values were obtained by the fitting of the mobility (fig.5) data as $\mu = \mu_0 \cdot \exp(\beta \cdot E^{1/2})$ at $E = 0$.

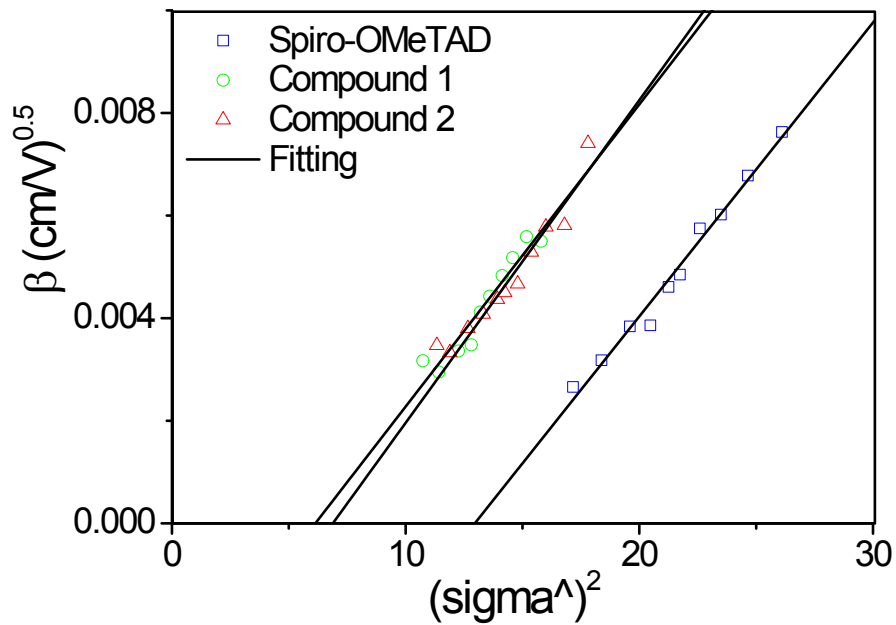
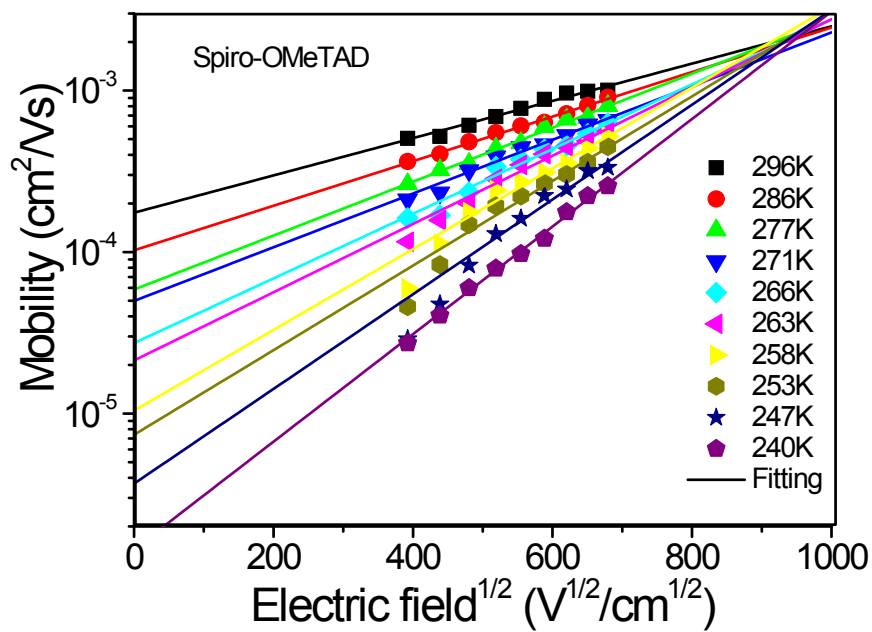


Figure S3. The temperature dependence of the field dependencies of the mobility ($\beta_i = f(\hat{\sigma}_i^2)$).



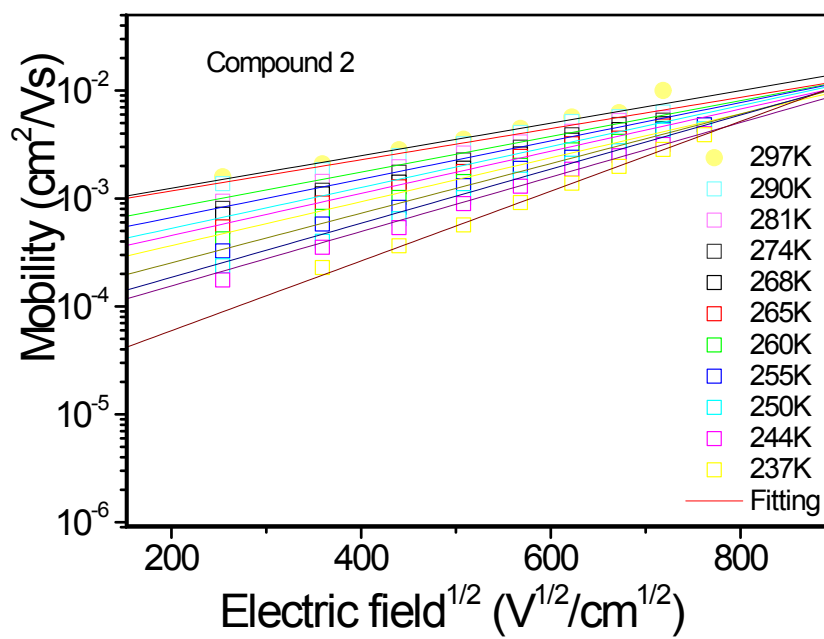
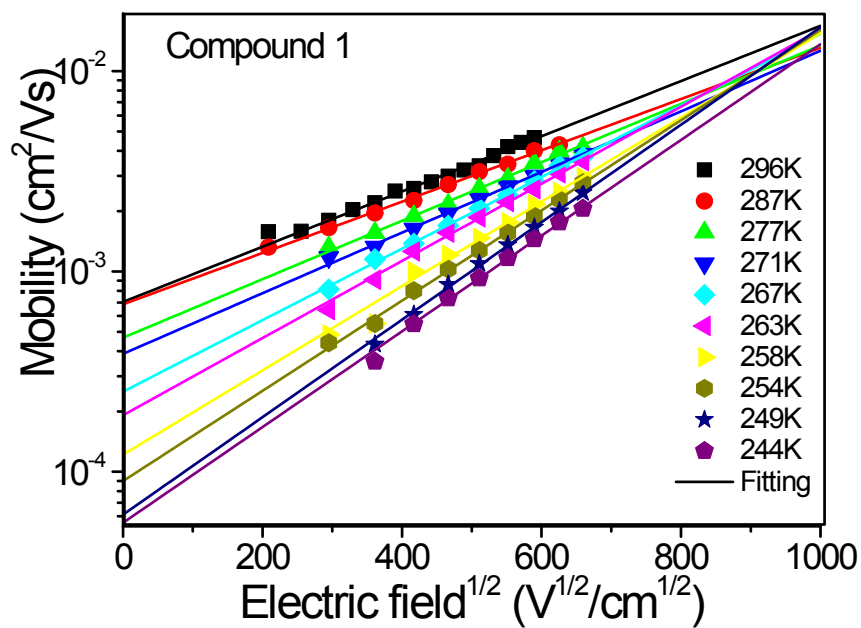


Figure S4. The field dependencies of the mobility at different temperatures.

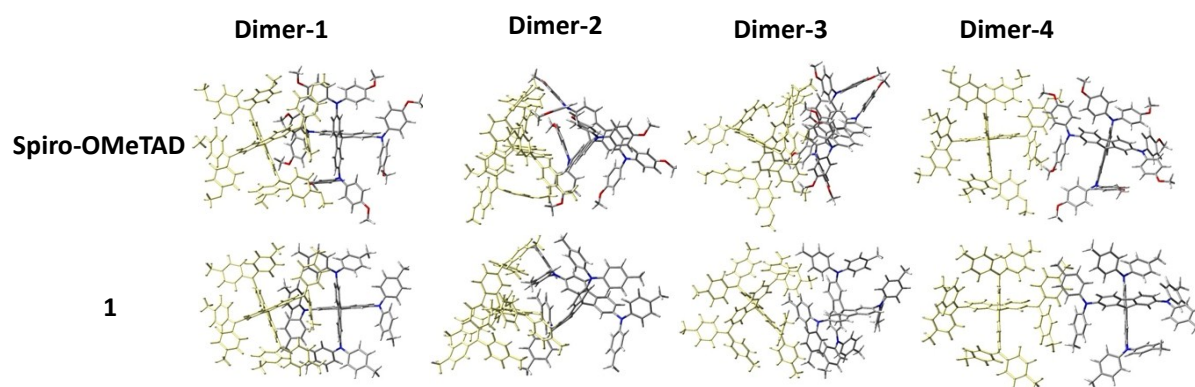


Figure S5. Geometries of four dimer types constructed with spiro-OMeTAD and compound 1, obtained at the ω B97XD/6-31G* level (“gas phase”). For clearer representation, one molecule of each dimer is highlighted in yellow. Note that this figure is identical to Figure 2 in the main text, but is reproduced here for the readers comfort.

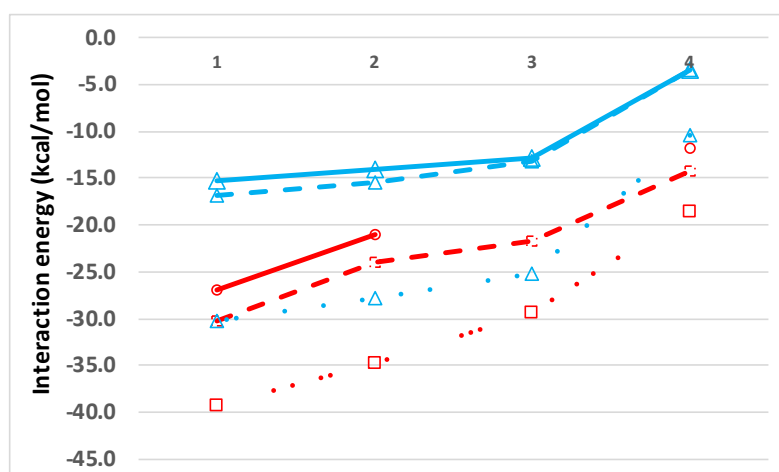


Figure S6. Comparison of interaction energies for each of dimers 1-4 for spiro-MeTAD compound 1 (in red) and spiro-OMeTAD (in blue). The lines are just guide for the eye, and have no physical meaning. The values joined by the dotted lines correspond to interaction energies without any correction, the dashed lines correspond to interaction energies corrected for the BSSE (basis set superposition error, counterpoise method), whereas the bold lines include the correction for the BSSE and ZPE (zero point energy). The frequency calculation for the Dimer-3 of spiro-MeTAD was impossible to obtain for technical reasons.

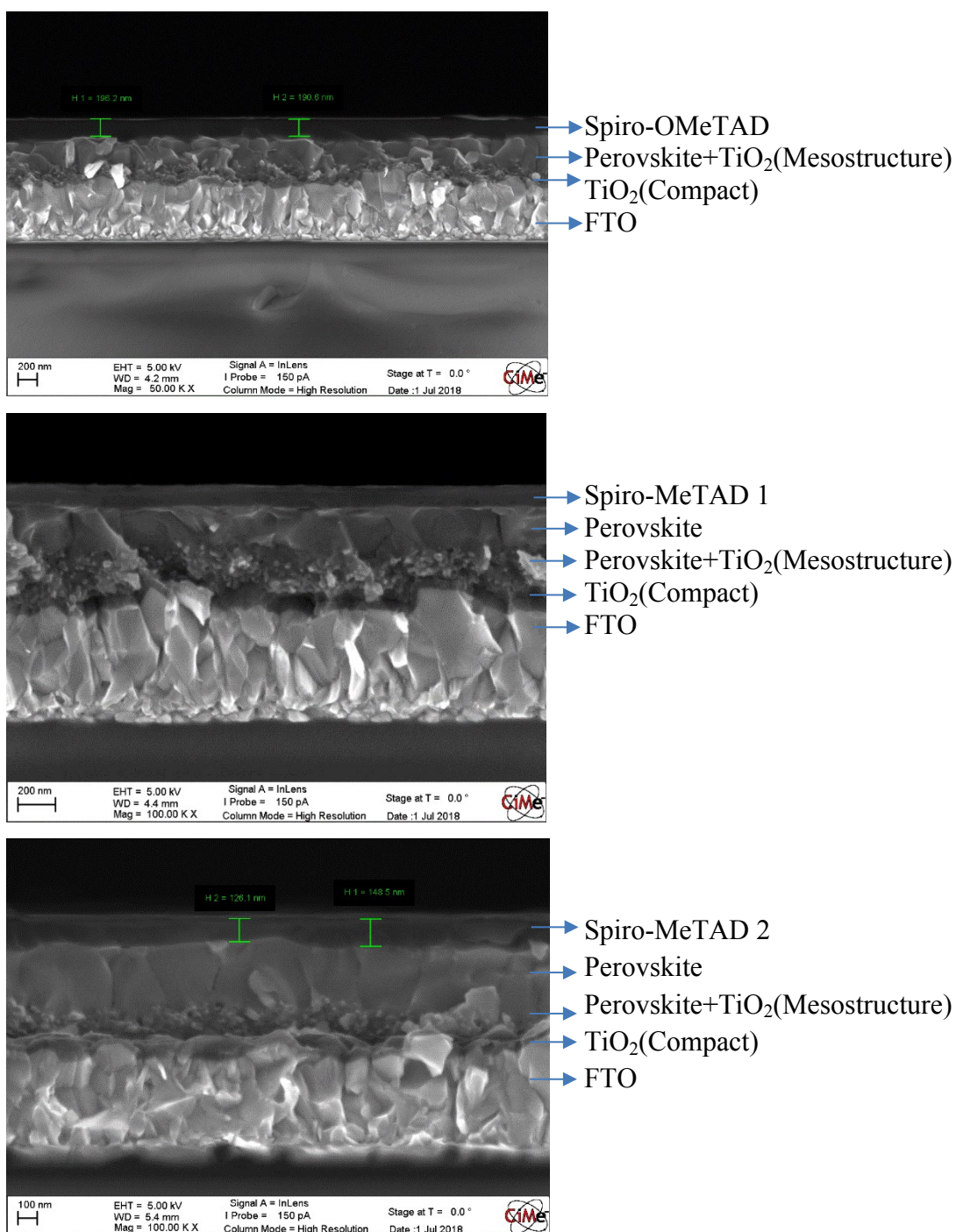


Figure S7. Cross-sectional SEM images of devices. Two HTM layer thickness are indicated in the case of spiro-OMeTAD (196.2 nm and 190.6 nm) and spiro-MeTAD 2 (126.1 nm and 148.5 nm).

II- Annex I

Choice of the method. The choice of the method was imposed by the very important size of the molecules: in the case of spiro-OMeTAD, the dimers contain 322 atoms, 1296 electrons, and by using 6-31G* basis set, 3062 basis functions. With these numbers, and by remembering that the geometry optimizations of the dimers converge very slowly due to noncovalent intermolecular interactions, the time needed for a single geometry optimization without frequency calculation was more than roughly one month. This time is additionally increased by the subsequent computations, concerning: (i) the frequency calculations, (ii) the correction of the interaction energies for the basis set superposition error (BSSE, counterpoise method), (iii) the time dependent DFT calculations for the optical properties, (iv) intramolecular interaction energies (requesting for geometry optimization of the cationic species) and electronic couplings between HOMOs of each molecule in each dimer, which are necessary for the discussion of the hole mobilities.

In view of the exorbitant computer time spent for our current study with the 6-31G* basis set, it becomes evident that using larger basis sets would be practically impossible. Nevertheless, it is worth mentioning that the ω B97XD/6-31G* level of theory is typical when considering important-size systems (see for instance Advanced Energy Materials 8 (12), 1702232), which can justify the use of this level of theory in our case (see also the point below).

Choice of the dimer geometries. The idea is the following: (i) four starting geometries were chosen by making sure that, when going from dimer-1 to dimer-4, the nature and number of molecular fragments in interaction between two molecules vary as much as possible. This allows obtaining a reasonably large spread of interactions energies, from the strongest to the weakest. As such, the impact of the calculation errors and of the small random geometrical variations is importantly reduced. (ii) In order to reliably compare intermolecular interaction energies between the two compounds, identical dimer geometries are needed. To this aim, the four dimer geometries were optimized initially for spiro-OMeTAD. Starting from these dimer geometries, and by replacing the methoxy groups by methyl groups, the same dimer types were subsequently optimized for spiro-MeTAD. The four dimer types are shown in Figure S5 (identical to Figure 2 in the main text): for each dimer-type (column), practically identical intermolecular interaction geometries can be observed for spiro-OMeTAD and compound **1**. This allows for a reliable and pertinent comparison of the interaction energy of the two compounds for each individual dimer-type, and justifies the use of the average value among the four dimer-types.

Pertinence of the trend of the intermolecular aggregation strengths. We firstly note that the aggregation strengths calculated in the present study are typical for non-covalent interactions. As shown in the manuscript, the average aggregation strengths range between 12kcal/mol for spiro-OMeTAD and 23 kcal/mol for spiro-MeTAD (dissociation energies + BSSE correction), which not only are relatively strong for noncovalent interactions, but also very different between them. This difference of 11 kcal/mol between the two average values is important, and allows for reliable and pertinent comparisons.

Very importantly, the large difference of 11 kcal/mol between the average aggregation strengths of 12 and 23 kcal/mol does not result from a rough cancellation between alternated trends through different dimer-types, but from a constant trend through the four dimer-types (**Figure S6**), with individual values ranging from the largest value of ~30 kcal/mol (spiro-MeTAD, dimer-1) to the smallest value of 3 kcal/mol (spiro-OMeTAD, dimer-4). The constant trend shown in Figure S6 indicates for all dimers stronger aggregation for spiro-MeTAD as compared to spiro-OMeTAD independently from the dimer geometry, thus allowing to safely conclude on the targeted trend.