

When neighbours make the difference

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Charge transfer processes between donor–acceptor complexes and metallic electrodes are at the heart of novel organic optoelectronic devices such as solar cells. In fact, molecular dyads allow the development of new architectures according to a win-win design strategy, thanks to the varied properties offered by organic semiconductors. On the one hand, the optical sensitivity of the photovoltaic cell can be tuned to the environmental light conditions by appropriate choice of the molecular pair. On the other hand, the intermolecular interactions can be trimmed by chemical functionalization of the respective molecules, in order to optimize the molecular coupling in the supramolecular assembly. The bottleneck of this emerging technology is represented by the interface with the supporting metal contact, where the charge signal is extracted.

Here we show that the charge transfer and the chemical properties of metal-organic interfaces based on single component organic layers cannot be naively extrapolated to the new molecular environments of supramolecular architectures, such as donor–acceptor binary assemblies. As a consequence, a detailed atomistic understanding of the hybrid junction between electrode and organic mixture (both from an electronic and structural point of view) is required for a rational design of functional donor–acceptor nanostructures with optimized properties.

Our study focused on binary supramolecular nanostructures on copper comprising fluorinated Copper-phthalocyanines ($F_{16}CuPc$) and diindenoperylene (DIP). The electronic and crystalline properties have been addressed by means of scanning tunnelling microscopy, synchrotron radiation spectroscopy measurements performed at ALOISA, and state-of-the-art ab-initio calculations. We have found that, with respect to the corresponding single component layers, the new environment of the binary mixture causes the donor molecule (DIP) to decouple electronically from the metal surface, while the acceptor ($F_{16}CuPc$) suffers strong hybridization with the substrate.

