

Extending the functionality of low-dimensional hybrid perovskites through the incorporation of charge-transfer complexes

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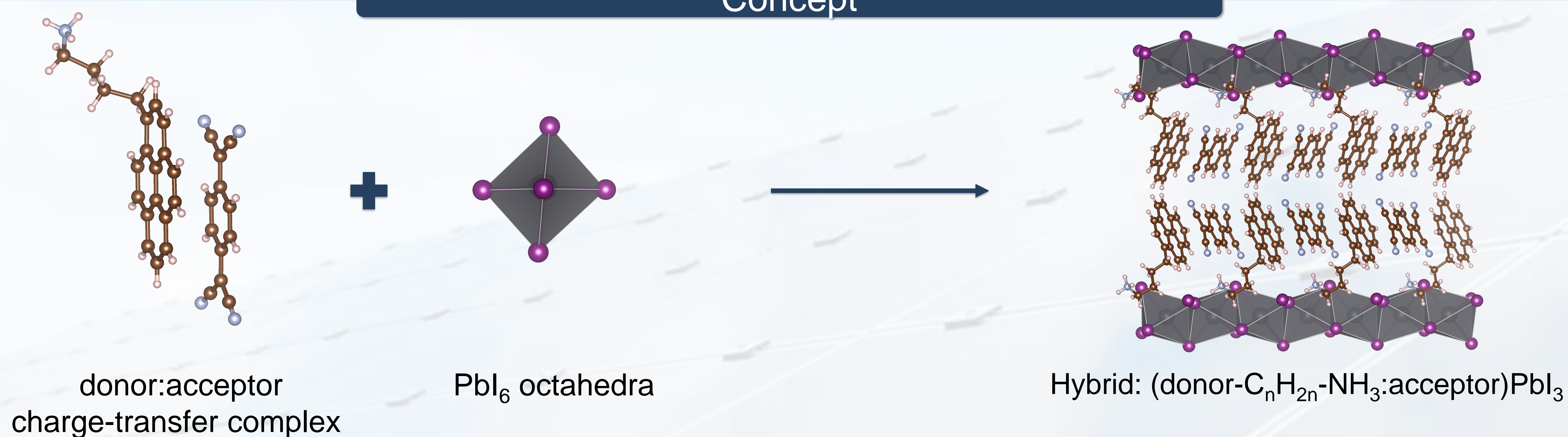
HyMaD fwo
HYBRID MATERIALS DESIGN

Introduction

Low-dimensional hybrid perovskites are emerging as a promising class of materials for use in optoelectronic applications. A significant advantage of the low-dimensional hybrids over the currently more extensively studied 3D hybrid perovskites, is the greater compositional flexibility of the organic layer. The structural constraints on the organic cation are much more limited for low-dimensional hybrids compared to their 3D counterparts and a large variety of possible molecules remains unexplored. An additional way to introduce functionality is through the use of intercalation. In this way, molecules that do not contain an ammonium tethering group can be incorporated into the organic layer of the hybrids. Mitzi et al. intercalated hexafluorobenzene molecules into phenethylammonium based 2D layered perovskites using the fluoroaryl-aryl interactions.¹ More recently, Smith et al. intercalated molecular iodine into hexylammonium based 2D layered perovskites in order to decrease the electronic confinement in the layered perovskite.²

We incorporate donor:acceptor charge-transfer complexes into the organic layer of low-dimensional hybrids.^{3,4} The organic layer of these hybrids contains donor molecules with an ammonium tethering group. Through self-assembly, small electron acceptor molecules intercalate into the organic layer. The structural, optical and charge-transport properties of the hybrid are compared to the properties of the free organic donor:acceptor charge-transfer complex.

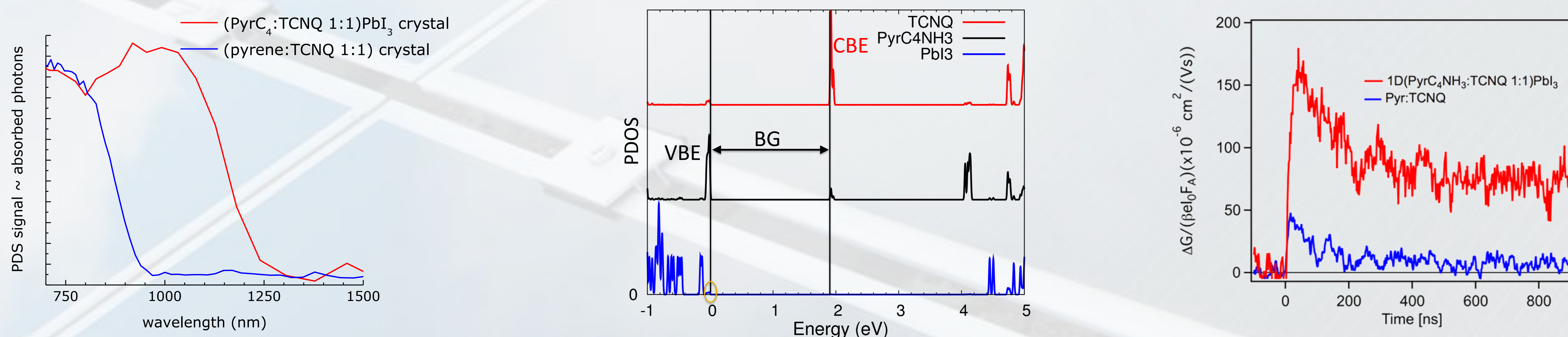
Concept



Comparison



Results



Conclusions

We showed that charge-transfer complexes (CTCs) can be incorporated into the organic layer of a 1D hybrid through self-assembly. The band gap of the 1D hybrid containing the CTC (~ 1.0 eV) is significantly red-shifted compared to the band gap of the equivalent free organic charge-transfer complex (~ 1.3 eV). Through *ab initio* modelling it is shown that this shift in band gap can mainly be explained by a templating effect of the inorganic lattice, which changes the stacking of the donor and acceptor molecules in the hybrid compared to the free charge-transfer complex. The valence band edge (VBE) and conduction band edge (CBE) of the hybrid are respectively dominated by pyrene occupied orbitals and TCNQ empty orbitals. However, occupied states of the inorganic lattice are located in very close energy proximity to the VBE. The 1D hybrid possesses a higher photoconductivity than the free organic CTC. This hybrid represents the first of a new class of hybrids containing CTCs with the potential for a high compositional versatility and a wide range of optical and electronic properties.

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