Supplementary Information

Impact of Organic-Inorganic Wavefunction Delocalization

on the Electronic and Optical Properties

of One-Dimensional Hybrid Perovskites

Xiaojuan Ni,† Sadisha Nanayakkara,† Hong Li,* and Jean-Luc Brédas*

Department of Chemistry and Biochemistry

The University of Arizona

Tucson, Arizona 85721-0041, United States

Emails: hongli2@arizona.edu

jlbredas@arizona.edu

Table of Contents

1. Geometric structures of (Cy7)PbI$_3$·2DMF and (VBB)PbI$_3$·2DMF

Table S1. Lattice parameters of (Cy7)PbI$_3$·2DMF and (VBB)PbI$_3$·2DMF, as optimized at the DFT-PBE level.

HOIP	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
(Cy7)PbI$_3$·2DMF	8.09	16.15	33.41	90	90	96
(VBB)PbI$_3$·2DMF	7.99	22.05	23.48	84	90	90

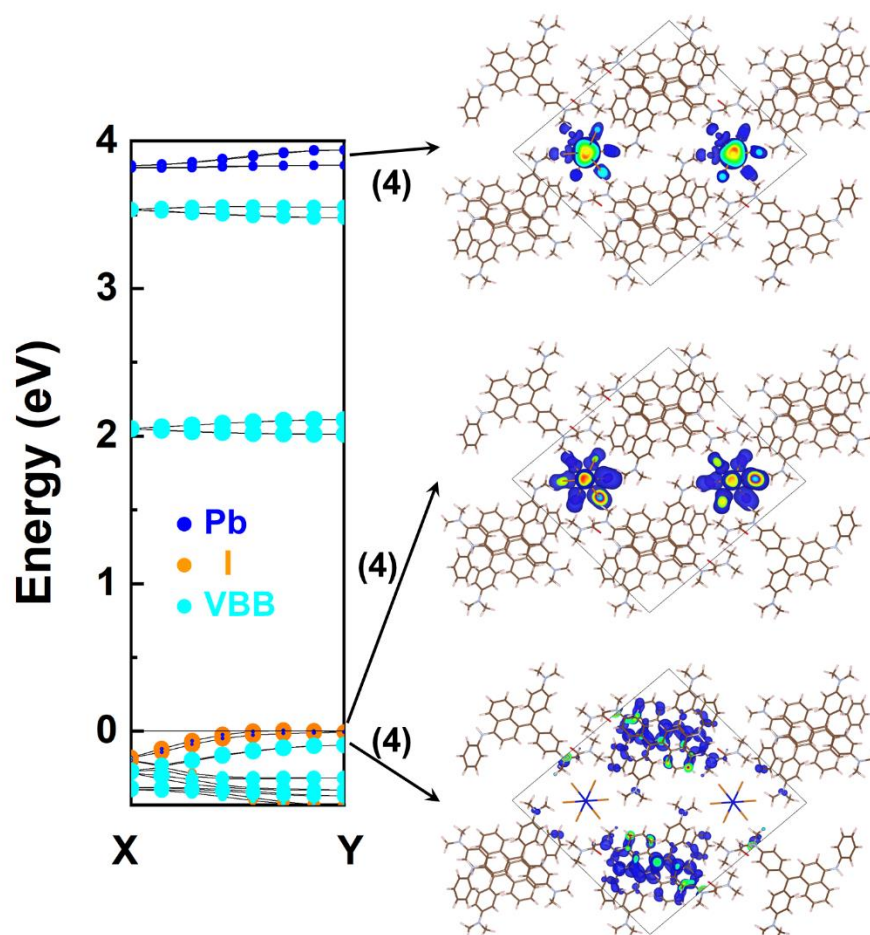## 2. Partial charge densities in (VBB)PbI$_3$·2DMF

Figure S1. HSE-SOC band structures along the X-Y k-path and partial charge densities of (VBB)PbI$_3$·2DMF. The values in parentheses indicate the number of eigenstates.

3. Tight-binding models

The Hamiltonian of a tight-binding model considering orbital hopping in the (Cy7)PbI$_3$·2DMF lattice (see **Figure 7a**) can be expressed as:

$$H = \sum_{\langle i \rangle} \varepsilon_i c_i^\dagger c_i \, \varepsilon_i - \left(\sum_{\langle i,j \rangle} t_1 c_i^\dagger c_j + \sum_{\langle\langle i,j \rangle\rangle} t_2 c_i^\dagger c_j + hc \right), \text{(S1)}$$

where ε_i represents the on-site energy; $c_i^\dagger$ and c_i denote the electron creation and annihilation operators at the i-th site, respectively; $\langle i,j \rangle$ denotes nearest-neighbor hopping with parameter t_1 and $\langle\langle i,j \rangle\rangle$ denotes next-nearest-neighbor hopping with parameter t_2. The detailed illustration of the hopping parameters is given in **Figure 7a**.

The electronic coupling strength between Cy7 and [PbI3], t_{in_or}, and the on-site energy of [PbI3], ε_{in}, are two parameters that we tune in the band-structure study, as shown in **Figure S2**. The contribution derived from Cy7 to the electronic states (indicated by the box in **Figure S2a**, which are predominantly derived from the inorganic framework) increases with the increasing value of t_{in_or} from 30 to 50 meV. The relative on-site energy of the inorganic component also plays an important role in determining the electronic hybridization between Cy7 and [PbI3] with a fixed value of t_{in_or}, as depicted in **Figure S2b**. When $t_{in\_or} = 39$ meV, by varying the value of [PbI3] on-site energy (ε_{in}) from -0.20 to -0.24 eV, the hybrid feature of the wavefunction of the boxed electronic states gradually reduces as we go from left to right. Therefore, we can identify that both the interaction between Cy7 and [PbI3] and the relative values of the on-site energy levels are responsible for the electronic coupling between the organic and inorganic components in these HOIPs.
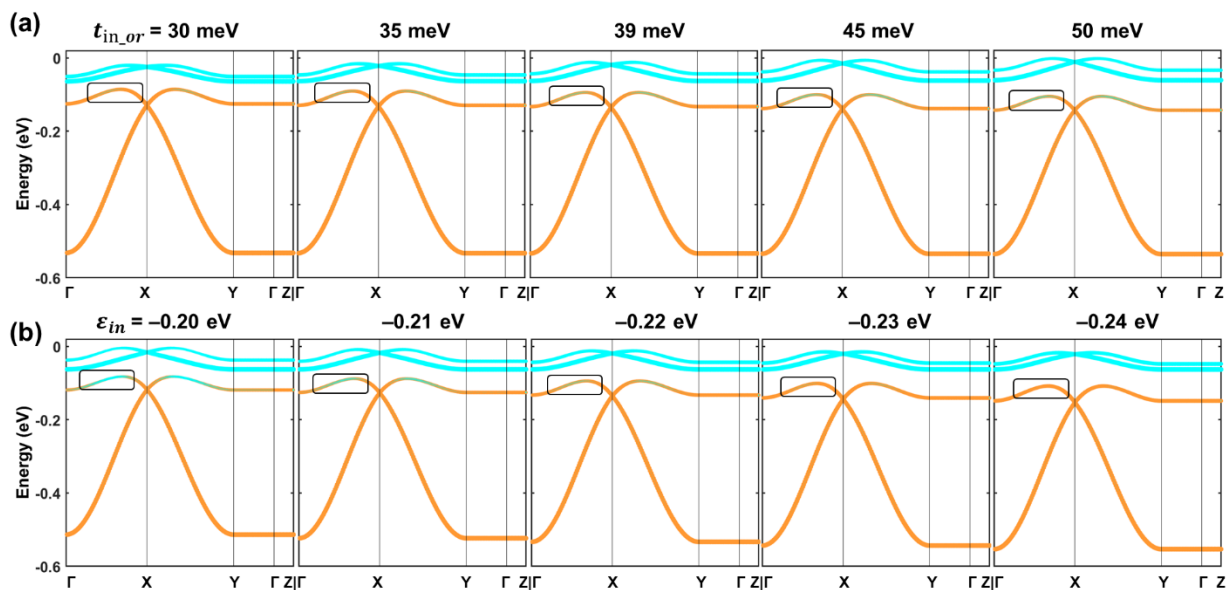
Figure S2. Band structures of (Cy7)PbI$_3$·2DMF obtained from TB models with the following parameters: (**a**) $\varepsilon_{or}=-0.05$ eV, $\varepsilon_{in}=-0.22$ eV, $t_{1\_in}=0.105$ eV, $t_{2\_in}=0.05$ eV, $t_{or}=0.008$ eV, $t_{in\_or}=30$, 35, 39, 45, and 50 meV; (**b**) $\varepsilon_{or}=-0.05$ eV, $t_{1\_in}=0.105$ eV, $t_{2\_in}=0.05$ eV, $t_{or}=0.008$ eV, $t_{in\_or}=39$ meV, and $\varepsilon_{in}=-0.20$, -0.21, -0.22, -0.23, and -0.24 eV. The cyan and orange colors represent the contributions from the organic and inorganic components, respectively.

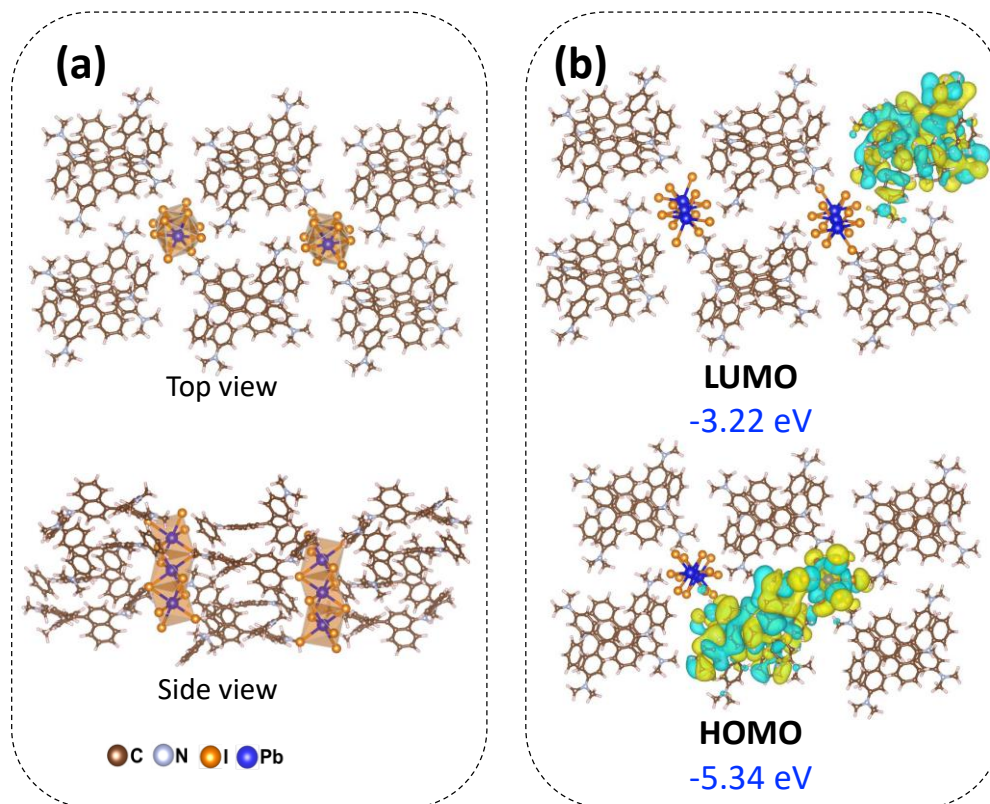## 4. Frontier molecular orbitals of the $(VBB)_{12}Pb_6I_{24}$ cluster

Figure S3. (**a**) Illustrations of the $(VBB)_{12}Pb_6I_{24}$ cluster model: top view and side view. (**b**) Frontier molecular orbitals of the $(VBB)_{12}Pb_6I_{24}$ cluster calculated at the HSE06 level. Isodensity surfaces with a contour of ±0.004 a.u. have been used to represent the positive (yellow) and negative (green) phases of the wavefunction.

5. Illustration of the molecular orbitals nearly degenerate with the HOMO and LUMO levels in the (Cy7)$_{12}$Pb$_6$I$_{24}$ cluster

level
nearly degenerate
with the LUMO

-3.39 eV

levels
nearly degenerate
with the HOMO

-5.03 eV   -5.05 eV   -5.05 eV

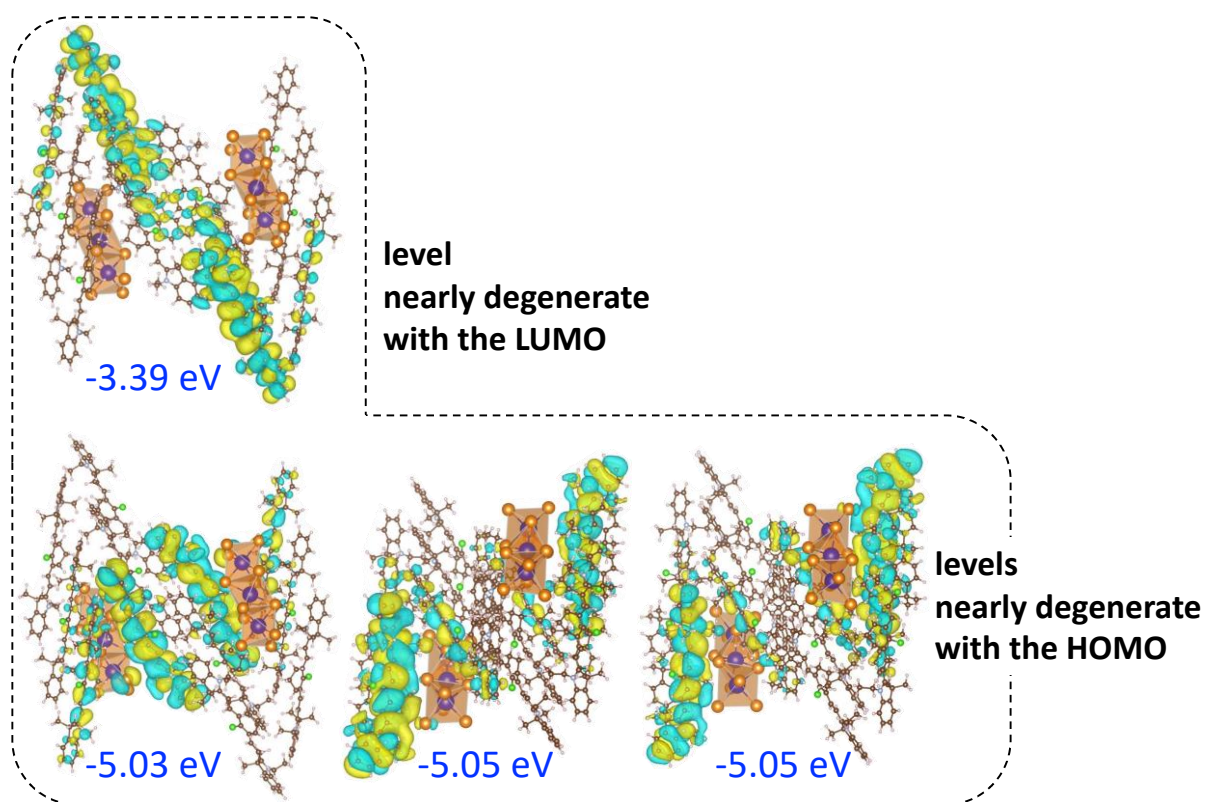**Figure S4.** Frontier molecular orbitals of the (Cy7)$_{12}$Pb$_6$I$_{24}$ cluster nearly degenerate with the HOMO and LUMO levels (depicted in **Figure S3**), as calculated at the HSE06 level. Isodensity surfaces with a contour of ±0.004 a.u. have been used to represent the positive (yellow) and negative (green) phases of the wavefunction.

6. Excited-state properties of the $(Cy7)_{12}Pb_6I_{24}$ cluster and Cy7-I salt

Table S2. Energy (eV), wavelength (nm), oscillator strength (f), electric transition dipole moment (μ, Debye), and charge-transfer contribution (%) from the inorganic to the organic fragment in the hole wavefunction of the low-lying singlet excited states, as calculated at the ωB97X-D level. The excited states with zero oscillator strength are excluded.

Electronic transition	Energy (eV)	Wavelength (nm)	f	μ (Debye)	Charge transfer contribution (%)
$(Cy7)_{12}Pb_6I_{24}$ cluster (DMF)					
S_1	1.79	693	0.19	5.4	1.31
S_4	1.82	680	0.33	6.9	1.17
S_5	1.84	675	2.15	17.6	1.07
S_8	1.89	656	0.93	11.4	0.25
S_{10}	1.99	624	1.65	14.8	0.89
S_{12}	2.08	597	18.64	48.7	1.26
Cy7-I complex (DMF)					
S_1	2.16	573	2.24	16.5	-

Table S3. Energies (eV), wavelengths (nm), oscillator strengths (f), and electric transition dipole moments (μ, Debye) of the low-lying singlet excited states, as calculated at the HSE06 level. The excited states with zero oscillator strength are excluded.

Electronic transition	Energy (eV)	Wavelength (nm)	f	μ (Debye)
$(Cy7)_{12}Pb_6I_{24}$ cluster (DMF)				
S_2	1.60	773	0.0162	1.6
S_3	1.63	759	0.0023	0.6
S_5	1.65	751	0.0002	0.2
S_6	1.65	751	0.0036	0.8
S_8	1.66	749	0.0001	0.2
S_9	1.66	748	0.0045	0.9
S_{10}	1.66	748	0.0002	0.2
S_{11}	1.66	747	0.0096	1.2
S_{12}	1.66	747	0.0001	0.1
Cy7-I complex (DMF)				
S_1	2.04	607	2.27	17.1