Charge Transfer States and Carrier Generation in 1D Organolead Iodide Semiconductors

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Supporting information

Table S1 Crystal data and structure refinement for $[(NDIC2)_2Pb_5I_{14}(DMF)_2]\cdot 4DMF$

	Compound name $[(NDIC2)_2Pb_5I_{14}(DMF)_2]\cdot 4DMF$
Empirical formula	$C_{13.50}\ H_{19.50}\ I_{3.50}\ N_{3.50}\ O_{3.50}\ Pb_{1.25}$
Formula weight	989.96
Temperature	100.0 K
Wavelength	1.34139 Å
Crystal system	triclinic
Space group	*P-1*
Unit cell dimensions	a = 11.2786(13) Å, α = 95.353(3)° b = 11.8512(13) Å, β = 95.858(3)° c = 17.6015(19) Å, γ = 94.332(3)°
Volume	2321.6(4) $Å^3$
Z	4
Density (calculated)	2.832 g/cm^3
Absorption coefficient	36.932 mm^{-1}
F(000)	1764
θ range for data collection	3.756 to 63.409°
Index ranges	-13<=h<=15, -15<=k<=15, -23<=l<=23
Reflections collected	142977
Independent reflections	10992 [R_{int} = 0.0701]
Completeness to θ = 25.242°	95.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10992 / 0 / 466
Goodness-of-fit	1.156
Final R indices [I > 2σ(I)]	R_{all} = 0.1090, wR_{all} = 0.3745
R indices [all data]	0.00149(13)
Largest diff. peak and hole	6.331 and -6.558 $e\cdot Å^{-3}$
$R = \Sigma\|\|F_o\|-\|F_c\|\| / \Sigma\|F_o\|$, $wR = \{\Sigma[w(\|F_o\|^2 - \|F_c\|^2)^2] / \Sigma[w(\|F_o\|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0174P)^2+22.3075P]$ where $P=(Fo^2+2Fc^2)/3$	

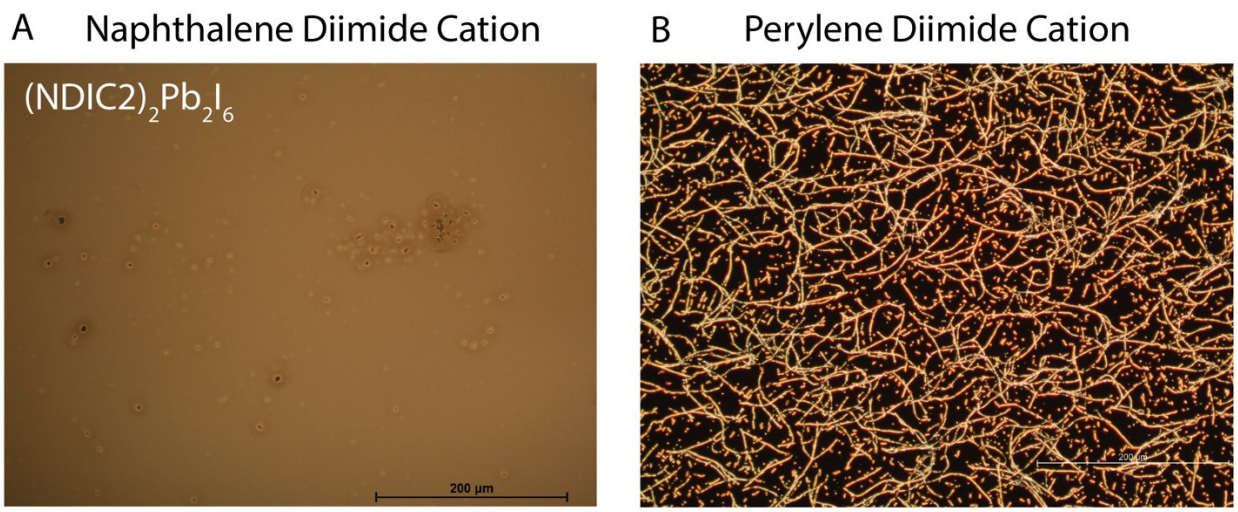
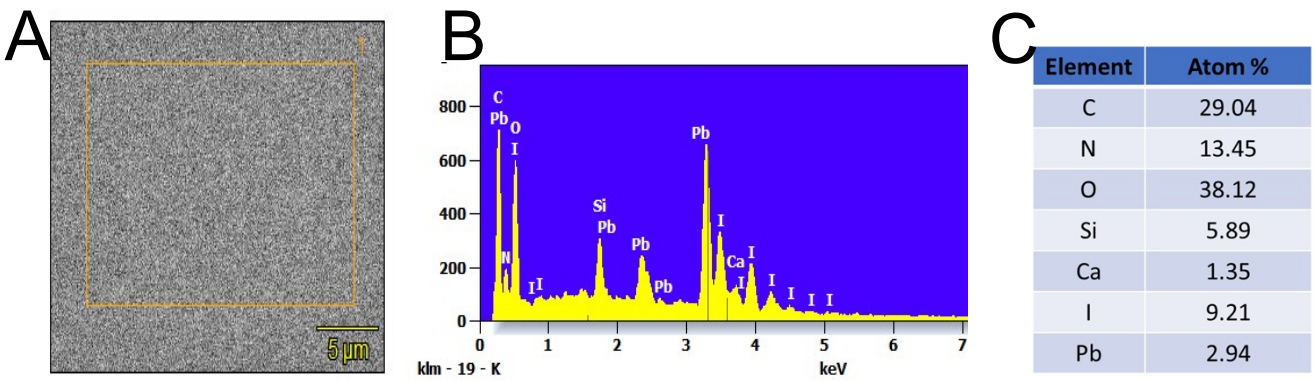


Figure S1. Optical micrographs to demonstrate that **A.** no phase segregation occurs in $(NDIC2)_2Pb_2I_6$ thin films using naphthalene diimide (NDI) A-site cations, whereas **B.** substantial phase segregation (wire formation) occurs when larger perylene diimide A-site cations are employed. In this case, π-stacking in the larger PDI-based cations drives the formation of pure PDI-based wires.



Element	Atom %
C	29.04
N	13.45
O	38.12
Si	5.89
Ca	1.35
I	9.21
Pb	2.94

Figure S2. Elemental mapping using energy-dispersive X-ray (EDX) spectroscopy on (NDIC2)Pb_2I_6 thin films. **(A)** SEM image of the area used to acquire the scan. **(B)** EDS spectrum. **(C)** Detailed distribution of the elemental composition and atomic %.

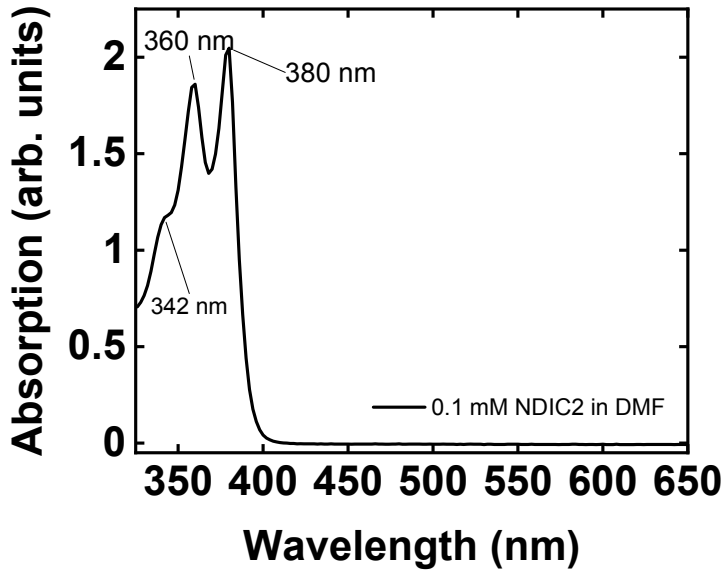


Figure S3. Solution-phase optical absorption spectrum for NDIC2-I_2 in DMF.

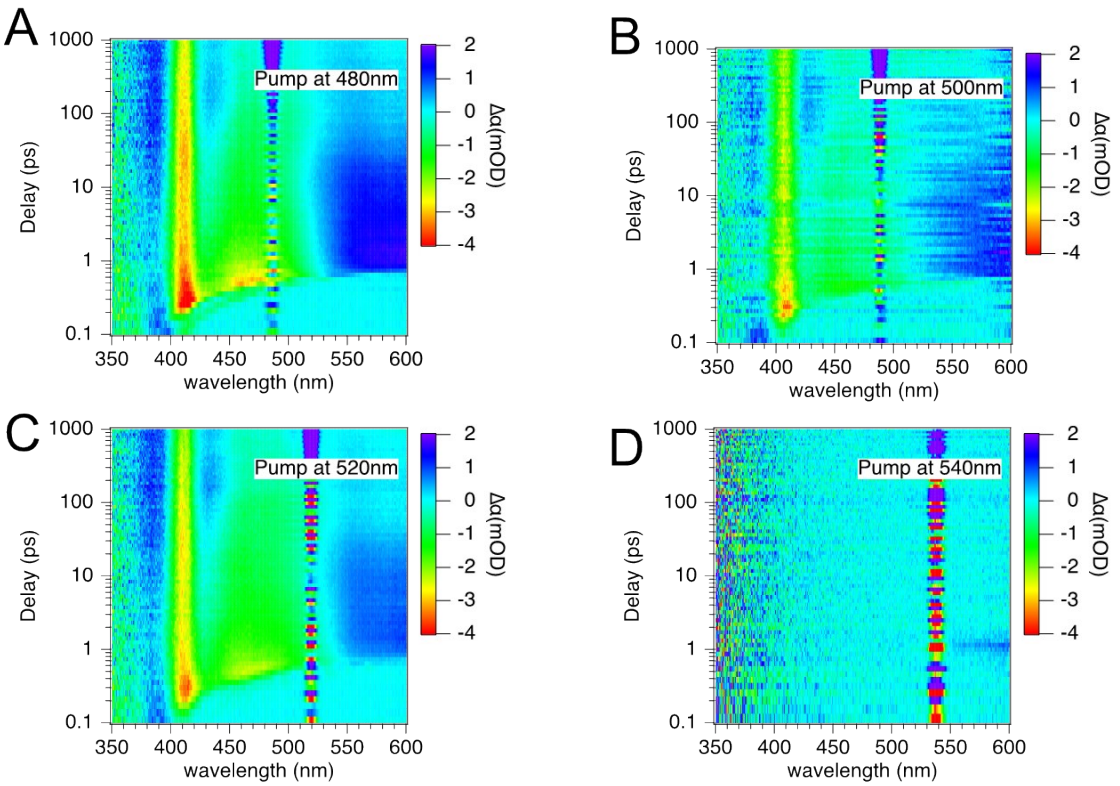


Figure S4. (A-D) TA decays pumped at 480, 500, 520, and 540 nm, respectively.

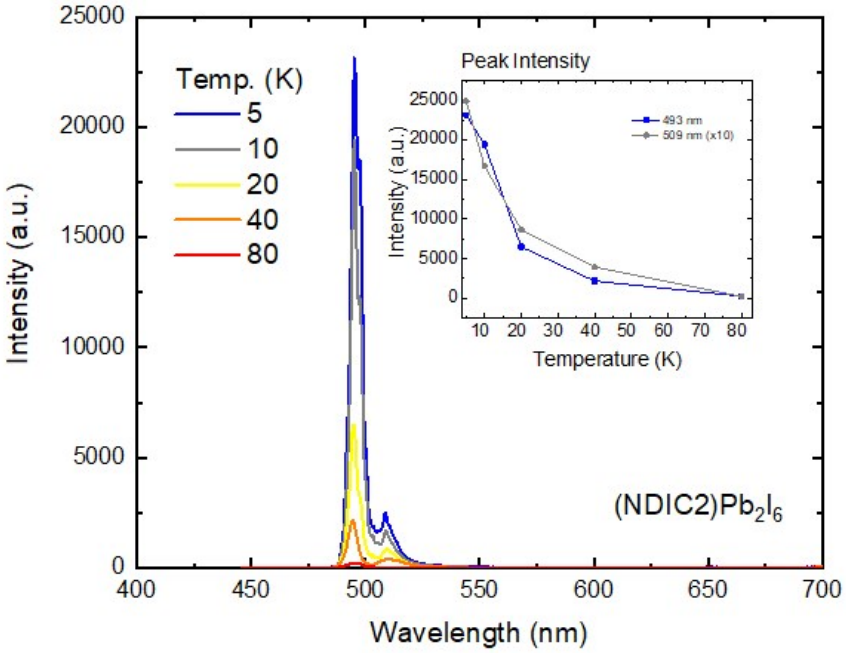


Figure S5. Temperature-dependent PL emission spectra for (NDI)Pb_2I_6 thin films (inset: peak intensity).

Computational methods

We use the all-electron electronic structure code FHI-aims[1-2] to perform first-principles hybrid density-functional theory calculations. The computations were carried out on the Bridges-2 supercomputer (Pittsburgh Supercomputing Center) through the Extreme Science and Engineering Discovery Environment (XSEDE). The calculations are based on numeric atom-centered orbital basis sets, using FHI-aims' "intermediate" numerical settings for basis functions, integration grids and for the electrostatic potential. A k-point grid of 4×4×3 points was used to discretize reciprocal-space integrals. Full relaxation of lattice parameters and atomic coordinates for the system was performed using the range separated hybrid HSE06 functional[3-4] plus the Tkatchenko–Scheffler (TS) pairwise dispersion scheme[5] for van der Waals interactions. For the structure optimization, the atomic ZORA level of scalar relativity was employed (Eqs. (55) and (56) of Ref. 1). For band structure and orbital calculations, we employed the HSE06 hybrid density functional[3-4] plus second-variational non-self-consistent spin–orbit coupling (SOC)[6] to predict the character of frontier orbitals. The k-point path is shown in Figure S6. The absorption spectrum in Figure S7 was calculated using the Lindhard formula and the independent particle approximation[7], based on DFT-HSE06+SOC. We provide the input structures for our calculations in the documented format of FHI-aims' geometry.in file[8]. Finally, a non-Aufbau occupation constrained DFT model[9-11] was implemented, constraining the CBM and VBM state's occupation number to 1.0 in the spin-unpolarized calculation (for the same geometry as the fully relaxed ground state structure, i.e., modeling a vertical excitation). The resulting density difference between ground state and simulated, static constrained state is shown in the main paper, Figure 7B. We note that this difference was calculated between scalar-relativistic self-consistent densities, i.e., omitting SOC effects (a self-consistent SOC implementation of the HSE06 density functional is not yet available in FHI-aims). The use of the scalar-relativistic formalism for the non-Aufbau density difference is justified since the main components contributing to the difference originate from light elements as well as I, but much less from the heavier, strongly spin-orbit coupled Pb 6*p* orbitals, which are largely unoccupied and are not expected to contribute significantly to the total-energy difference and density difference.

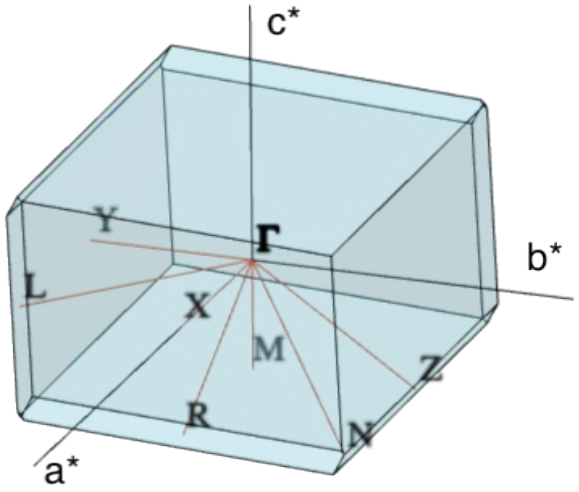


Figure S6. The high symmetry points and k-point path used in the band structure plot generated by the graphical interface for materials science (GIMS) application[12].

Computationally Optimized Structure

Table S2 compares the unit cell dimensions of the XRD-refined structure and the unit cell dimensions predicted by DFT-HSE06+TS. The percentage differences between the computational and experimental structural parameters are within 1%.

Table S2 The HSE06+TS computational lattice parameters compared to the XRD-based experimental lattice parameters for $[(NDIC2)_2Pb_5I_{14}(DMF)_2]\cdot 4DMF$.

Unit cell	**a(Å)**	**b(Å)**	**c(Å)**	$\alpha(°)$	$\beta(°)$	$\gamma(°)$	**Unit cell volume(Å^3)**
XRD resolved structure	11.2786(13)	11.8512(13)	17.6015(19)	95.353(3)	95.858(3)	94.332(3)	2321.6(4)
HSE06+TS structure	11.190	11.955	17.527	95.07	95.66	94.17	2316.20
Difference	-0.8%	+0.9%	-0.4%	-0.3%	-0.2%	-0.2%	-0.2%

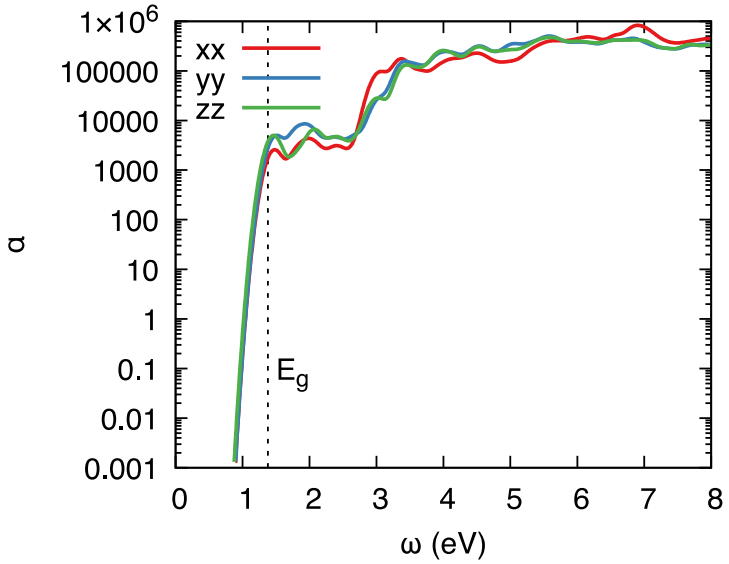


Figure S7. The calculated independent particle absorption spectrum for $[(NDIC2)_2Pb_5I_{14}(DMF)_2]\cdot 4DMF$ at the level of DFT-HSE06+SOC. The shallow foot between 1.5-2.5 eV indicates some residual absorption of the CT state even at the independent particle level. The underestimation of the fundamental gap compared to the actual CT state energy is attributed to the HSE06+SOC single particle eigenvalues, which underestimate the LUMO energy of the molecular species.

FHI-aims geometry.in file for the XRD-derived structure (input to electronic structure theory)

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FHI-aims geometry.in file for the DFT-HSE06+TS optimized structure

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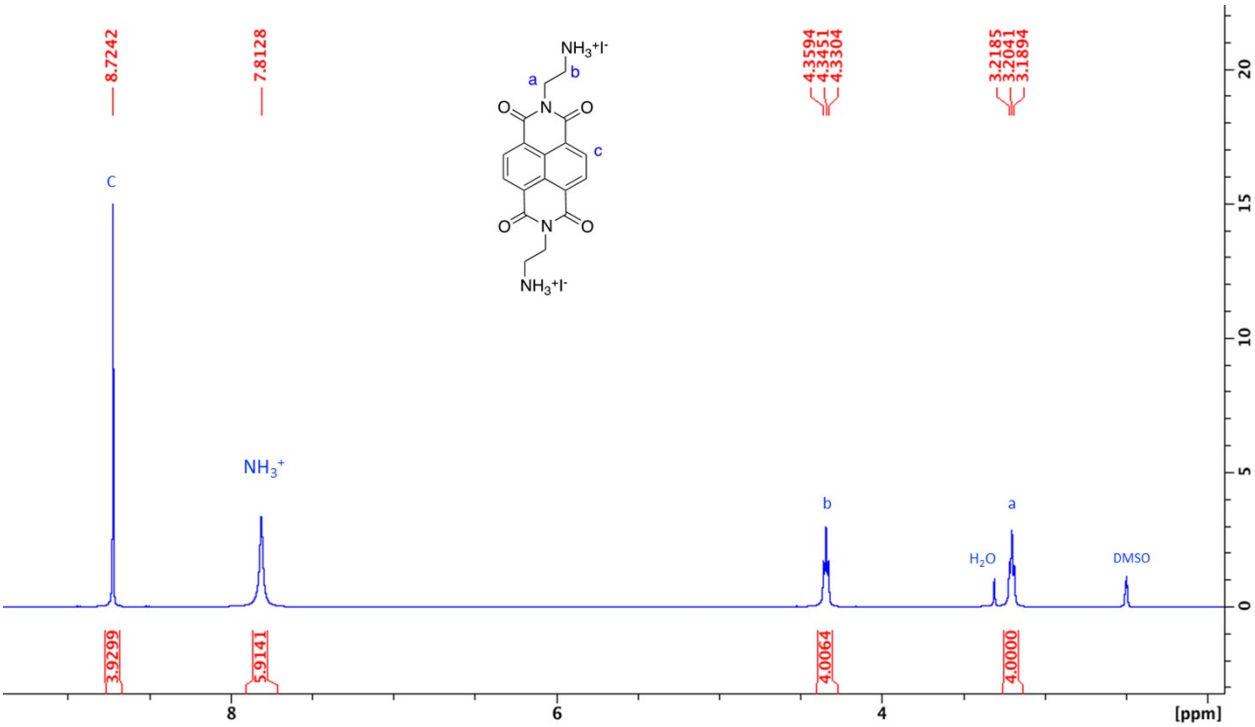

Figure S8. H1-NMR data of 2,7-bis(2-ammoniumethyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone iodide.

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