Synthesis, structural, linear and nonlinear optical studies of inorganic-organic hybrid semiconductors (R-$C_6H_4CHCH_3NH_3)_2PbI_4$, (R=CH_3, Cl)

Mohammad Adnan[a], Kotla Nageswara Rao[a], Jitendra Nath Acharyya[a], Dinesh Kumar[b], Kshetra Mohan Dehury[a] and G. Vijaya Prakash[a*]

[a] Nanophotonics Lab, Department of Physics, Indian Institute of Technology Delhi, New Delhi 110016, India.
[b] Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India.

Supplementary Information

Table S1.

Crystal Data	MPEPI	CEPI
Empirical Formula	$C_{18}H_{26}I_4N_2Pb$	$C_{16}H_{22}Cl_2I_4N_2Pb$
Formula weight	985.245 (g mol^{-1})	1028.62 (g mol^{-1})
Temperature	273K	298K
Wavelength	O.71073Å	0.71073Å
Crystal System	Orthorhombic	Monoclinic
Space Group	$Cmc2_1$	P 21/C
Unit cell dimensions	a=32.544 (7) Å;b=9.316 (2) Å c=8.6028(19) Å α=β=γ=90°	a=16.200(3)Å;b=9.2695(2)Å c=8.6314(13)Å β=96.738(2)°
Volume	2608.2 $Å^3$	1287.19 (4)$Å^3$
Z	4	2
Density (Calculated)	2.509mg m^{-3}	2.652mg m^{-3}
Crystal	Rod shape with hexagonal cross-section	Fragment, Dark yellow
Crystal Size	0.1x0.1x0.1mm^3	0.3x0.06x0.04mm^{-3}
Data Collection		
Absorption Coefficient	11.208 mm^{-1}	11.562mm^{-1}
F (000)	1768	920
Theta Range for data collection	2.274-28.288°	2°-25°
Reflections Collected	14082	2270
Independent reflections	3192	2200
Completeness to θ=27.48°	99.5%	99.99%
Absorption Correction	Semi empirical from equivalents	Multi Scan
Max. and Min Transmission	0.400 and 0.400	0.111 and 0.059
Refinement Method	Full-matrix least squares on F^2	Phi and Omega scans
Data/Restraints/Parameter	3129/1/120	2200/0/117
Final R-indices[F^2 >2σ(F2]	R1=0.0288, wR2=0.0569	0.0253
R-indices (all data)	R1=0.0330, wR2=0.0576	0.0267

R-factor (%)	2.88	2.53

Frames and data were collected at T= 298 K and 273K for MPEPI and CEPI respectively by ω, ψ, and 2θ-rotation at 10s per frame with SAINT. The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[1] Structure solution, refinement and data output were carried out with SHELXTL.[2] All the non-hydrogen atoms were refined anisotropically. All calculations were carried out using Wingx- crystallographic package.[3] Single crystal structure was examined using the Adsym subroutine of PLATON[4] to verify that no additional symmetry could be used to the model. The C–H hydrogen atoms were located in geometrically calculated positions by using a riding model. Hydrogen bonding interactions in the crystal lattice were calculated using SHELXTL and Diamond.[2,5] Molecular graphic images were created with Diamond.

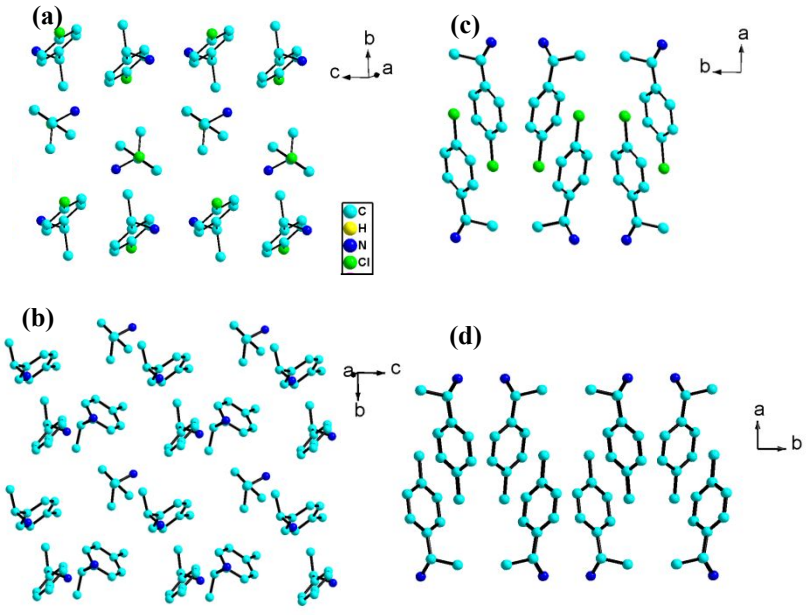

Figure S1. (a) Shows the double layer of organic ammonium in CEPI when viewed along a axis with a slight tilt (b) Shows the double layer view of organic ammonium cation when viewed along a axis. (c) And (d) presents a clear view of two different orientations of the organic in a single layer of CEPI and MPEPI respectively.

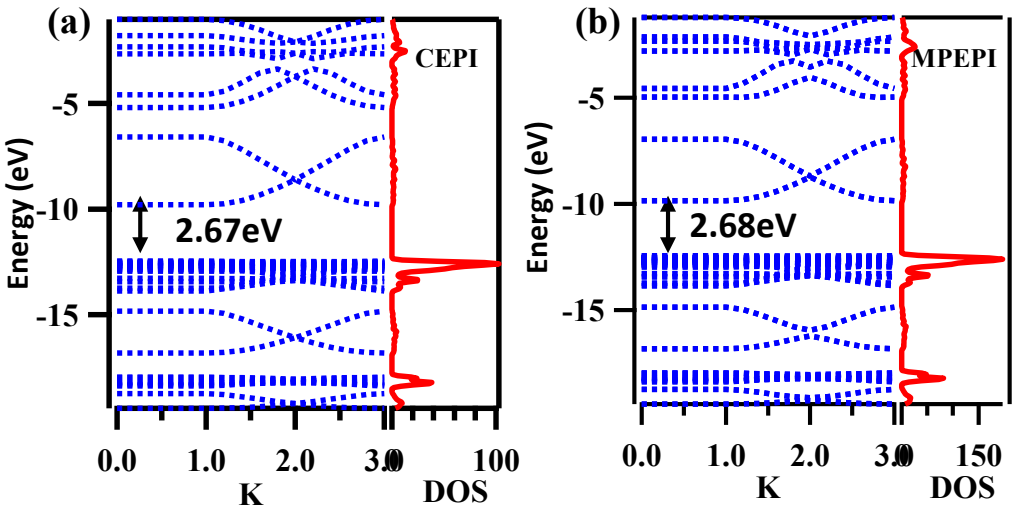

Figure S2. (a) & (b) Shows band structure diagram and band gap of CEPI and MPEPI respectively extracted from extended hückel tight binding calculations.

Extended hückel tight binding calculation's [CAESAR^{TM}V2.0] are used to evaluate the band structure of both the IO hybrids from their crystallographic data. The estimated band gaps of the both CEPI and MPEPI are 2.66eV and 2.68eV respectively [Figure S2]. These results are in agreement with the exciton emission properties shown by them. In our earlier reports we tried correlating the band gap difference associate with these IO hybrid systems with the change in the Pb-I-Pb bond crumpling angle.[6] The difference in band gaps observed here and Pb-I-Pb bond crumpling in corresponding materials crystal structure are well in agreement.

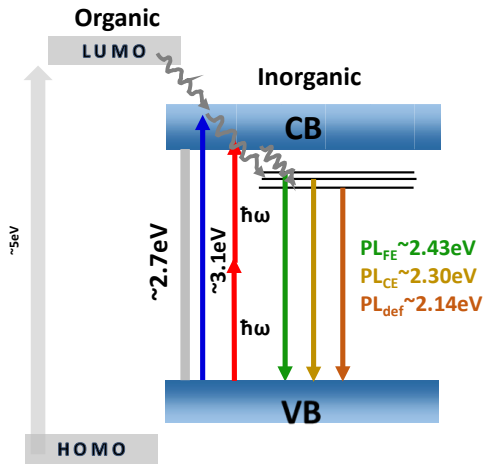

Figure S3. Schematic energy level representation of inorganic-organic hybrid semiconductor.

Reference:

[1] Bruker Analytical X-ray Systems. SAINT-NT, version 6.04; *Bruker AXS*: Madison, WI, **2001**.

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[3] Farrugia, L. WINGX, version 1.80.05; University of Glasgow: Glasgow, **2009**.

[4] Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, the Netherlands, **2005**.

[5] Brandenburg, K. DIAMOND, version 2.1e; Crystal Impact GbR: Bonn, Germany, **2001**.

[6] Pradeesh, K.; Rao, K.N.; Vijaya Prakash, G. Synthesis, structural, thermal and optical studies of inorganic-organic hybrid semiconductors. *J. Appl. Phys*. **2013**, 113, 083523.