Optoelectronic Modulation via Isomerism-Induced Structural Effects in Low-Dimensional Bismuth Halide Perovskites

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Supplementary information

S1. Experimental Details

Materials

Bi_2O_3 (Nano powder 90-210nm) was purchased from sigma Aldrich, hydroiodic acid (57 wt% in H_2O, 99.95%) was purchased from sigma Aldrich, o-phenylene diamine, m-phenylene diamine and p-phenylene diamine (98%) were purchased from TCI, H_3PO_2 was purchased from TCI. All chemicals were used without further purification.

Synthesis of (m-PDA)$_2$Bi$_2$I$_{10}$ (MPDA)

An amount of 930 mg (2mmol) of Bi_2O_3 powder was dissolved in 5 mL of hydroiodic acid and 0.5 mL of hypo phosphorous acid solution by heating under stirring for 5−10 min at ∼130 °C until the solution turned clear bright yellow. 0.5 mL of hydroiodic acid and 0.5 mL of hypo phosphorous acid was added to 216 mg (2 mmol) of meta-phenylenediamine in a separate vial under stirring. The protonated *m*-PDA solution was added into the previous solution under heating at 200 °C and stirring for 5 min [1]. Red plate-like crystals precipitate (65% of maximum theoretical yield) during slow cooling to room temperature

Synthesis of (o-PDA)$_2$Bi$_2$I$_{10}$ (OPDA)

An amount of 930 mg (2mmol) of Bi_2O_3 powder was dissolved in 5 mL of hydroiodic acid and 0.5 mL of hypo phosphorous acid solution by heating under stirring for 5−10 min at ∼130 °C until the solution turned clear bright yellow. 0.5 mL of hydroiodic acid and was added to 216 mg (2 mmol) of ortho-phenylenediamine in a separate vial under stirring. The protonated *o*-PDA solution was added into the previous solution under heating at 200 °C and stirring for 5 min. Red wire-like crystals precipitate (69% of maximum theoretical yield) during slow cooling to room temperature.

Synthesis of (p-PDA)$_2$Bi$_2$I$_{10}$.6H$_2$O (PPDA)

An amount of 230 mg (0.5mmol) of Bi_2O_3 powder was dissolved in 4.5 mL of Deionized water and 1.25 mL of hydroiodic acid solution by heating under stirring for 5−10 min at ∼130 °C until the solution turned clear. 4.5 mL of absolute ethanol was added to 54 mg (2 mmol) of para-phenylenediamine in a separate vial under stirring. The protonated *p*-PDA solution was added into the previous solution under heating at 130 °C and stirring for 5 min. Red plate-like crystals (48% of maximum theoretical yield) precipitate during slow cooling to room temperature

S2. Methods and instrumentation:

UV-visible Absorption Spectroscopy

UV-visible absorption spectra were collected using Shimadzu UV-1800 spectrometer. The excitation spectra were corrected for lamp and detector response respectively. All experiments were performed at room temperature.

X-ray Diffraction (XRD)

Powder XRD patterns were collected from a Rigaku Ultima IV X-Ray diffractometer operated with an X-ray generator voltage and current of 50 kV and 60 mA respectively and using a Cu Kα source (λ =1.54187 Å). 1M solution of single crystals were dissolved in DMF and were spin-coated on a clean glass substrate and then annealed at 130^{o}C before acquiring the spectra at room temperature. Data analysis was performed with the Rigaku PDXL data processing software.

Single crystal X-ray Diffraction (SCXRD)

The single crystal data of the respective materials have been obtained through X–ray diffraction analysis. The crystals were mounted on a Gemini A Ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector for data collection. X–ray intensity data were collected with graphite monochromated MoKa radiation (kĽ0.71073 Å) at 295(2) K with □ scan mode. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm (CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.37.46) were applied. All anisotropically using full–matrix, least squares. All hydrogen atoms were added geometrically and refined as "riding" on the adjacent carbon with individual isotropic temperature factor equal to 1.2 times the value of equivalent temperature factor of the parent atom. Olex2 2 and SHELXS 3 programs were used for all calculations. The molecular graphic designs and packing diagram were performed using OLEX2 software.

Ultraviolet Photoelectron Spectroscopy (UPS)

UPS analysis patterns were obtained from Thermo Scientific NEXSA Surface Analysis. UV Source used for this characterization was of HeI (21.2eV) HeII (40.8eV). Powder samples were used for this characterization.

Computational details

We conducted comprehensive theoretical studies using density functional theory (DFT) with the advanced Vienna Ab initio Simulation Package (VASP)[2]. DFT is particularly adept at accurately predicting solid-state properties that align closely with experimental results. To investigate core electron behaviour, we employed Projected Augmented Wave (PAW) pseudopotentials. For structural optimization, we utilized the Generalized Gradient Approximation (GGA) developed by Perdew, Burke, and Ernzerhof (PBE)[3, 4]. A kinetic energy cutoff of 500 eV was established following thorough convergence testing. The Brillouin zone was sampled in k-space using the Monkhorst-Pack scheme with a 3x3x1 K-point grid. During structural optimization, we enforced strict convergence criteria for energy and forces at 10^{-6} eV and 10^{-2} eV/Å, respectively, to guarantee robust and reliable results.

Table S1: Crystal parameters of PPDA, MPDA and OPDA derived from SCXRD.

Parameters	**OPDA**	**MPDA**	**PPDA**
Space group	P21/c	P21/n	P21/n
Crystal structure	Monoclinic	Monoclinic	Monoclinic
Volume	1952.9	1748.9	2046.4
a, b, c (Å)	8.72, 19.56, 13.95	10.75, 8.48, 19.86	11.47,12.89, 14.96
α, β, γ (°)	90, 124.88, 90	90, 105.05, 90	90,112.39,90
Hall group	-P 2ybc	-P 2yn	-P 2yn
Sum formula	C12 H20 Bi2 I10 N4	C12 H20 Bi2 I10 N4	C12 H32 Bi2 I10 N4 O6
Mr	1907.28	1907.28	2015.38
Dx, gcm^{-3}	3.243	3.622	3.271
Z	2	2	2
F000	1632.0	1632.0	1752.0

F000'	1607.84	1607.84	1727.84
h,k,l_{max}	12, 26, 19	14, 11, 27	15, 17, 20
N_{ref}	5330	4856	5673
T_{min}, T_{max}	0.123, 0.508	0.082, 0.125	0.231, 0.446
T_{min}'	0.069	0.005	0.059

Table S2: Calculated bond length of PPDA, MPDA and OPDA. A more detailed crystallographic data is provided in the **Table S1** of supporting information (SI).

Bond length (Å)	***OPDA***	***MPDA***	***PPDA***
Bi-I$_1$	3.020	3.222	3.267
Bi-I$_2$	2.945	3.204	3.099
Bi-I$_3$	2.915	3.310	2.943
Bi-I$_4$	3.089	2.918	2.920
Bi-I$_5$	3.290	2.976	3.064
Bi-I$_6$	3.271	2.964	3.243

S3: Ultraviolet Photoelectron Spectroscopy measurements

a) Work Function Determination: All the three as synthesized single crystal compounds were studied using UPS analysis under zero bias voltage. The work function (Φ) was calculated from the high-binding energy cutoff using the He I radiation energy of 21.22 eV.

For PPDA, the high-binding energy cutoff and VBM w.r.t fermi energy was observed at 15.45 eV and 0.53 eV (Fig.5a). Therefore, Work Function = 15.45 eV − 21.22 eV = −5.77 eV versus vacuum.

For MPDA, similar calculations were performed, yielding a work function of – 5.76 eV versus vacuum.

For OPDA, similar calculations were performed, yielding a work function of – 5.74 eV versus vacuum.

b) Valence Band Maximum (VBM): The position of the VBM was determined using the low energy tail of the UPS spectrum[5] (Figure 5b).

For PPDA, the VBM was found to be 0.53 eV below the Fermi level. Therefore,

VBM = -5.77-0.53 = − 6.30 eV versus vacuum.

For MPDA, the VBM was found to be 0.71 eV below the Fermi level. Therefore,

VBM = -5.76 eV – 0.71 eV = − 6.47 eV versus vacuum.

For OPDA, the VBM was found to be 1.18 eV below the Fermi level. Therefore,

VBM = -5.74 eV – 1.18 eV = − 6.92 eV versus vacuum.

c) Conduction Band Minimum (CBM): By using the optical bandgap from the spectra (although indicative of excitonic bandgap observed to overlap), CBM was determined using the relation: CBM = VBM + Optical Bandgap.

For PPDA, CBM = − 6.30eV + 2.04 eV = − 4.26 eV versus vacuum.

For MPDA, CBM = − 6.47 eV + 2.18 eV = − 4.29 eV versus vacuum.

For OPDA, CBM = − 6.92 eV + 2.21 eV = − 4.71 eV versus vacuum.

Electron affinity = E_{vac} – CBM (E_{vac} = 0 eV for all the three compounds)

S4: EDX measurement of thin films

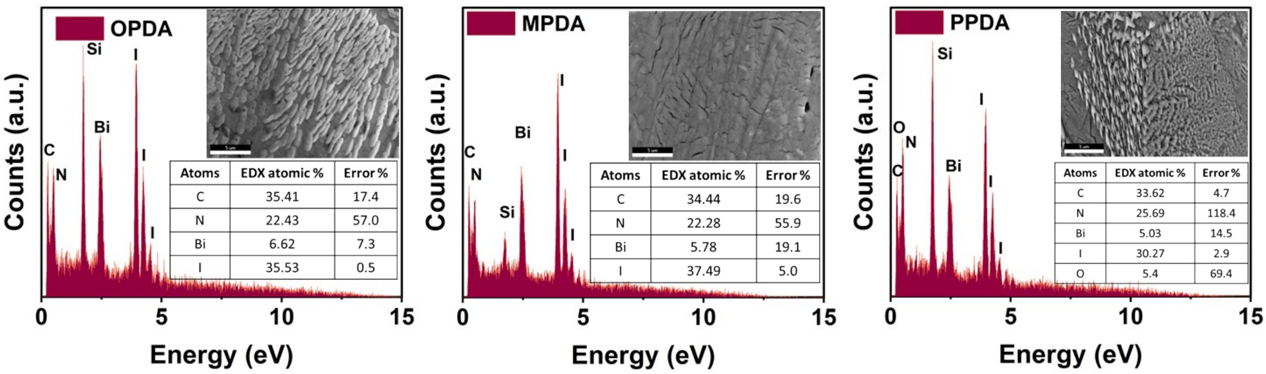

Figure S1: EDX measurement of thin films of OPDA, MPDA and PPDA respectively**.**

References

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