Pressure-Induced Structural and Optoelectronic Modulations in 2D Dion-Jacobson Hybrid Lead Iodide Perovskites with a Rigid Spacer

Aditya KUTTY (University of Western Ontario, Canada),
Jesse RATTÉ (University of Western Ontario, Canada),
Rongfeng GUAN (University of Western Ontario, Canada),
Jingyan LIU (University of Western Ontario, Canada),
Sean TAO (University of Western Ontario, Canada),
Yanqian LIN (University of Western Ontario, Canada),
Matthew P. HAUTZINGER (National Renewable Energy Laboratory, USA),
Willa MIHALYI-KOCH (University of Wisconsin-Madison, USA),
Song JIN (University of Wisconsin-Madison, USA),
Yang SONG* (University of Western Ontario, Canada)
*Correspondence: yang.song@uwo.ca

Abstract

Two-dimensional hybrid organic-inorganic perovskites (HOIPs) are known for their enhanced chemical and thermal stability relative to three-dimensional variants, positioning them as promising materials for advanced optoelectronic applications. External pressure provides an effective route to modify their structures and tune their optoelectronic responses. This study examines the high-pressure behavior of the Dion-Jacobson 2D HOIP DPDAPbI□, which incorporates the rigid organic spacer N,N-dimethylphenylene-p-diammonium (DPDA). Combining photoluminescence, UV-visible absorption, vibrational spectroscopy, and in situ synchrotron powder X-ray diffraction, we identify an isostructural phase transition near 1.5 GPa, marked by a pronounced change in photoluminescence intensity linked to free-exciton emission. Synchrotron X-ray diffraction reveals significant anisotropic compression along the c-axis, while structural analysis indicates the rare occurrence of reduced lead-iodide octahedral distortion below 2 GPa, contrasting with the increased octahedral distortion commonly reported in lead-based 2D HOIPs. Density functional theory calculations elucidate the structural origins and mechanisms driving the pressure-induced phase transition and optoelectronic tuning. These findings highlight the critical interplay between rigid organic spacers and inorganic octahedra in modulating high-pressure optoelectronic properties, offering design insights for future 2D HOIPs with tailored functionalities.

Keywords: 2D hybrid organic-inorganic perovskites; Dion-Jacobson; high pressure; photoluminescence; UV-visible absorption; octahedral distortion; bandgap