Poster

Rationalizing the chiroptical behaviour of chiral hybrid metal halides: the role of composition and crystal structure

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Introducing chiral cations into hybrid organic-inorganic metal halides (HOIMHs) is paving the path for innovative materials combining the benefits of the chiral molecules, as the second-order non-linear optical response [1], and the adjustable absorption and luminescence properties deriving from the HOIMHs structures [2,3]. The heightened design flexibility allows for the creation of materials with customizable structural and functional properties, such as high spin selectivity, increased circular dichroism, improved stability, and more. Despite the growing interest in this area, many fundamental questions persist regarding the influence of chemical composition and structural parameters on the photophysical properties and chirality transfer mechanisms, and their understanding is a bottleneck for significant progresses in the field.

In this scenario our investigation aims on attaining novel series of chiral HOIMHs, wisely modulating the constituents and evaluating the impact on the crystal structure thus on the chiroptical properties. To this aim we have synthesized and characterized the 2D (*R/S*/rac)ClMBA$_2$SnI$_4$ (ClMBA=1-(4-chlorophenyl)ethanamine), displaying a remarkable bandgap as low as 2.12 eV, a broad emission due to self-trapped exciton formation and a Rashba type band splitting in the chiral samples [4], thus we have tentatively correlated the octahedra distortions with the chiroptical features by a comparison with similar lead and lead-free 2D chiral perovskites from literature. We then move to Ge^{II} synthesizing the 1D (*R/S*)ClMBA$_3$GeI$_5$, observing an enhanced octahedra distortion index *vs*. Pb- and Sn-based HOIMHs, and performed the optical characterization to rationalize the role of Ge^{II} *vs*. Sn^{II} in the chiroptical behaviour. In a different work we have employed (*S*)-3-aminopiperidine obtaining the bromide and iodide series with Ge^{II}, Sn^{II} and Pb^{II} [5,6], as well as Cu^{II}, and are currently carrying out the photophysical characterization aiming to correlate the results with the difference in dimensionality and crystal structure imparted by the modulation of metal ion and/or halogen. Moreover, we are tuning the chiral cations by synthesizing *ad hoc* (2*R/S*,2'*R/S*)-1,1'-azanediylbis(butan-2-ol) and coupling it with Pb^{II} and Sn^{II} and are now putting efforts to elongate the organic chain and evaluate the effect of its steric hindrance. By taking also advantage of theoretical calculations for the interpretation of the results we focus on unveiling new parameters to correlate the chemical and structural properties with the chiroptical features, providing beneficial tools for the design of novel materials for photodetection, chiral photonics, spintronics, energy harvesting, etc.

[1] Kauranen, M.; Busson, B.; Van Elshocht, S.; Verbiest, T.; Persoons, A.; Nuckolls, C.; Katz, T. J. (2000). *Optics & Photonics News*, **11**, 24.

[2] Jena, A. K.; Kulkarni, A.; Miyasaka, T. (2019). *Chem. Rev*., **119**, 3036.

[3] Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos, P.; Lu, Z.; Kim, D. H.; Sargent, E. H. (2016). *Nature Nanotechnology*, **11**, 872.

[4] Coccia, C.; Morana, M.; Mahata, A.; Kaiser, W.; Moroni, M.; Albini, B.; Galinetto, P.; Folpini, G.; Milanese, C.; Porta, A.; Mosconi, E.; Petrozza, A.; De Angelis, F.; Malavasi, L. (2024). *Angew. Chem. Int. Ed.,* **63**, e202318557.

[5] Peng, Y.; Yao, Y.; Li, L.; Liu, X.; Zhang, X.; Wu, Z.; Wang, S.; Ji, C.; Zhang, W.; Luo, J. (2019) *Chem. Asian J*., **14**, 2273.

[6] Fu, D.; Xin, J.; He, Y.; Wu, S.; Zhang, X.; Zhang, X.-M.; Luo, J. (2021) *Angew. Chem. Int. Ed*., **60**, 20021.

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