Supplementary information

Unmasking The Magic of Magic Blue in Perovskite Doping

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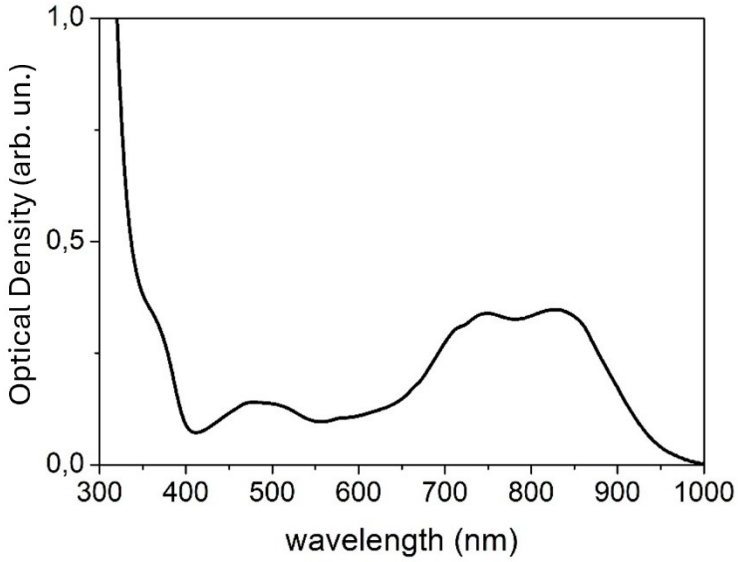

Figure S1. Absorption spectrum of a MB film on glass, encapsulated. The film thickness is ca. 20 nm.

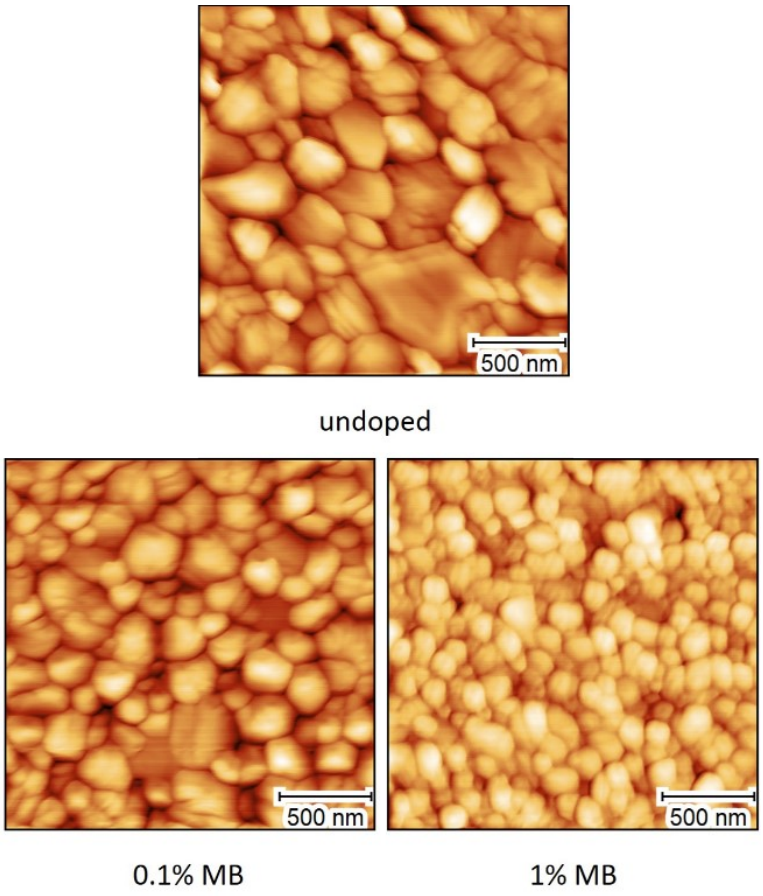

Figure S2. AFM images for the undoped MAPI and doped with 0.1% and 1% of MB.

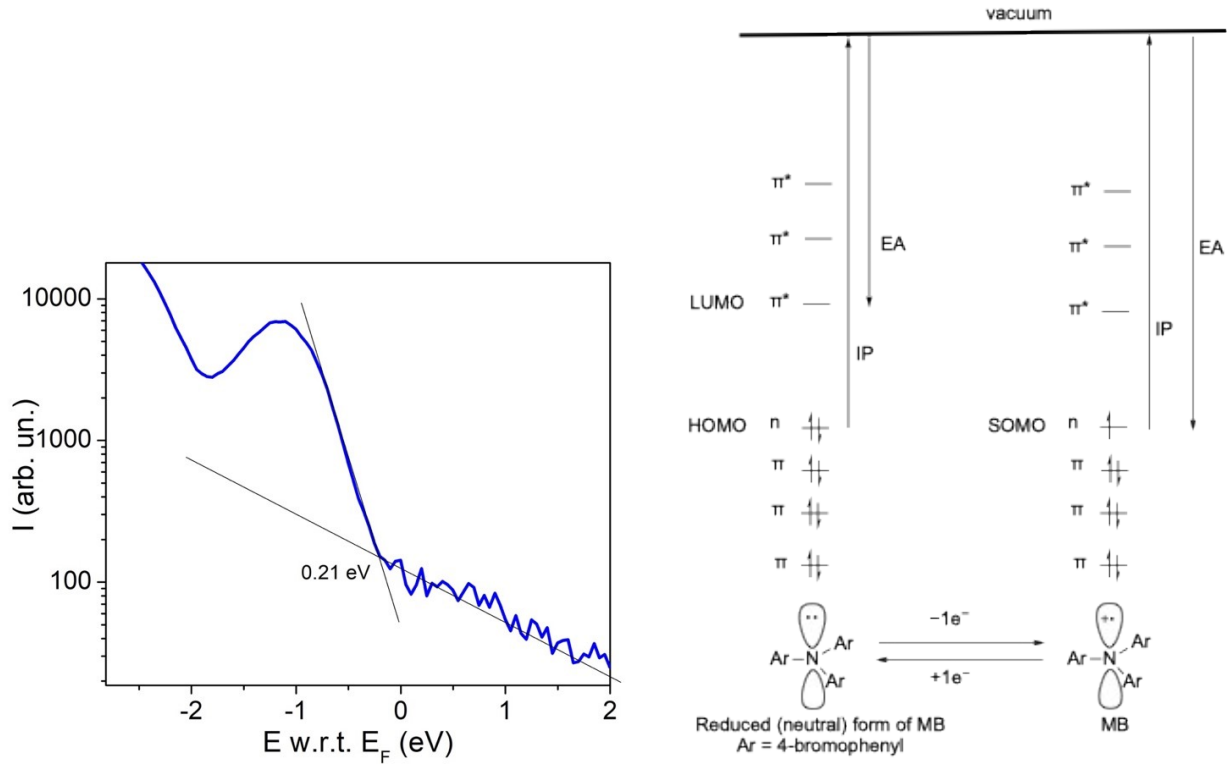

Figure S3: Left: UPS spectrum of a thin film of Magic Blue. Fermi level is 0.21 eV above occupied states (SOMO or HOMO). Right: Simplified molecular orbital diagram depicting the ionization potential (IP) and electron affinity (EA) of MB and its neutral triarylamine precursor. The energy level of the SOMO does not take into account the reorganization energy or electron repulsion.

The highly oxidizing MB is a persistent radical cation obtained from its neutral tri-arylamine precursor through chemical one-electron oxidation, usually using a strong chemical oxidant. As shown in Fig S3, the HOMO of the neutral amine precursor is located on the nitrogen lone pair. Upon oxidation, the latter undergoes hybridization to an sp^2 center that is (partly) conjugated to one (or more) of the aryl substituents. As shown, the IP and EA of MB are equal because no correction is introduced to take into account the lowered electron – electron repulsion or reorganization energy of the radical cation. This can be substantial and, in some cases, lowers the energy of the SOMO below that of the highest doubly occupied molecular orbital (SOMO – HOMO inversion)[1]. In this case, ionization then occurs from the doubly-occupied HOMO.

[1] S. Kasemthaveechok, L. Abella, J. Crassous, J. Autschbach and L. Favereau, *Chem. Sci.*, 2022, **13**, 9833-9847.