Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Origin of Absorption Edge Fine Structure in Pb-Based Organic-Inorganic 1D Perovskites

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SUPPORTING INFORMATION

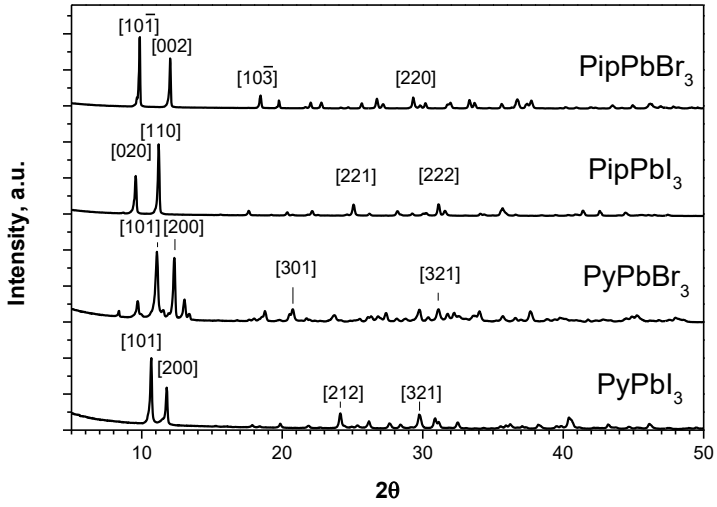

Figure SI1. Experimental XRD patterns of the 1D perovskites examined.

It is known that all four of our 1D perovskites demonstrate at 77 K very broad emission (500 – 850 nm) with a maximum at 625-650 nm, excited in the range of intrinsic absorption.[1-3] Therefore, while recording the DR spectra at cryogenic temperatures in the range of the absorption edge and higher energies, the integrating sphere recorded both diffusively reflected light and light of the photoluminescence (PL). It was shown in our previous study[4] that specially selected glass filters placed into the integrating sphere over the UV-vis light detector provided for the PL registration during the measuring of the DR spectra in the range of the absorption edge.

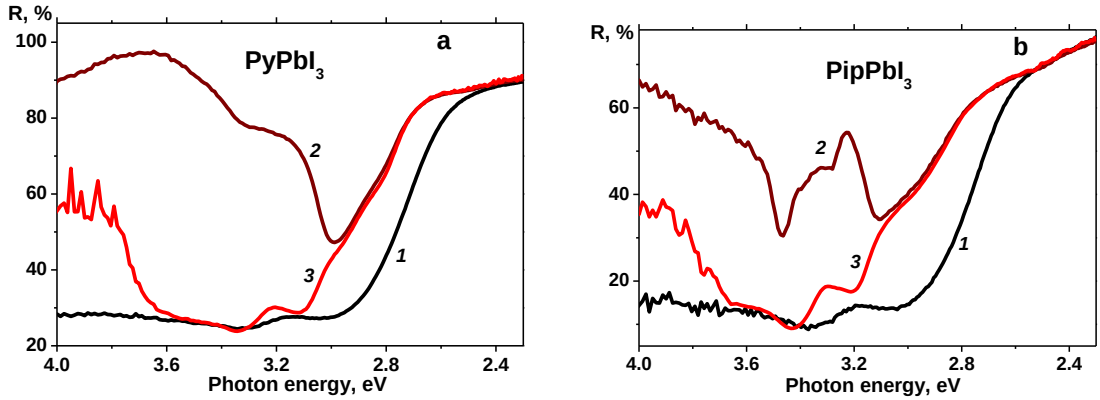

Figure SI2. DR spectra of $PyPbI_3$ (a) and $PipPbI_3$ (b) recorded at room temperature (curves ***1***), at 100 K (curves ***2***), and at 100 K with glass filter (curves ***3***). Glass filters: in (a) and (b) PS11+CZC21

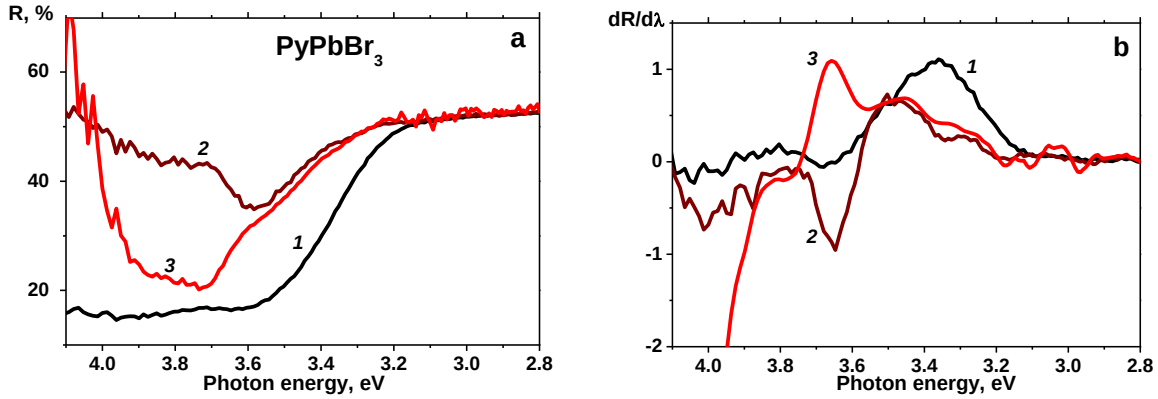

Figure SI3. (a) DR spectra of $PyPbBr_3$ recorded at room temperature (curves ***1***), at 100 K (curves ***2***), and 100 K with glass filter UFS-2 (curves ***3***). (b) First derivatives of the DR spectra are relative to wavelength in (a).

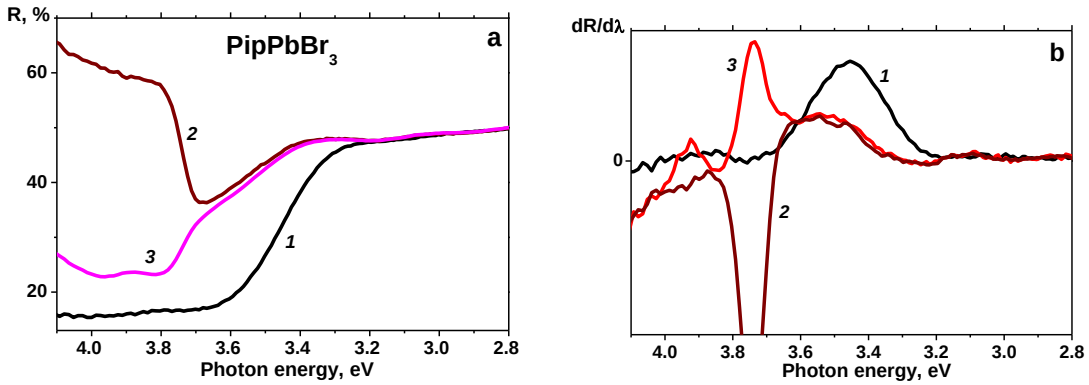

Figure SI4. (a) DR spectra of $PipPbBr_3$ recorded at room temperature (curves ***1***), 100 K (curves ***2***), and at 100 K with glass filters FS6+PS11 (curves ***3***). (b) First derivatives of the DR spectra in (a) with respect to wavelength.

Figure SI2, curves ***3*** show that in the case of both iodides, the selected glass filters precluded the PL registration in the DR spectrum at 100 K up to 3.6 eV. In the case of 1D bromides, the selected glass filter/filters suppressed the PL. In the sub-absorption edge region ($h\nu < 3.6$ eV) but did not provide complete suppression of the PL in the range $h\nu > 3.7 – 3.8$ eV (curves 3 in Figure S3a and S4a). Along with this, non-suppressed PL don't create any features in the sub-absorption edge region of the absorption/reflectance spectra. Comparison of curves ***2*** and ***3*** in **Figure SI3b** and **Figure SI4b** clearly shows that the features of the absorption edge manifested at first derivatives of the DR spectra at $h\nu < 3.5$ - 3.6 eV as maxima exist independently of the PL suppression. It is essential for the present work since just these features at the perovskite's absorption edge are the main subject of the present study.

Phase transitions and thermal/photodegradation can manifest in perovskites' diffuse reflectance (DR) spectra. Phase transition was well observed in the temperature dependence of the DR spectra of $MAPbBr_3$.

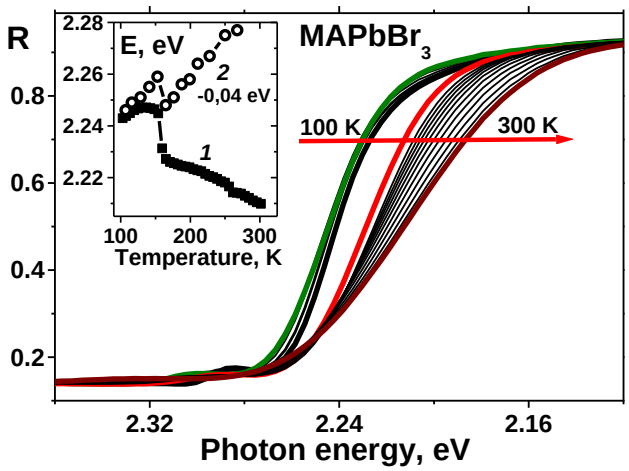

Figure S5. Temperature dependence of the DR spectra of 3D perovskite $MAPbBr_3$. The inset displays the temperature dependence of the bandgap, E_{bg} (curve ***1***), and the excitonic feature's spectral position, E_{ex}, (curve ***2*** shifted down at 0.04 eV).

Well documented in the literature, the phase transition in $MAPbBr_3$ occurs at ~150 K (at 158 K in the insert). It manifests in the DR spectra as a sharp shift of the absorption edge and corresponding sharp changes in E_{bg} and E_{ex}. As **Figure 2 A-D** in the main text shows, similar temperature behavior of the DR spectra was not observed for any of the materials studied. The temperature shift of the absorption edge in the DR spectra of all 1D perovskites is always monotonic.

The thermal decomposition (degradation) of halide iodides perovskites is well documented in the literature. Degradation (photo and dark) of iodide perovskites was extensively studied for $MAPbI_3$.[5-7] This phenomenon manifests in the absorption/DR spectra as an additional shoulder or edge at 2.4 – 2.5 eV. It was established that the final product of $MAPbI_3$ degradation was PbI_2. A single crystal of PbI_2 has a E_{bg} = 2.47 eV at 100 K.[8]

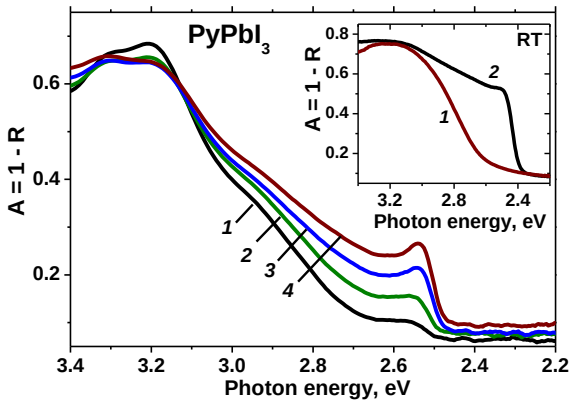

Figure SI6. The absorption spectra, A = 1 – R, of $PyPbI_3$ diluted in $BaSO_4$ (concentration = 1.56%) at 100 K: initial state (curve ***1***) and the state after exposure in cryostat vacuum at room temperature 1 day (curve ***2***), 4 days (curve ***3***), 6 days (curve ***4***). The insert shows the absorption spectra of $PyPbI_3$ diluted in $BaSO_4$ (concentration = 25%) at room temperature. Curve ***1*** – initial state, curve ***2*** – after prolonged exposure of the sample at ambient conditions under Illumination by daylight (the sample was placed near a laboratory window). Only a skinny surface layer of such a sample had yellow coloration, while XRD data for the entire sample, ~0.7 mm thick, showed no trace of PbI_2.

Such absorption bands or any additional features are not observed in the DR spectra of our samples.

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