Supporting Information

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Enhanced Stability of MAPbI₃ Perovskite Films with Zirconium Phosphate-Phosphonomethylglycine Nanosheets as Additive

Nadir Vanni, Diletta Morelli Venturi, Eros Radicchi, Giulia Quaglia, Elena Cambiotti, Loredana Latterini, Filippo De Angelis,* and Ferdinando Costantino*
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Figure S1. XRD pattern of ZPGly (black) and exfoliated ZPGly (red)

Figure S2. SEM images of PVK
Figure S3. SEM images of PVK@ZPGly

Figure S4. SEM images of MIX
Figure S5. TEM images of a) PVK, b) PVK@ZPGly, and c) MIX (bar scale is 100 nm).

Figure S6. IR spectra of PVK (black), ZPGly (pink), PVK@ZPGly (red) and MIX (green).

The IR spectrum of PVK sample (Figure XX1, black line) shows peaks in the range 600-1750 cm\(^{-1}\) attributed to N-H bending out-of-plane (695 cm\(^{-1}\)), C-N stretching (792, 1044, 1143 cm\(^{-1}\)), N-H wagging (906-959 cm\(^{-1}\)), N-H bending and stretching (1416, 1573, 1651, 1504-1550, 2137 cm\(^{-1}\)), C-H bending and stretching (1468, 2712, 2958, 3184 cm\(^{-1}\)). The O-H stretching is centred at 3489 cm\(^{-1}\) in combination with C-OH in-plane bending at 1353 cm\(^{-1}\).\(^{[1-3]}\)
IR spectrum of ZPGly (pink line) shows an intense band between 950 and 1200 cm\(^{-1}\) is attributable to the P-O stretching. The O-H stretching vibration is observed with a broad band over 3000 cm\(^{-1}\). The band at 3002 cm\(^{-1}\) is due to the C–H stretching. The band at 1739 cm\(^{-1}\) is related to the C=O stretching in a –COOH group, accompanied by the bands at 1427 (O–H bending) and 1244 cm\(^{-1}\) (C–O stretching), further evidence of the presence of protonated – COOH groups. The region below 900 cm\(^{-1}\) presents different peaks due to bending and stretching modes of Zr-O. [4]

Figure S7. XRPD patterns of a sample of perovskite degraded at 70% RH and kept at ambient humidity for 10 days.
Figure S8. VT-XRPD pattern of the trend of reflection (211) during heating to 70 degrees of a sample of PVK (a) and MIX (b)

Electrolyte I/I₃ Stability

The first appearance of the category of perovskite in the photovoltaic field was as dye in a dye-sensitized solar cell device. The overwhelming drawback was that the liquid electrolyte dissolved the perovskite in just a few minutes. Therefore, in this work we have tested the stability of the coated perovskite with the goal of recreate a more stable DSSC device using the perovskite. To perform the test, we took samples of PVK and of protected perovskite (both PVK@ZPGly and MIX) with similar thickness, and we cover them with the liquid electrolyte making sure that the samples remained covered by the liquid for at least one hour. As expected, the sample of PVK dissolved due to the electrolyte in less than one minute, making impossible even to record a XRPD pattern after the test (Figure S9).

Instead, the samples of coated perovskite did not dissolve after more than one hour in contact with the electrolyte, making also possible to record XRPD spectra before and after the test. These are basically identical, which indicates that the sample was not damage by the liquid electrolyte. (Figure S10, left)

In the case of MIX spectrum (Figure S10, right) after the contact with the electrolyte the most intense peaks of the perovskite are well preserved and increased in intensity while some
of the low intensity peaks disappeared suggesting that the perovskite underwent a
dissolution/recrystallization process leading to a preferred orientation of the basal planes

Figure S9. Images of a sample of PVK a) before and b) after the contact with liquid
electrolyte.

Figure S10. XRD spectra of a sample of PVK@ZPGly (left box) and of MIX (right box)
before and after the exposition with liquid redox-active electrolyte \( \Gamma/\Gamma_3^- \).

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