Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information for

Multiscale morphology design of hybrid halide perovskite through polymeric template

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NMR experimental details

Optimization of $MAPbI_3$ concentration

NMR characterization was firstly performed with $MAPbI_3$ to polymer weight ratio of 36:1, in the solvent mixture THF/DMF/DMSO (3.3:1:1), according with the preparation of the blend. For each mixture, the blend was constituted by 79.94 mg of $MAPbI_3$ (0.129 mmol, 184 mM) and 2.19 mg (3.13 mgmL^{-1}) of polymer. However any NMR parameter of $MAPbI_3$ did not undergo significant changes due to the presence of polymers, which could be, anyway, explained on considering that above experimental conditions correspond to very high molar ratios of $MAPbI_3$ to polymer (4000:1 in the case of $MAPbI_3$/PS mixture). In these conditions the molar fraction of bound $MAPbI_3$ is too low in comparison with free molar fractions to bring about detectable parameters changes. In addition, precipitation occurred, that introduced some lack of reproducibility in data analysis.

For these reasons, $MAPbI_3$/polymer blends were prepared and analyzed by keeping unchanged the content of polymers and decreasing the concentration of $MAPbI_3$ from 184 mM (114.20 mgmL^{-1}) to 10 mM (6.20 mgmL^{-1}). Data reported in the paper are relative to this concentration.

Diffusion coefficient

Diffusion coefficients (D) represent global size-dependent parameters and on the basis of the Stokes–Einstein equation[1] [Equation (1), k is the Boltzmann constant, η is the solvent viscosity and T is the temperature in K], can be correlated to the hydrodynamics radius (r_H).

$$D = \frac{kT}{6\pi\eta r_H}$$

(1)

By virtue of the above dependence, diffusion coefficients are extremely sensitive to variations in the apparent molecular sizes that are produced by complexation processes.

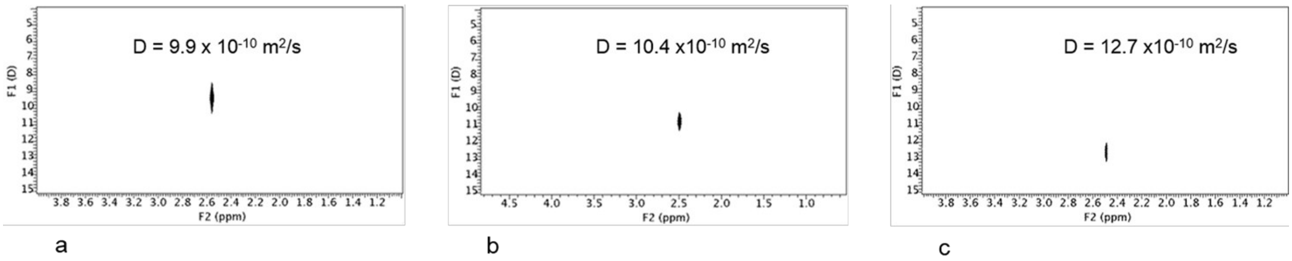

Figure S1. Expansion of DOSY maps (600 MHz, THF/DMF/DMSO 3.3:1:1, 298 K) of P3 at different concentration: 184 mM (a), 10 mM (b) and 2 mM (c).

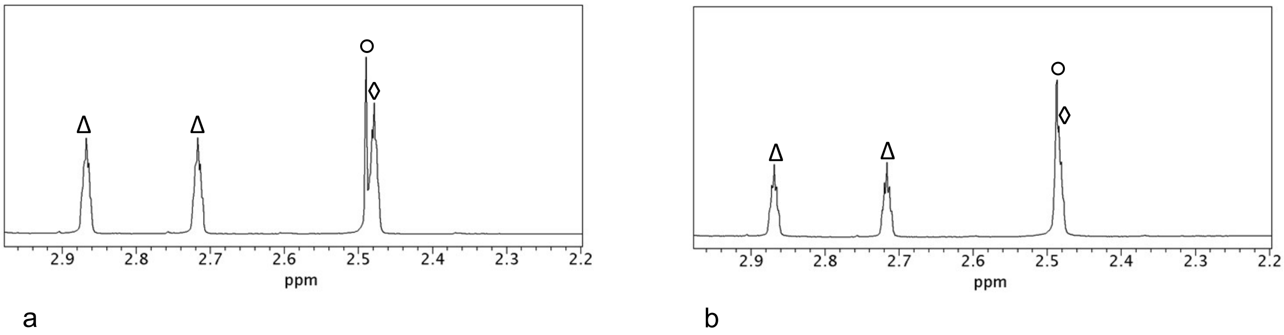

Figure S2. Expansion of ^{1}H NMR (600 MHz, THF/DMF/DMSO 3.3:1:1, 298 K) of $MAPbI_3$ (2 mM, a) and of mixture $MAPbI_3$/MEH-PPV (b, molar ratio P3/MEH-PPV 0.83:1); ◊, DMSO-d_6; ○, methyl of $MAPbI_3$; Δ, DMF-d_7.

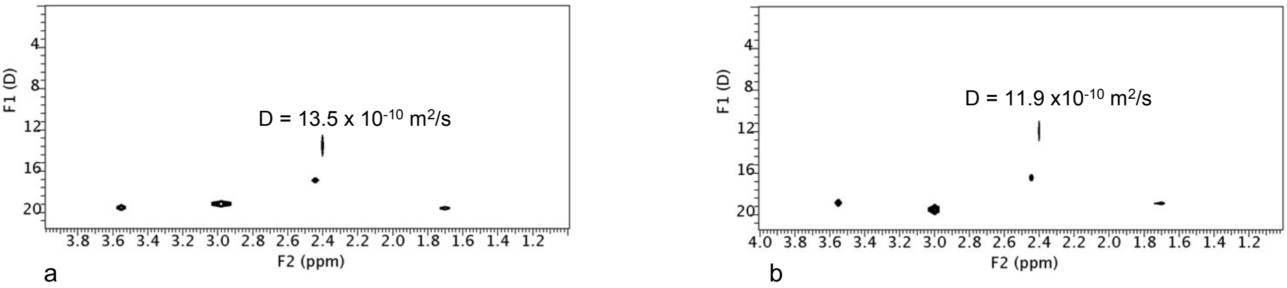

Figure S3. Expansion of DOSY maps (600 MHz, THF/DMSO 5:2, 298 K) of (a) $MAPbI_3$ (2 mM) and (b) of $MAPbI_3$ in the presence of MEH-PPV (molar ratio $MAPbI_3$/MEH-PPV 176:1).

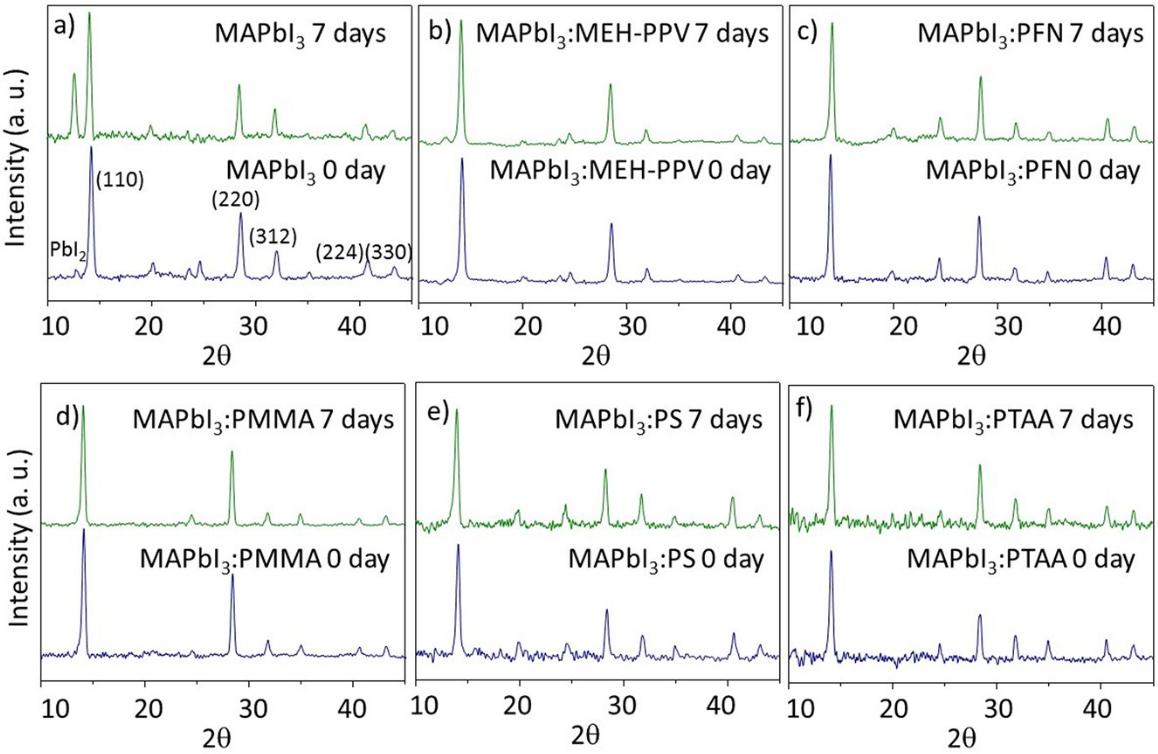

Figure S4. X-Ray diffraction pattern of (a) $MAPbI_3$ and $MAPbI_3$:polymer (b) MEH-PPV, (c) PFN, (d) PMMA, (e) PS, (f) PTAA thin films, which were exposed to ambient air.

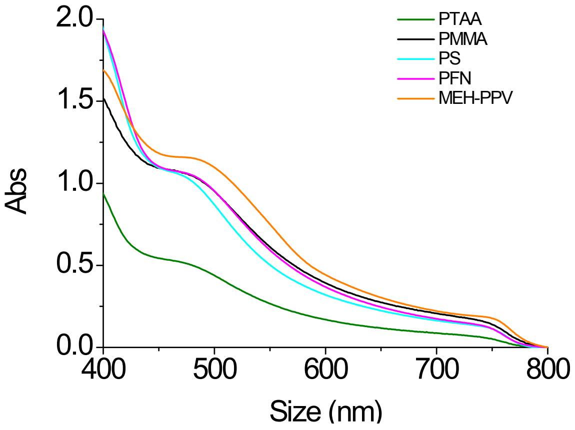

Figure S5. UV-vis spectra of MAPbI$_3$:polymer mixtures thin films.

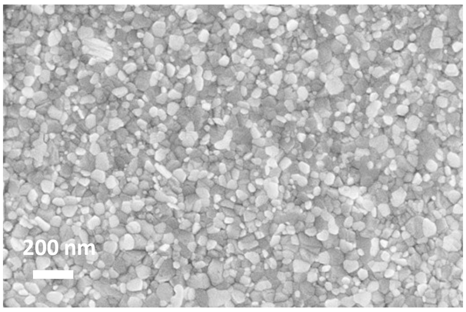

Figure S6. SEM image of MAPbI$_3$ film deposited on PEDOT:PSS.

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[1] a) Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D.; Gale, P. A.; Steed, J. W. *Supramolecular Chemistry: From Molecules to* Nanomaterials; Gale, P.; Steed, J., Eds.; Wiley and Sons: Chichester, U.K., 2012; Vol. 2, pp. 319-330. b) Morris, G. A. *Multidimensional NMR Methods for the Solution State*; Morris, G. A.; Emsley, J. W., Eds.; Wiley and Sons: Chichester, U.K., 2010; pp. 515-532. c) Morris, G. A. *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley and Sons: Chichester, U.K., 2002; Vol. 9, pp. 35–44.