

[Supporting Information]

Polymer Macroligands Passivate Halide Perovskite Surfaces

Mykyta Dementyev,^a Lindsay F. Jones,^a Michael C. Brennan,^{c,d} Tod A. Grusenmeyer,^c Seth D.

Waugaman,^c Robert T. Mathers,^c Robert J. Hickey^{a,b*}

^aMaterials Science and Engineering, The Pennsylvania State University, University Park, PA,
16802, USA

^bMaterials Research Institute, The Pennsylvania State University, University Park, PA, 16802,
USA

^cAir Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air
Force Base, Dayton, Ohio 45433, USA.

^dAzimuth Corporation, 2079 Presidential Dr. #200, Fairborn, OH 45342, USA.

^eChemistry, The Pennsylvania State University, New Kensington, PA, 15068, USA

*Corresponding Author, Email: rjh64@psu.edu

% Yield Study

To investigate the amount of the polymer in the resulting composite material, we performed a yield study. The final experimental weight of the composite material was compared to the theoretical yield of the perovskite/polymer sample after precipitation of the method outlined in this manuscript.

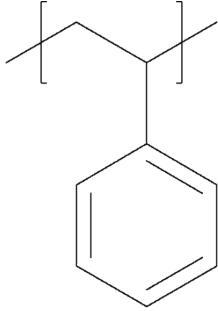
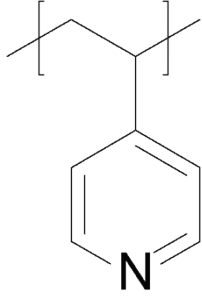
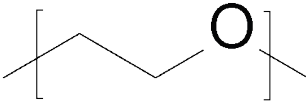
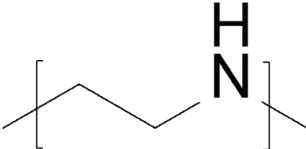
Table S1. Percent yields of polymer/perovskite hybrid materials

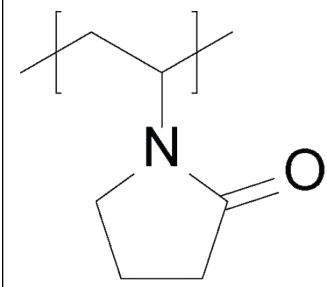
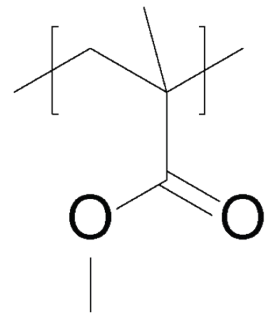
Polymer/Perovskite System	Perovskite + Polymer (%)	Polymer Yield (%)
PEI ($M_w = 100,000$ g/mol) / MAPbBr ₃	88.8 ± 0.7	66.0 ± 2.8
PEO / MAPbBr ₃	90.5	72.0
P4VP / MAPbBr ₃	97.8	~100
PS / MAPbBr ₃	71.8	~0
PMMA / MAPbBr ₃	71.6	~0
PVP / MAPbBr ₃	~100	~100
MAPbBr ₃	96.6	N/A

Differential scanning calorimetry characterization

Differential scanning calorimetry (DSC) measurements (TA instruments Q2000) were used to determine the glass transition temperature (T_g), melting (T_m), and crystallization (T_c) temperatures of polymer materials used in this work. To prepare samples, the polymer was added to a DSC pan, made by DSC Consumables, and hermetically sealed. A reference (empty) pan was also prepared. Polymers were heated first at 20 °C/min to 150 °C, cooled at 10 °C/min to 30 °C (except PEO, which was cooled to 0 °C), and heated again at 10 °C/min to 150 °C. After each step, the sample was held for 10 min at the target temperature.

Table S2. Molecular characteristics and structure of polymer materials used in OIP materials

Polymer	Molecular Weight (g/mol)	T_g (°C)	Repeat Unit
PS	4,000 ^a	53 °C	
P4VP	60,000 ^b	157 °C	
PEO	100,000 ^b	$T_c = 37$ °C ^c	
PEI	100,000 ^b	60 °C	

PVP	10,000 ^b	90 °C	
PMMA	11,600 ^b	90 °C	

^a Number-average molecular weight (M_n) was determined by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as the mobile phase. The SEC trace is plotted in **Figure S1**.

^b Reported molecular weights are from Sigma-Aldrich.

^c Only the melting and crystallization temperatures (T_m and T_c , respectively) were measured for PEO. The expected T_g for PEO is approximately -70 °C.

TRPL Fittings

Biexponential decay fitting model was used with the formula

$$y = y_0 + A_1 e^{-\frac{(x-x_0)}{t_1}} + A_2 e^{-\frac{(x-x_0)}{t_2}} \quad (1),$$

where y_0 is the fitting parameter, A_1 and A_2 are weighted parameters, x_0 is the offset parameter, while t_1 and t_2 are decay parameters.

Table S3. Fitted coefficients from the biexponential fit to the TRPL data

	x_0	y_0	A_1	t_1 (ns)	A_2	t_2 (ns)
PEI	67	0.09	0.95	19	0.24	212
PVP	78	0.08	0.48	39	0.43	176
P4VP	83	0.01	0.46	82	0.49	495

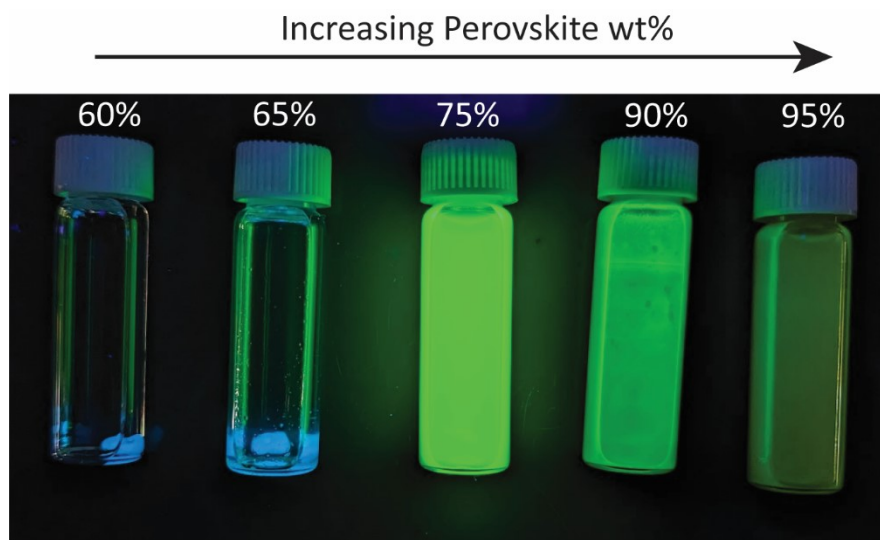


Figure S1. Photoluminescence image of PEI samples under a UV lamp at 365 nm prepared with varying weight percent of MAPbBr₃. The values stated above each vial indicate the perovskite weight percent.

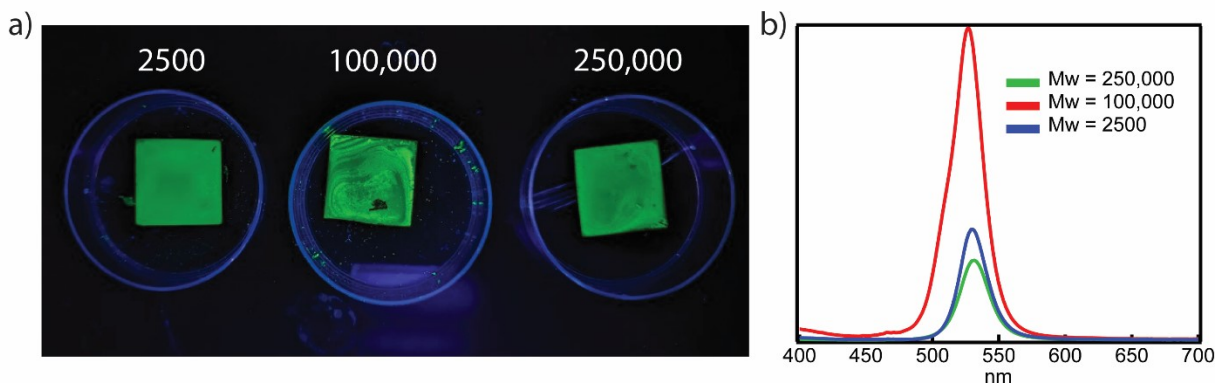


Figure S2. Emission fluorescence analysis of composite perovskite films prepared PEI over a range of molecular weights from 2,500 g/mol to 250,000 g/mol. a) fluorescence of composite films under 365 nm UV lamp excitation and b) emission fluorescence scan from 400 nm to 700 nm with 365 nm excitation.

Sample preparation for equivalent molar fraction of nitrogen containing functional groups

Samples were prepared by dissolving perovskite precursors (MABr: 0.2501 mmol / 0.0280 g; PbBr₂: 0.2507 mmol 0.0920 g) and polymers with normalized number of nitrogen functional groups (PEI: 0.3599 mmol / 0.0155 g; P4VP: 0.3599 mmol / 0.0378 g; PVP: 0.3599 mmol / 0.0400 g), resulting in a 0.59 mole fraction of N to PbBr₂. The molar mass of the polymer repeat unit was used to calculate the moles of nitrogen.

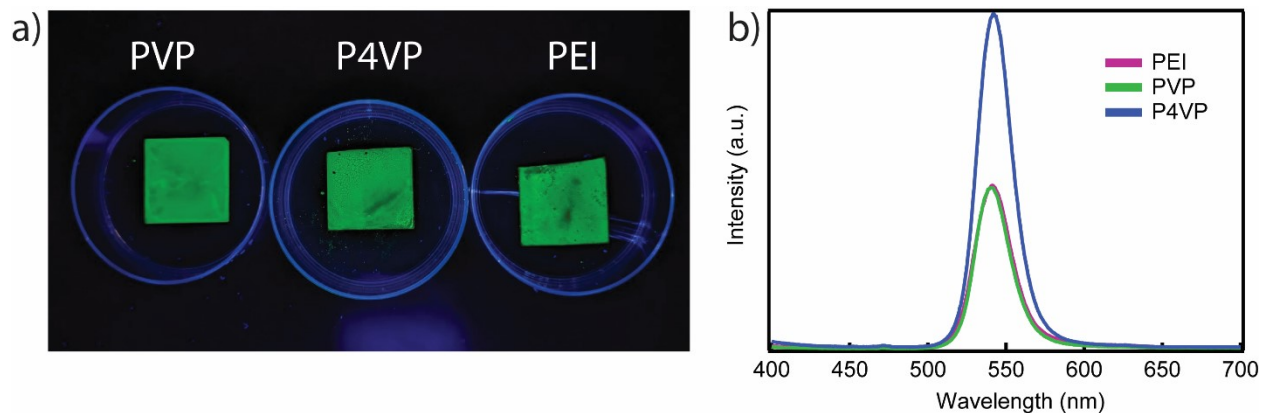


Figure S3. Emission fluorescence analysis of composite perovskite films prepared with PEI, P4VP, and PEI using a 0.59 mole fraction of N to PbBr_2 . a) Images of fluorescent composite films exposed to a 365 nm UV lamp and b) emission fluorescence spectra of the samples using 365 nm excitation.

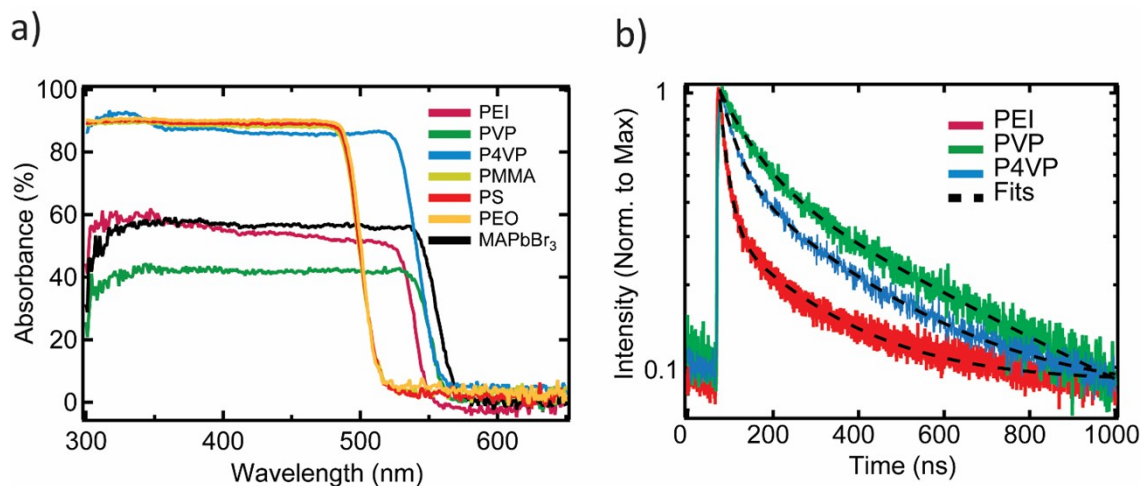


Figure S4. a) Absorbance of composite films prepared with PEI, PVP, P4VP, PMMA, PS, and PEO compared to the absorbance of the neat perovskite sample. b) Time-resolved PL study of composite samples prepared with nitrogen-containing polymers PEI, PVP, and P4VP. Dashed lines represent biexponential fits for TRPL data. Fit parameters are given in **Table S3**.

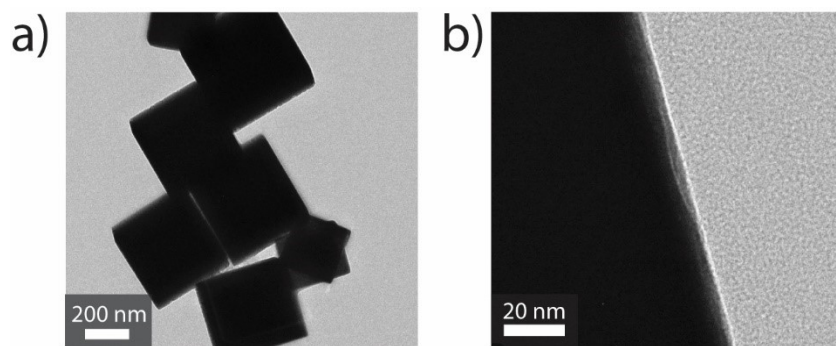


Figure S5. TEM images of synthesized polymer/perovskite materials. TEM images of neat MAPbBr₃ film. Samples were prepared by drop casting the precipitate solution on TEM grids and vacuum drying overnight. a) shows TEM image of neat perovskite at 200 nm resolution and b) shows TEM image of neat perovskite at 20 nm resolution.

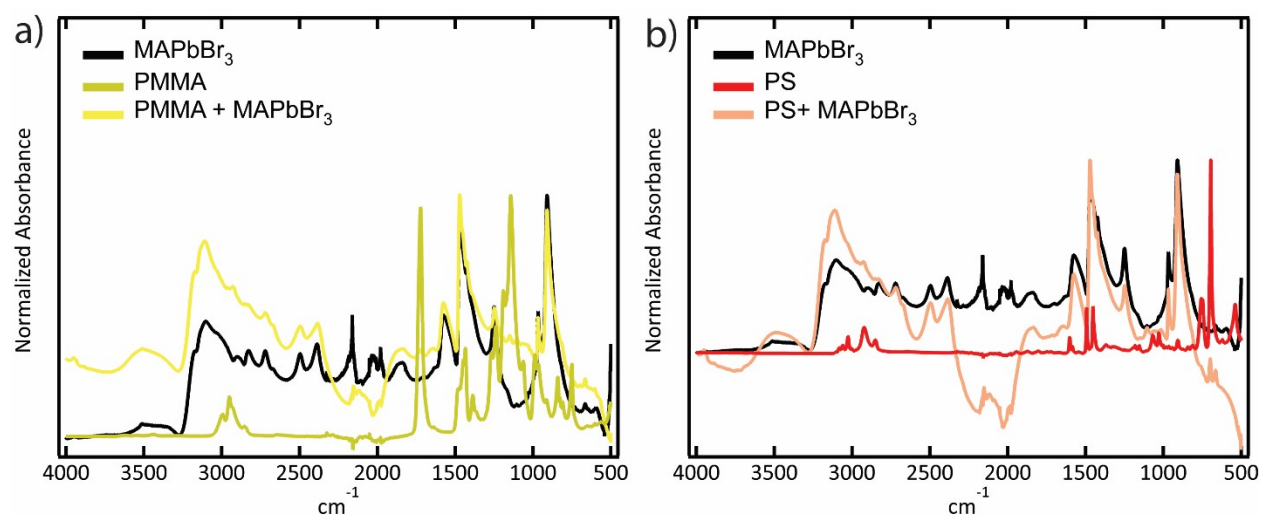


Figure S6. FTIR spectra of composite materials and individual perovskite and polymer components. Spectra of neat MAPbBr₃ samples compared to FTIR spectra of neat polymers PMMA a) and PS b), and the corresponding perovskite/polymer composite samples.

Size exclusion chromatography

The molecular weight of the PS used in this work was characterized by the size exclusion chromatography (SEC) instrument with THF as a mobile phase.

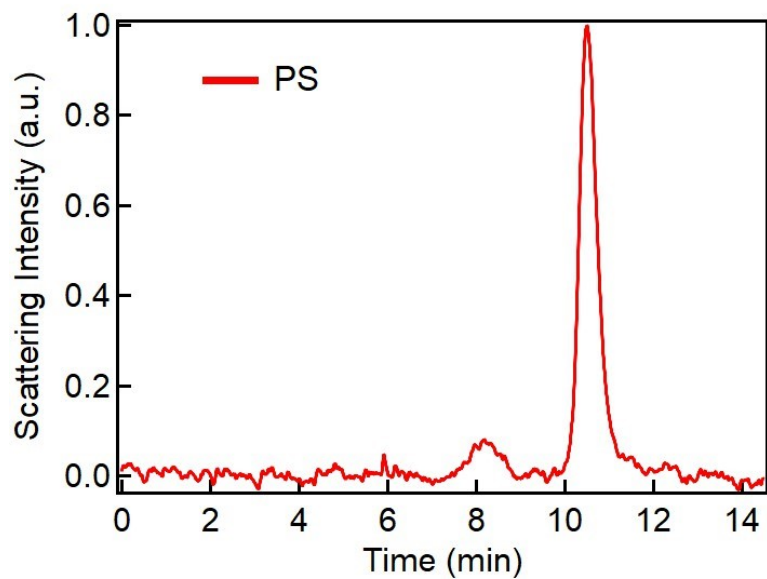


Figure S7. Size exclusion chromatography of synthesized PS via RAFT polymerization.

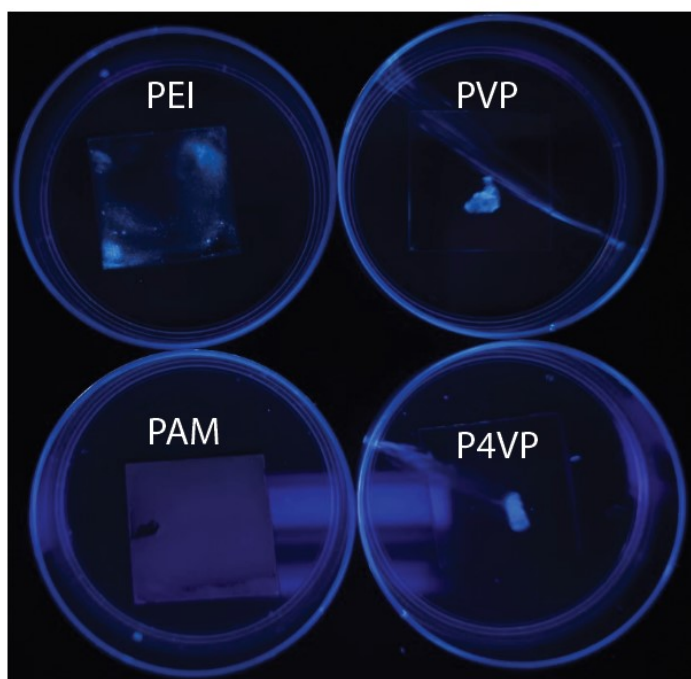


Figure S8. UV photographs of neat polymer films on glass slides prepared identically to the composite perovskite/polymer films.