SUPPORTING INFORMATION

Reducing hole transporter use and increasing perovskite solar cell stability with dual-role polystyrene microgel particles

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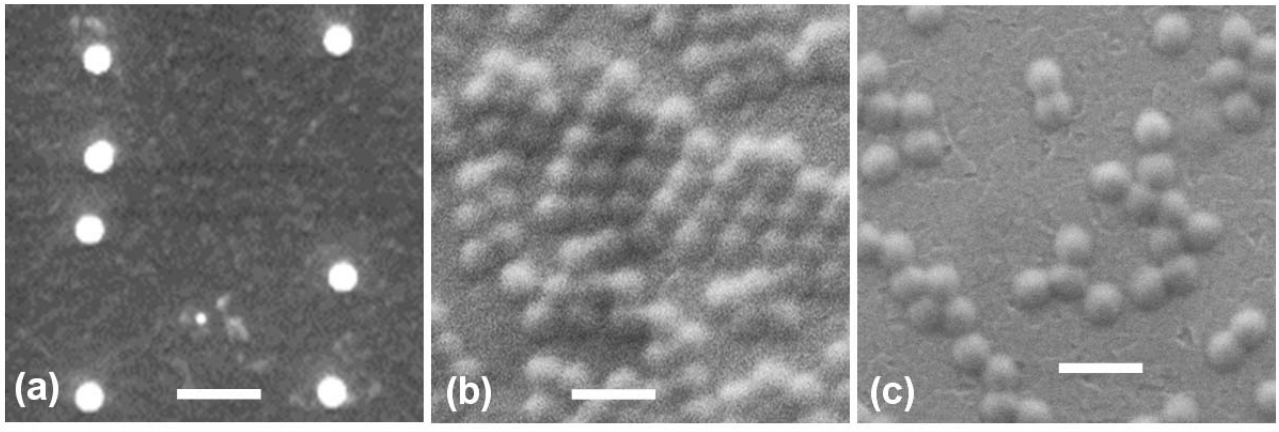
SUPPLEMENTARY DISCUSSION AND FIGURES

Microgel characterisation

The microgel (MG) particles were prepared using surfactant-free emulsion polymerisation in water which is a well-known method for preparing sub-micrometer sized polymer particles[1]. Because water is a poor solvent for PS the particles were prepared in their non-swollen (latex) form. The number-average diameter of the particles deposited from water as determined by SEM (d_{SEM}) was 280 nm (Fig. S1). The particles were freeze-dried from water and re-dispersed in toluene or chlorobenzene (CBZ). (Toluene was the solvent used for the P3HT-based films; whereas, CBZ was used for the PTAA- and Spiro-based films - See Fig. 1.) The d_{SEM} value increased slightly to 300 nm for particles deposited from toluene. The d_{SEM} value for MGs deposited from CBZ was 514 nm.



Dispersant	d_{SEM} (CV) / nm[a]	d_z / nm[b]
Water	280 (5.7)	281
Toluene	300 (6.7)	529
CBZ	514 (1.2)	712

[a] CV is the coefficient of variation.
[b] z-average diameter.

Fig. S1 Representative SEM images are shown for PS MGs deposited onto glass from (a) water, (b) toluene and (c) CBZ. The scale bars in (a) to (c) represent 1 μm. (d) DLS data for PS MG particles dispersed in water, toluene and CBZ. Particle size data obtained from the SEM and DLS data are shown in the table.

DLS data for the particles dispersed in water, toluene and CBZ are shown in Fig. S1d and the table. The values for the z-average diameter (d_z) for the MGs dispersed in water and toluene were 281 and 529 nm, respectively. The d_z value for the particles dispersed in CBZ was 712 nm. The latter values

are larger than the respective d_{SEM} values because the particles contracted upon drying. From the d_z values the particle volume swelling ratio ($Q_p = (d_z/d_{z(water)})^3$) was calculated as ~ 6.7 and 16.3, respectively, for the MGs dispersed in toluene and CBZ. Clearly, the particles swelled strongly in these two solvents. This trend for Q_p is expected because the polymer-solvent interaction parameter for polystyrene in CBZ is lower than that for toluene[2].

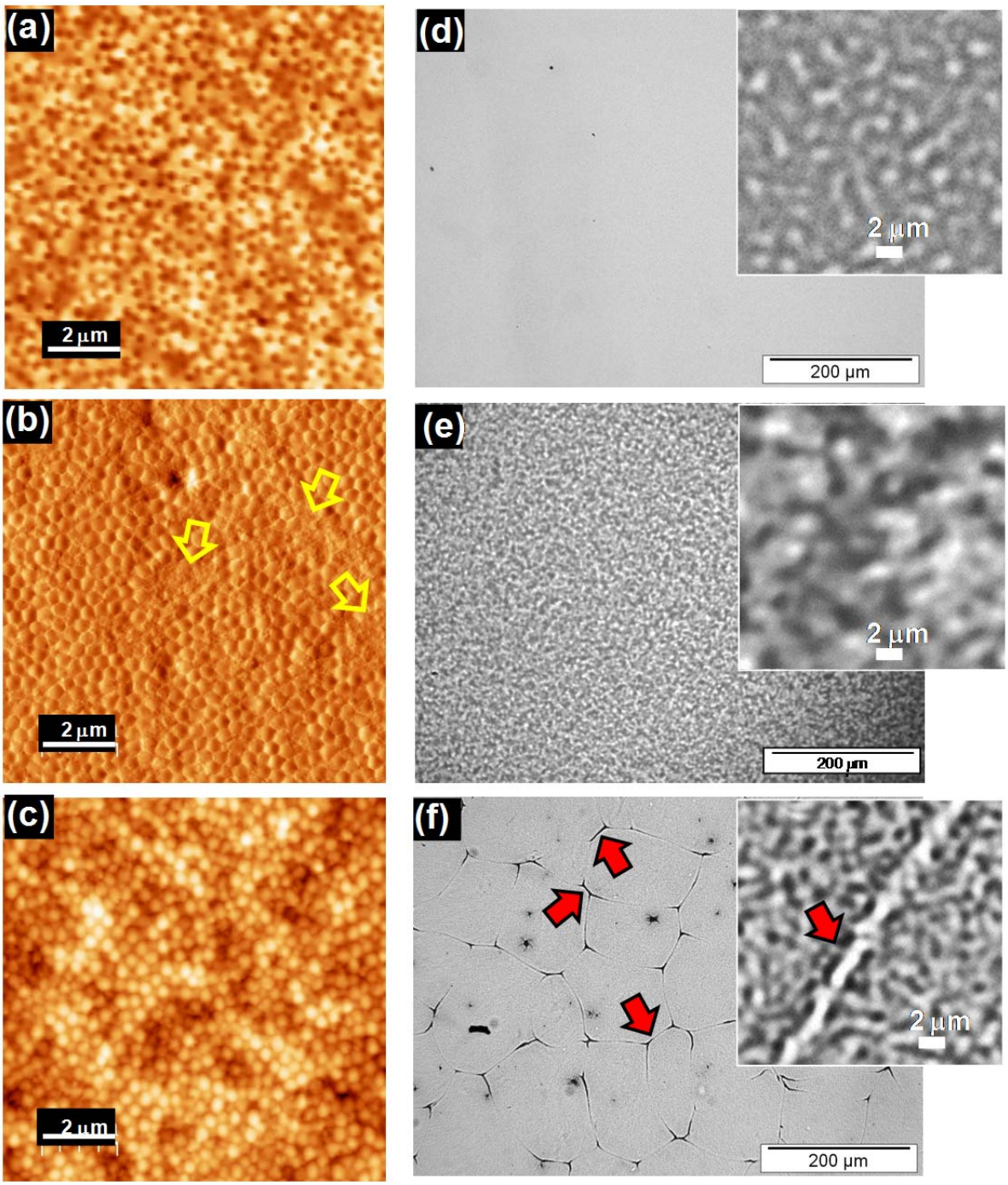


Fig. S2 Lower magnification AFM images (left hand column) and larger area optical micrographs (right hand column) for PTAA-MG (a and d), P3HT-MG (b and e) and Spiro-MG (c and f) composite films. The yellow arrows in (b) highlight P3HT-rich regions. The red arrows in (f) highlight micro-cracks.

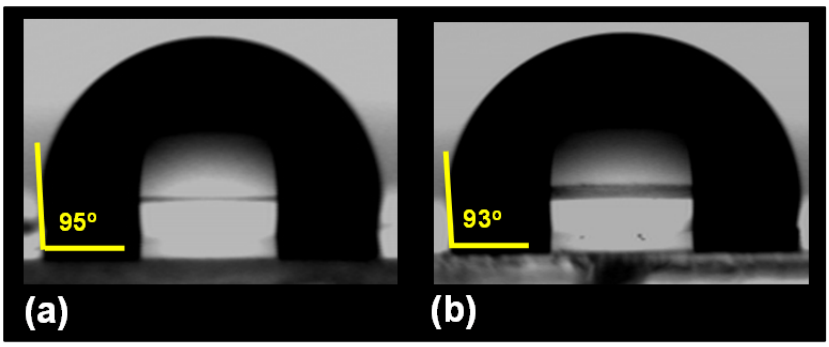


Fig. S3 Contact angle measurements for water on (a) P3HT-MG and (b) P3HT films, respectively.

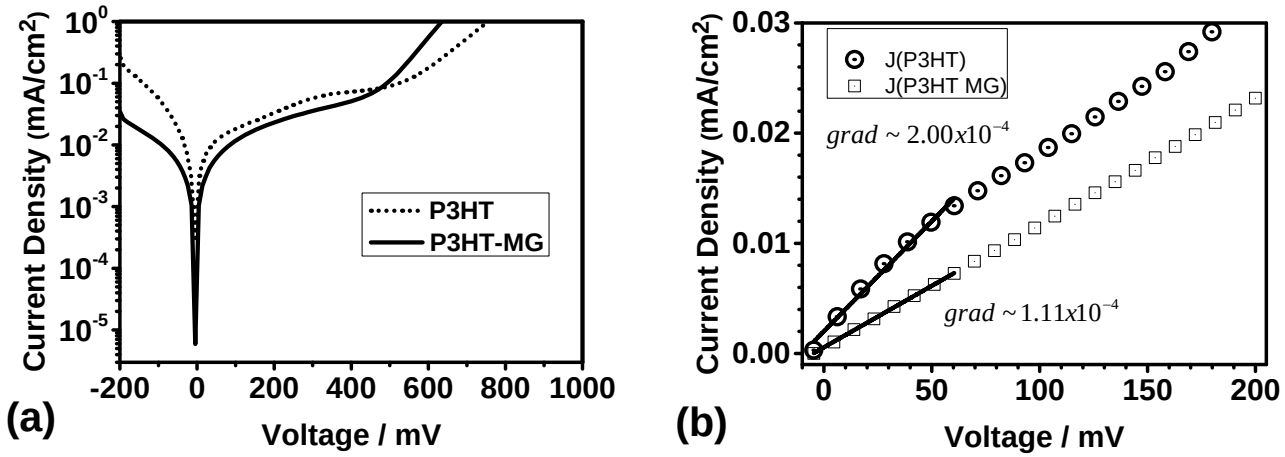


Fig. S4. (a) Dark current density – voltage curves for PSCs with HTMs of P3HT or P3HT-MG. (b) Data re-plotted from (a) to enable determination of the shunt resistances. The reciprocal of the gradients for the PSCs with P3HT and P3HT-MG for these devices gave calculated shunt resistances of 5,000 and 9,000 Ω cm^2, respectively.

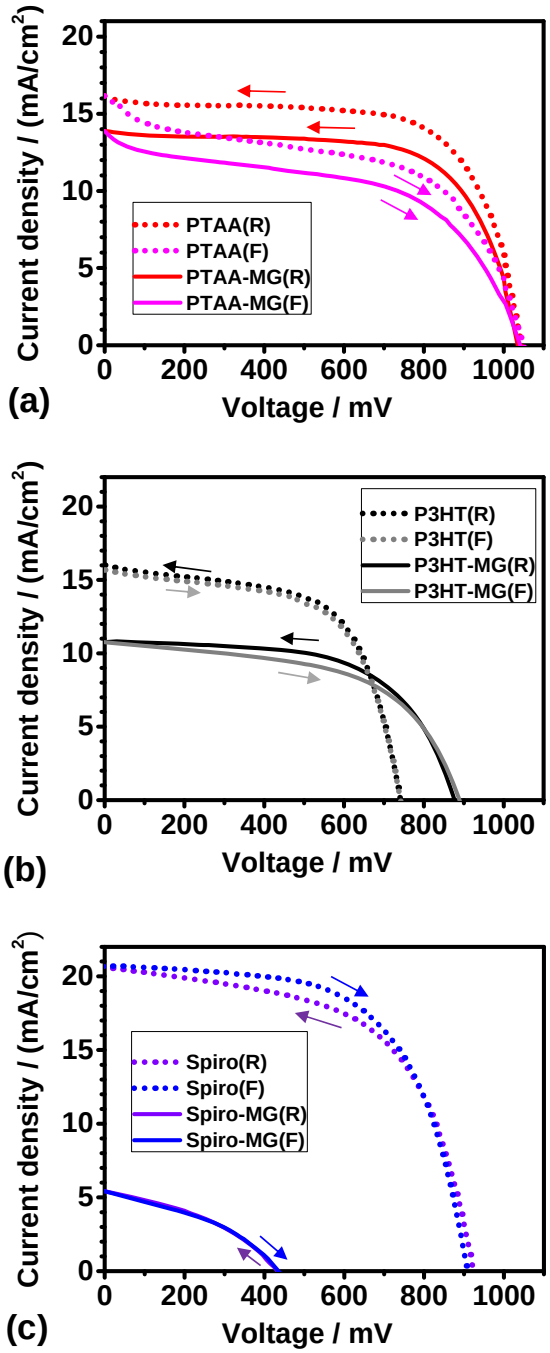


Fig. S5. J-V curves for devices from Fig. 3(a) - (c) showing forward and reverse scans.

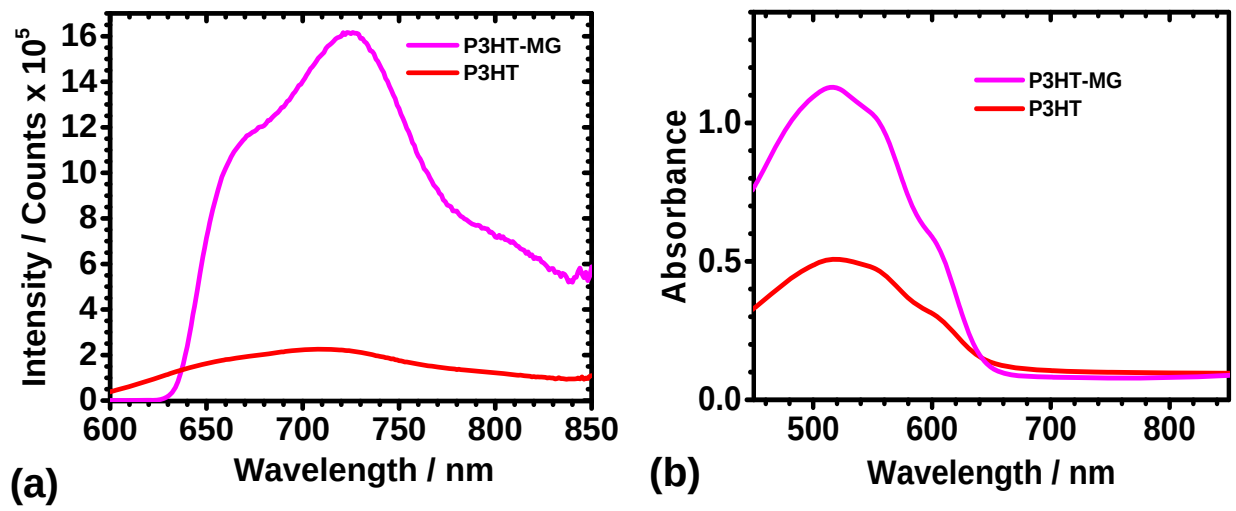


Fig. S6. (a) PL spectra and (b) UV-visible spectra for P3HT and P3HT-MG films on glass. The excitation wavelength for the PL spectra used was 480 nm. The PTAA and PTAA-MG films did not give significant UV-visible or PL spectra over the wavelength ranges shown here.

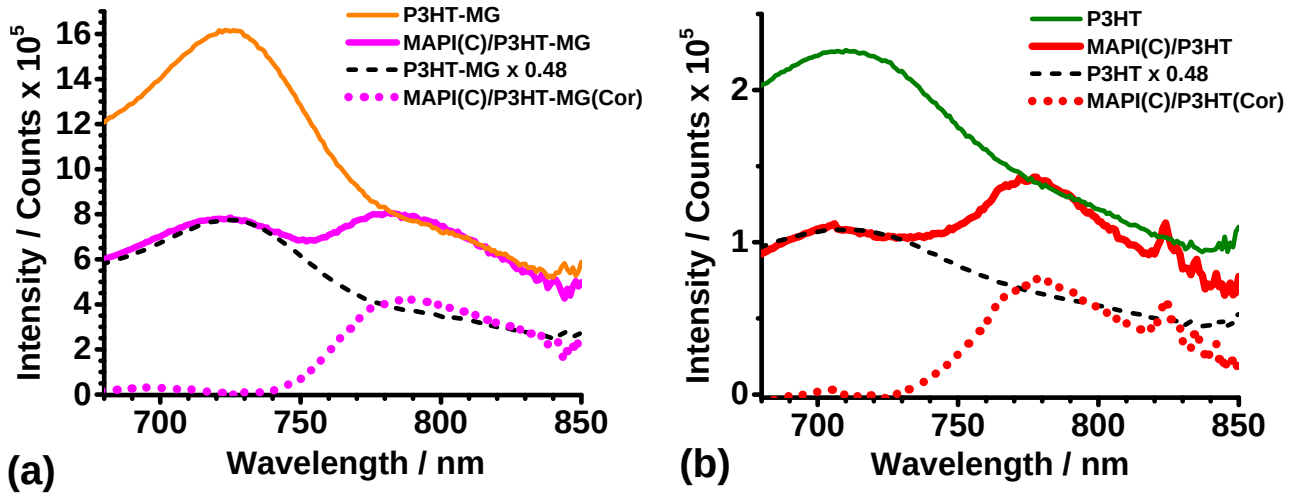


Fig. S7. Measured and corrected PL spectra for (a) films containing P3HT-MG and (b) films containing P3HT. The spectra for P3HT-MG and P3HT were multiplied by 0.48 which gave good fits to the P3HT parts of the MAPI(C)/P3HT or MAPI(C)/P3HT-MG spectra (black dashed lines). The reduced spectra were subtracted from the spectra for MAPI(C)/P3HT or MAPI(C)/P3HT-MG spectra, respectively, to provide the corrected spectra (thick dotted lines).

Achieving uniform microgel films using spin-coating

As a preliminary study to determine the MG concentration required to form uniform coatings, MG particles dispersed in toluene were spin-coated onto glass. The coverage was estimated from optical micrographs (Fig. S8a - e). Gaps between deposited islands of particles vanished and full coverage for the films occurred at a MG concentration (C_{MG}) of 3.0 %. The AFM image (Fig. S8f) shows the films consisted of overlapping MGs. The variation of %Coverage with C_{MG} determined from optical the microscopy data is shown in Fig. S8g.

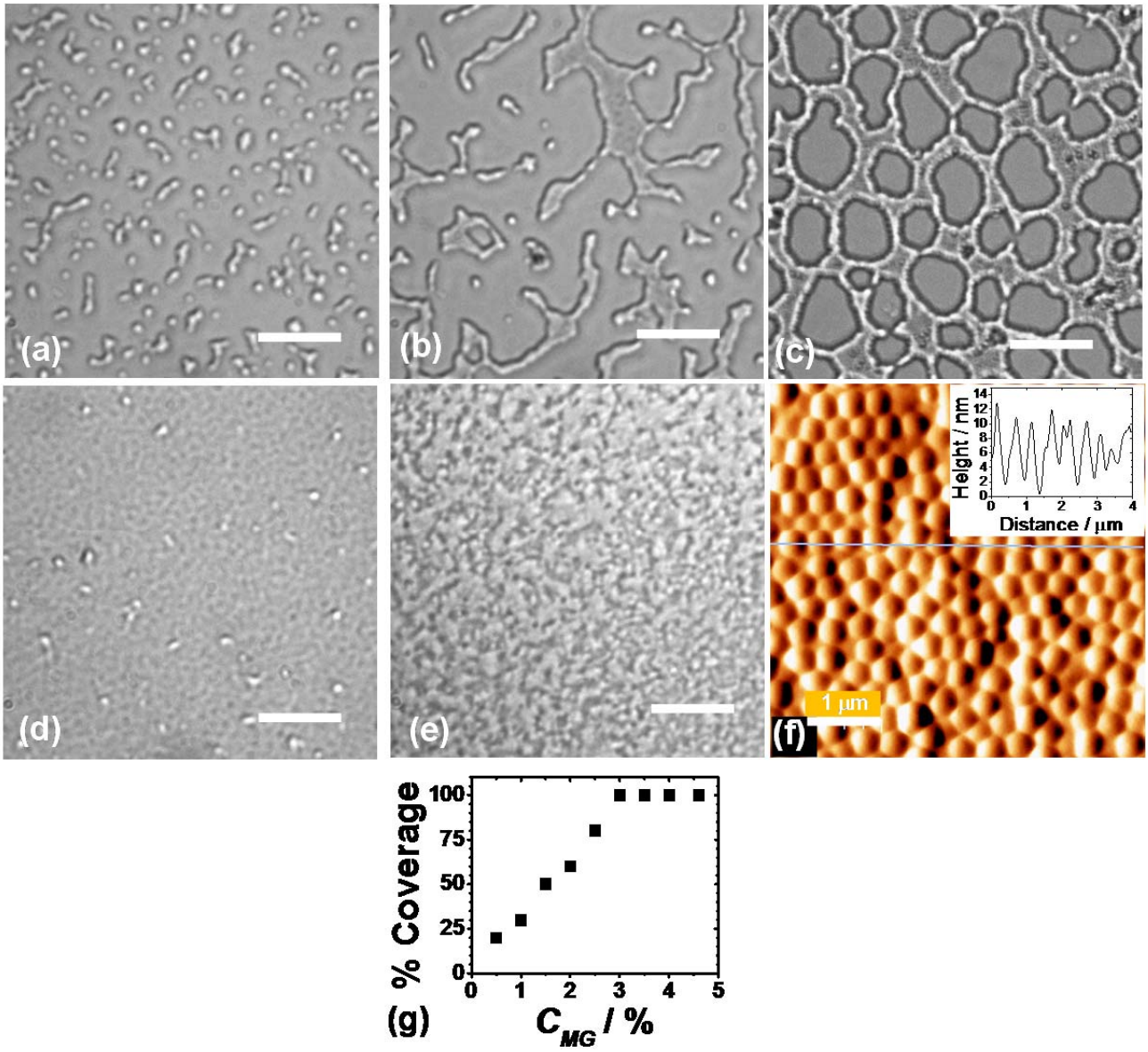


Fig. S8. MG films deposited from toluene dispersions onto glass using concentrations of 0.5% (a), 1.5% (b), 2.0% (c), 3.0% (d) and 4.6% (e and f). Optical micrographs are show in (a) to (e). A tapping mode AFM image and line profile are shown in (f). The scale bars for the optical micrographs correspond to 20 µm. (g) Variation of surface coverage with MG concentration.

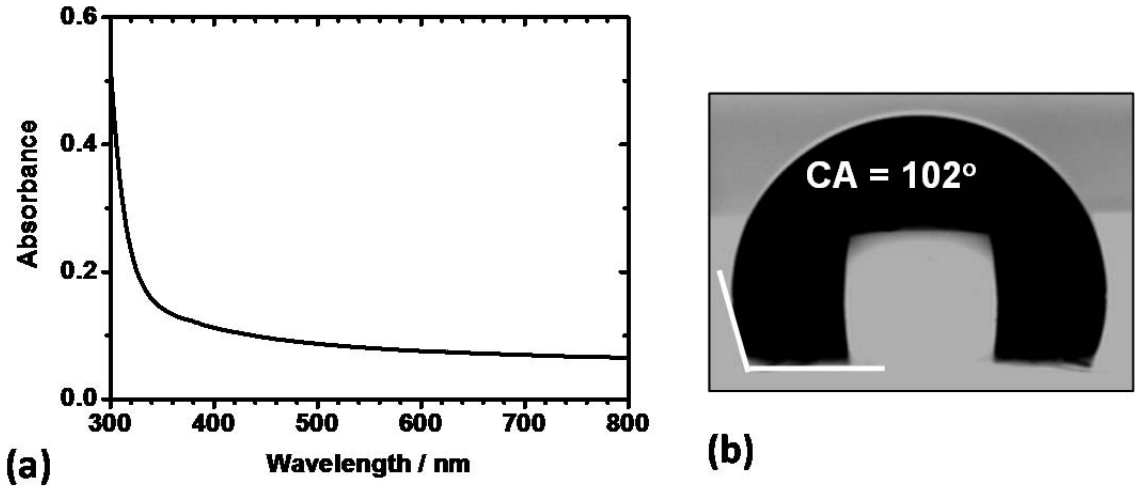


Fig. S9. (a) UV-visible spectrum of a MG film deposited on glass. (b) Contact angle measurement for a MG film deposited on ITO/bl-TiO_2 surface. The C_{MG} value was 4.6%.

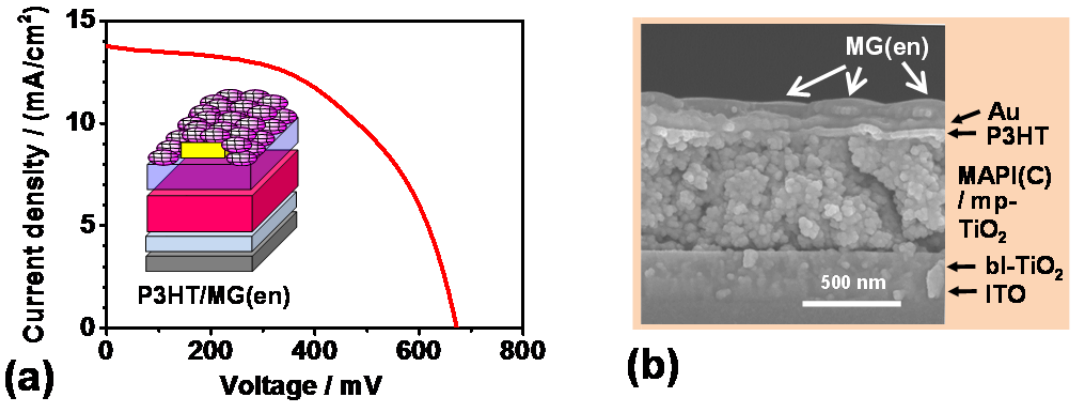


Fig. S10. (a) J-V curve and schematic for a PSC encapsulated by a MG film. (b) Cross-sectional SEM for the device from (a). The arrows in (b) highlight flattened MG particles.

Table S1. PSC performance data.

Device HTM	J_{sc} **(mA/cm^{-2})**	V_{oc} **(mV)**	**FF (%)**	**PCE (%)**
PTAA-MG	13.73 ± 0.28	960 ± 34	66.7 ± 2.0	8.79 ± 0.46
PTAA	17.08 ± 0.46	988 ± 51	66.6 ± 1.6	11.23 ± 0.51
P3HT-MG	10.93 ± 0.56	872 ± 15	55.8 ± 3.9	5.31 ± 0.44
P3HT	14.66 ± 0.62	706 ± 21	64.0 ± 3.8	6.64 ± 0.65
Spiro-MG	4.00 ± 1.50	416 ± 11	38.3 ± 1.8	0.60 ± 0.12
Spiro	21.40 ± 1.20	875 ± 18	46.1 ± 2.0	8.62 ± 0.34
P3HT/MG(en)	13.45 ± 0.48	675 ± 30	55.7 ± 3.0	5.06 ± 0.45

References

1. B.R.Saunders, and B.Vincent. *Adv. Coll. Interf. Sci.* 1999, **80**, 25.
2. L. A. Errede. *J. Appl. Polym. Sci.* 1992, **45**, 619-631.