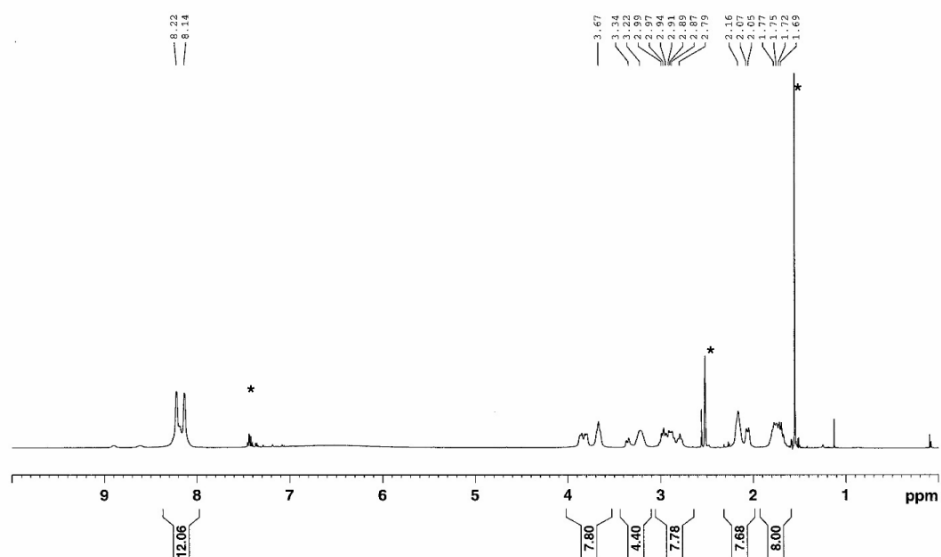
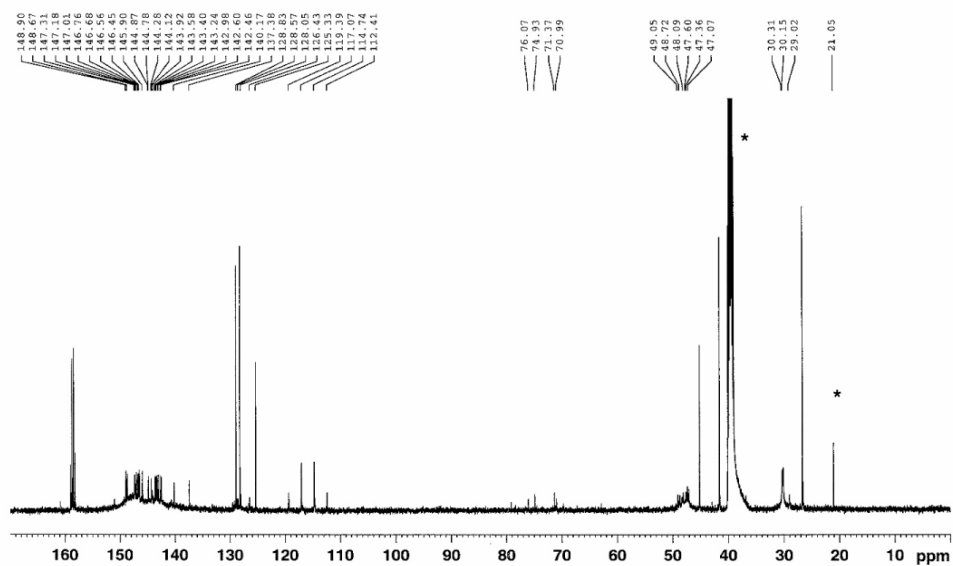


# Controlling Film Morphology in Conjugated Polymer:Fullerene Blends with Surface Patterning

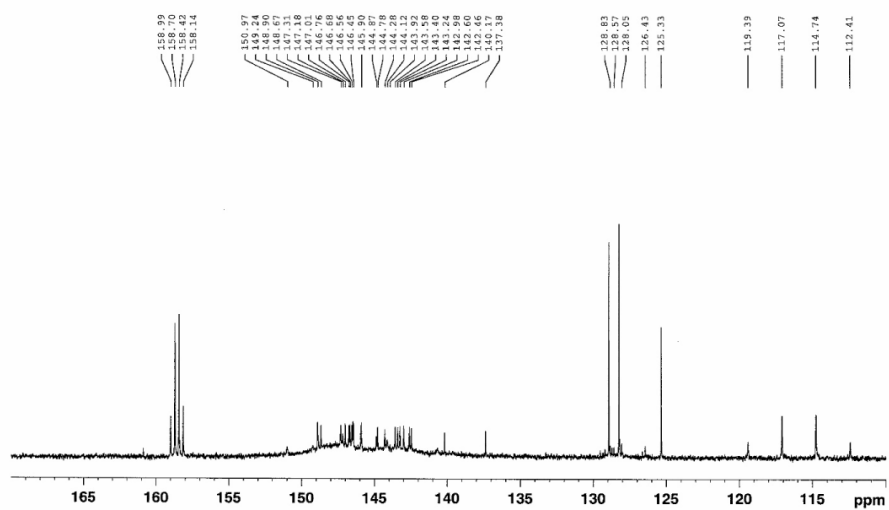
Lee Y. Park,<sup>\*, ‡</sup> Andrea M. Munro<sup>§</sup> David S. Ginger<sup>\*, §</sup>



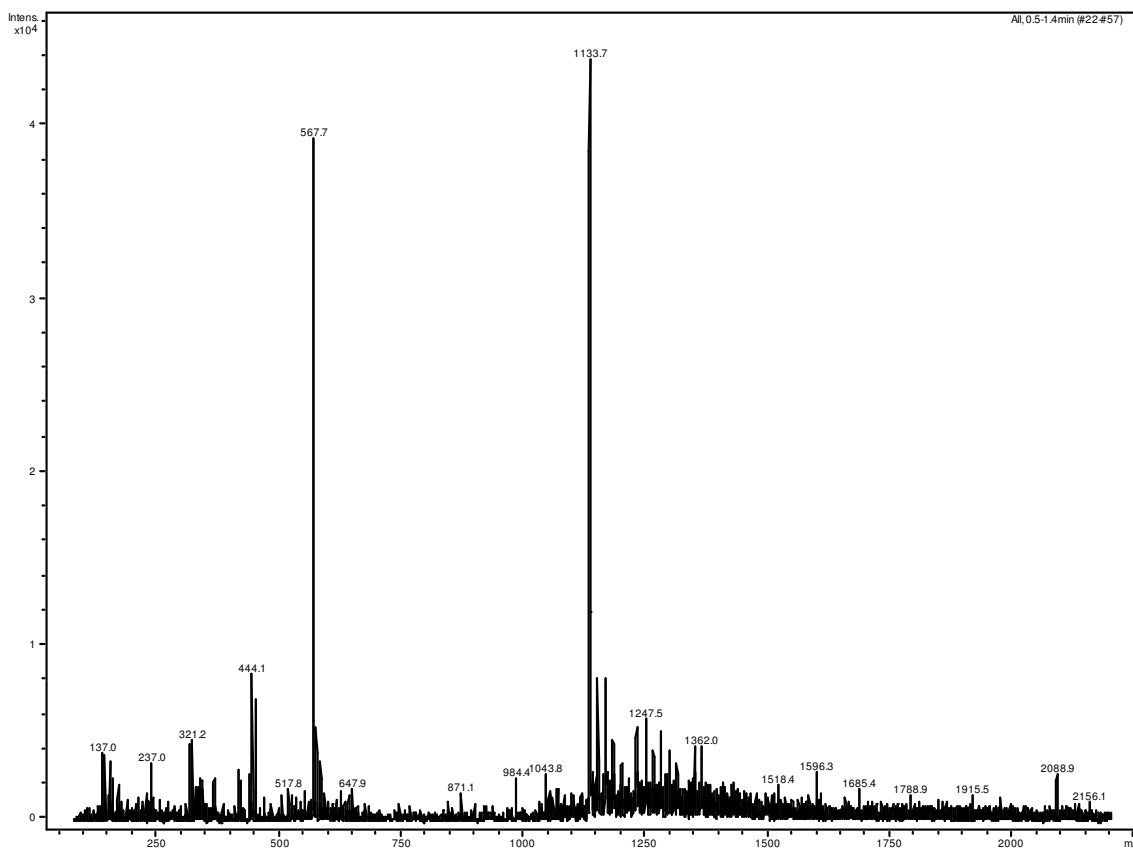
**Figure S1**  $^1\text{H}$  NMR ( $\text{d}_6\text{-DMSO}$ , 500 MHz) of **2** (collected on a Bruker 500 MHz Avance Spectrometer.) Residual solvent signals are marked with an asterisk.



**Figure S2**  $^{13}\text{C}$  NMR ( $\text{d}_6\text{-DMSO}$ , 500 MHz) of **2** (collected on a Bruker 500 MHz Avance Spectrometer.) Residual solvent signals are marked with an asterisk.



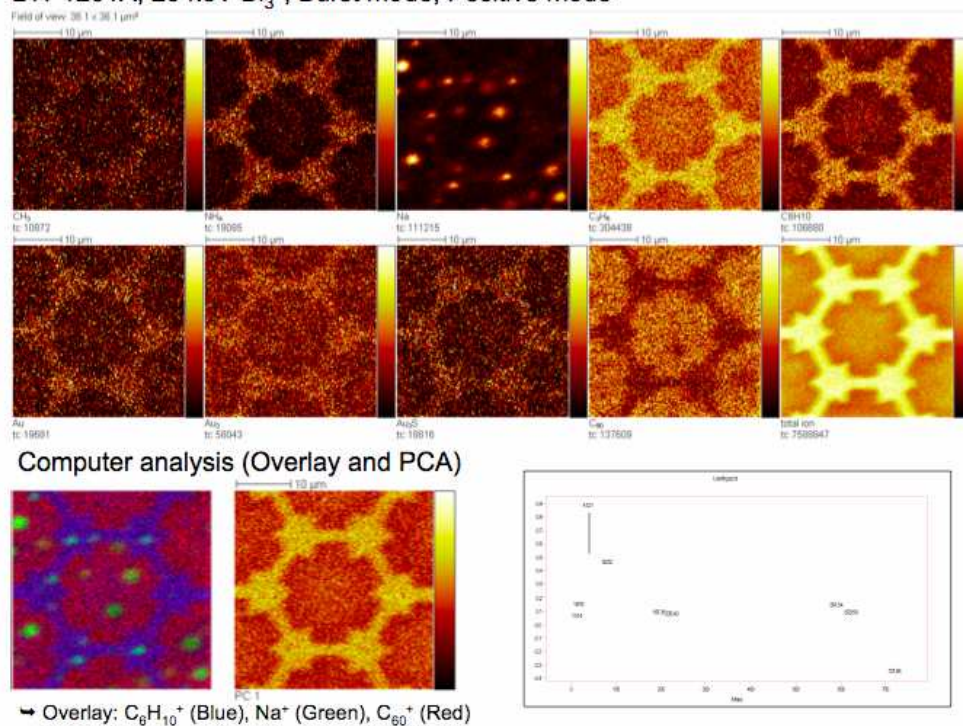
**Figure S3**  $^{13}\text{C}$  NMR ( $\text{d}_6\text{-DMSO}$ , 500 MHz) of **2**, expanded.



**Figure S4** ESI-MS of **2** obtained by direct infusion of the sample (from a solution in a mixture of DMSO and acetonitrile) on a Bruker Esquire LC ion trap mass spectrometer.

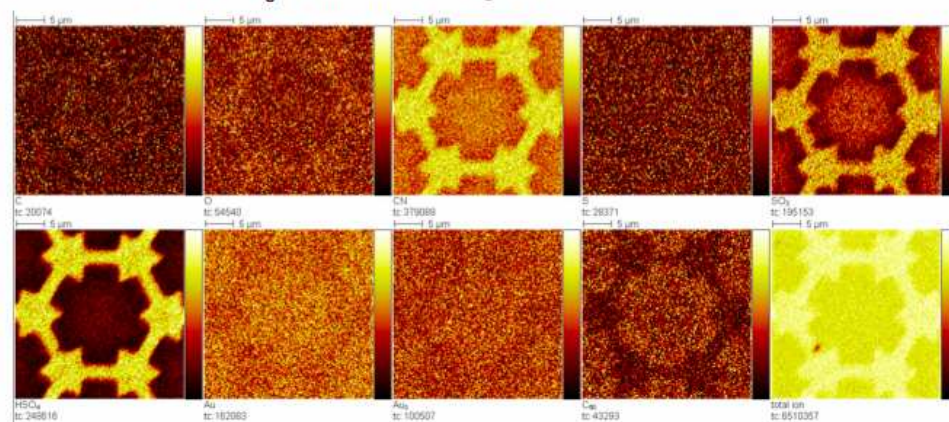


LYP1251A, 25 keV Bi<sub>3</sub><sup>+</sup>, Burst mode, Positive mode

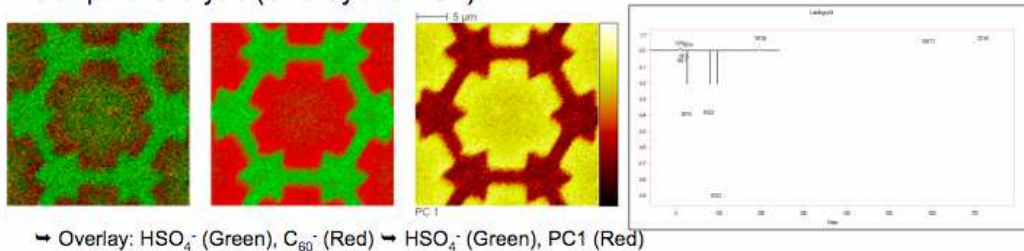


**Figure S6** ToF-SIMS maps for Au surface patterned with fullerene as illustrated in Figure 2, backfilled with HSpyr

LYP1251A, 25 keV Bi<sub>3</sub><sup>+</sup>, Burst mode, Negative mode



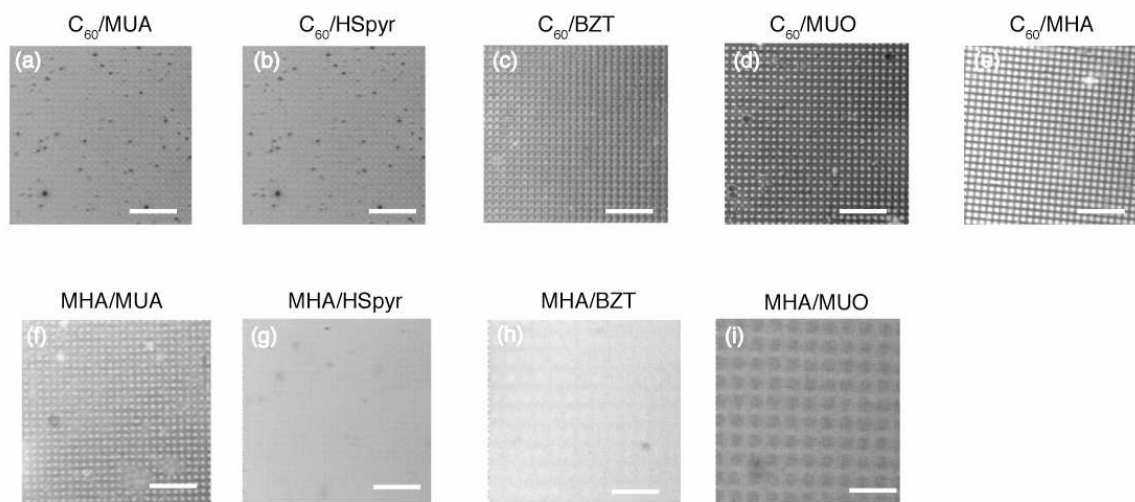
Computer analysis (Overlay and PCA)



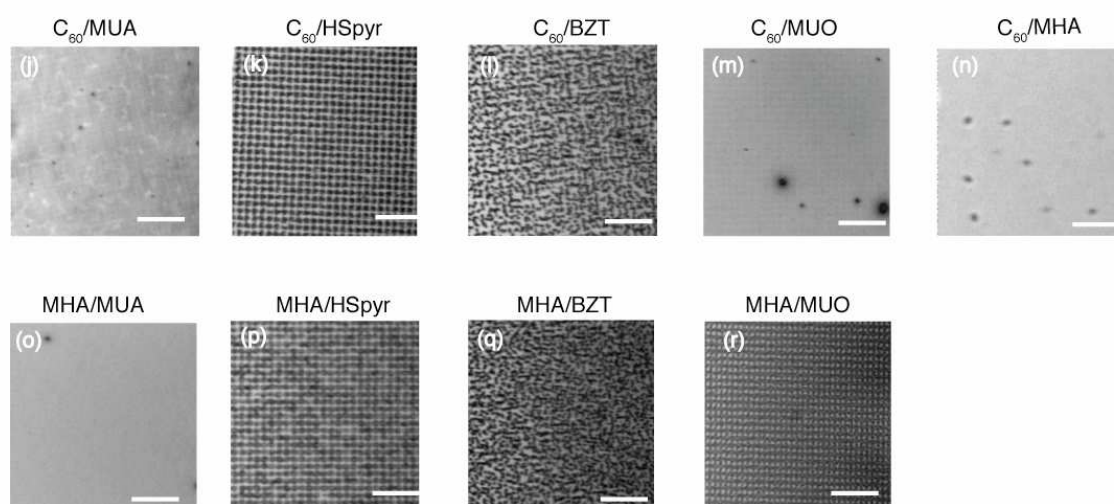
**Figure S7** ToF-SIMS maps for Au surface patterned with fullerene as illustrated in Figure 2, backfilled with HSpyr



# MDMO-PPV:PCBM



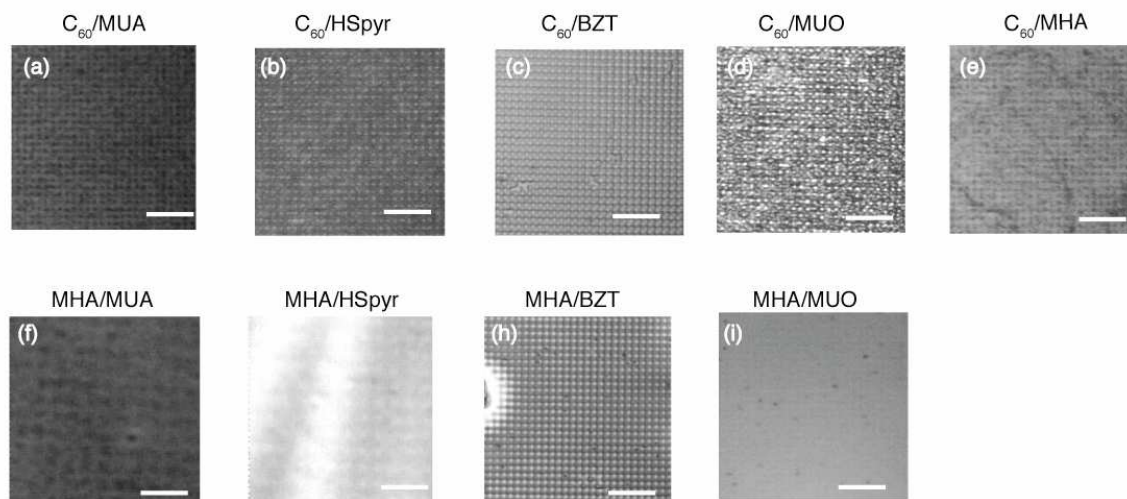
# P3HT:PCBM



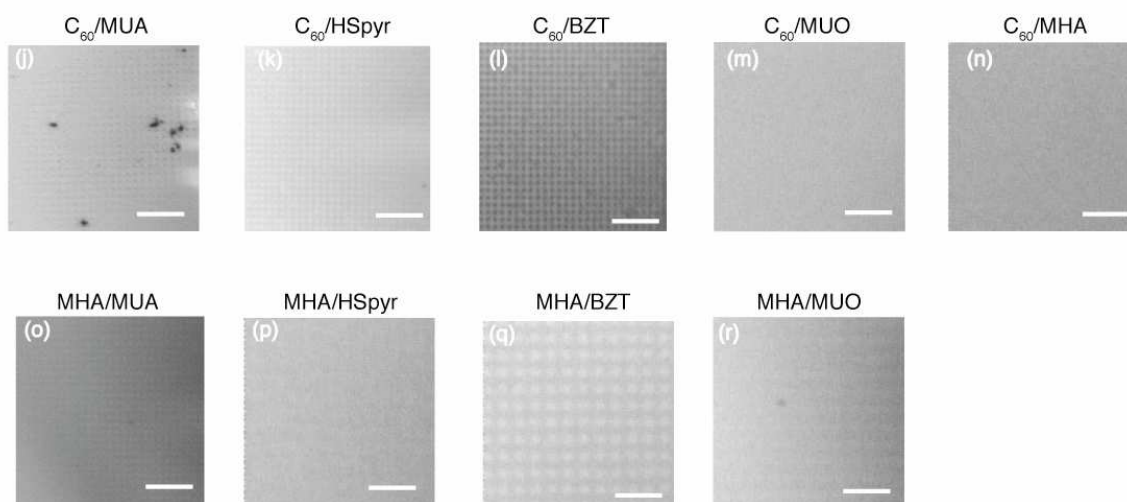
**Figure S8** Optical Microscopy Images of MDMO-PPV:PCBM and P3HT:PCBM films, cast onto patterned surfaces, after annealing. Scale bars in (a)-(g), (j)-(r) ~30  $\mu\text{m}$ ; in (h), (i) ~10  $\mu\text{m}$



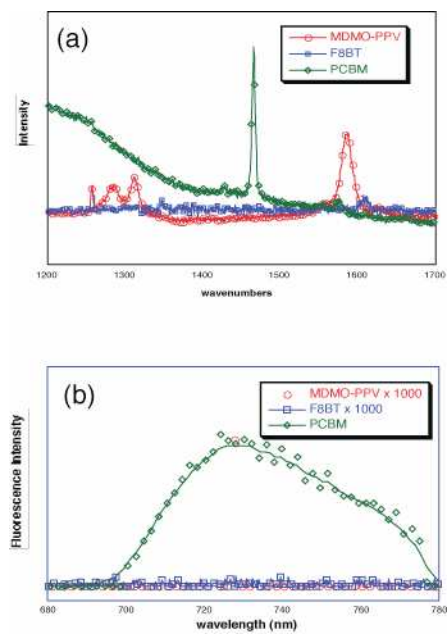
# F8BT:PCBM



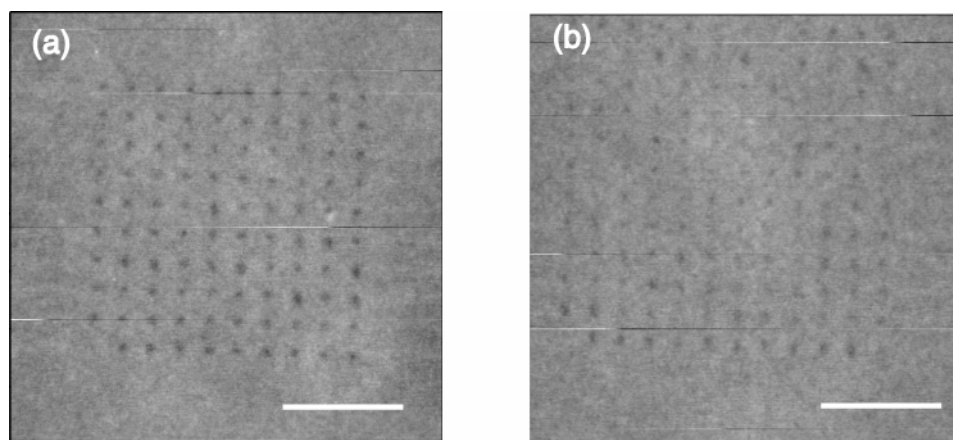
# PFB:PCBM



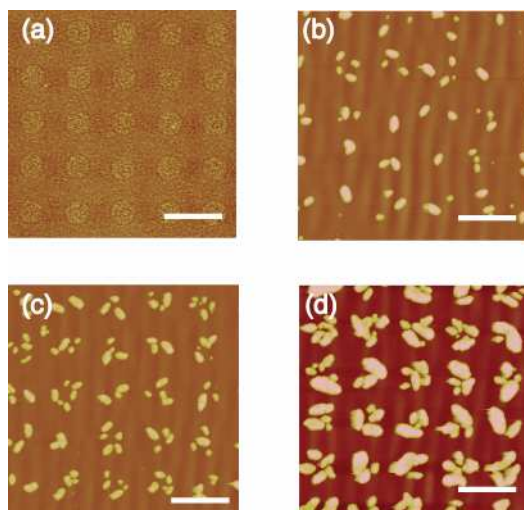
**Figure S9** Optical Microscopy Images of F8BT:PCBM and PFB:PCBM films cast onto patterned surfaces, after annealing. Scale bars in (a)-(e), (h)-(p)  $\sim 30\ \mu\text{m}$ ; in (f), (g), (q), (r)  $\sim 10\ \mu\text{m}$



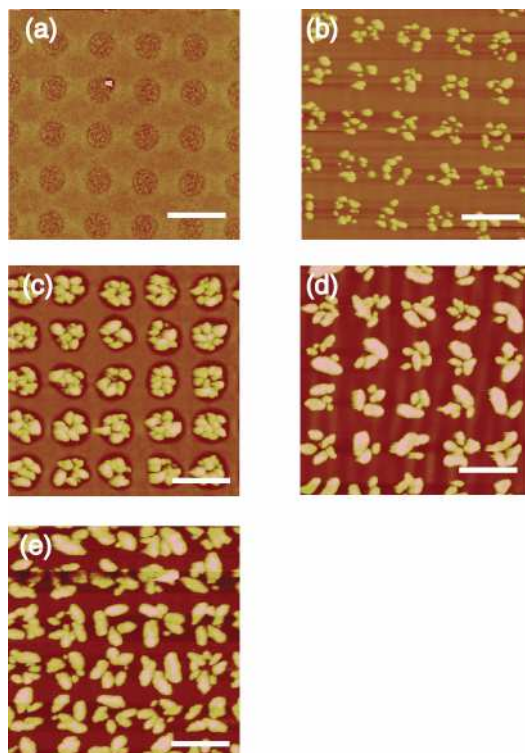
**Figure S10** (a) Raman spectra of MDMO-PPV, F8BT, and PCBM (b) Fluorescence spectra of MDMO-PPV, F8BT, and PCBM (excitation  $\lambda = 632$  nm)



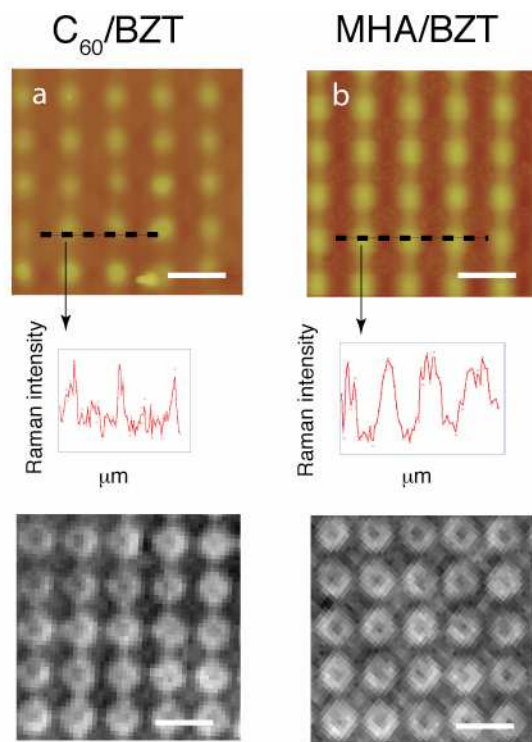
**Figure S11** AFM topography images (AC mode) of 200 nm thick MDMO-PPV:PCBM films on DPN-patterned surfaces (MHA/HSpyr) (a) DPN features ~200 nm in diameter (b) DPN features ~130 nm in diameter. Scale bars are 5  $\mu\text{m}$ .



**Figure S12** AFM topography images (AC mode) for annealed films (130 °C, 30 min) of varying P3HT:PCBM composition (w:w ratios) cast onto MHA/HSpyr patterned substrates: (a) P3HT alone; (b) 2:1; (c) 1:2; (d) 1:2 . Scale bars are 5 microns; vertical scale (z) in (a) is 15 nm; (b)-(d) 200 nm.



**Figure S13** AFM topography images (AC mode) showing the evolution of morphology of P3HT:PCBM film on MHA/HSpyr surface with variation in annealing conditions (a) 115 °C, 30 min (b) 120 °C, 40 min, (c) 130 °C, 30 min, (d) 125 °C, 30 min followed by 130 °C, 30 min, (e) 130 °C, 90 min. Scale bars are 5 microns in all cases. Vertical (z) scale for (a) 25 nm, for (b)-(d) 200 nm.



**Figure S14** Comparison of AFM topography (top row), Raman line scans (middle row) of peak intensity (cps) at  $1460\text{ cm}^{-1}$  across regions indicated by the black dashed lines in the AFM images, and fluorescence images (bottom row) resulting from excitation at  $\lambda = 632\text{ nm}$  (exposure time = 0.2 sec) for F8BT:PPV/PCBM films prepared and annealed in the usual way on (a)  $C_{60}/BZT$  and (b)  $MHA/BZT$ . The black arrows indicate the center of a dot in the AFM image and the corresponding position in the Raman line scan; lateral scales of all images are equivalent, with scale bars =  $5\text{ }\mu m$ . Vertical scale =  $200\text{ nm}$  for both samples.

**Table S1** Summary of behaviors observed for PPV:PCBM films.

<b>PPV:PCBM films</b>	Patterning visible by Bright Field	Net Aggregation of Material (AFM)	Brighter PCBM Fluorescence	Higher PCBM Raman Signal Intensity
C <sub>60</sub> /MUAm	Yes	P <sup>a</sup>	B	
C <sub>60</sub> /HSPyr	Yes	B <sup>b</sup>	P	P
C <sub>60</sub> /BZT	Yes	B	B and P	B
C <sub>60</sub> /MUO	Yes	P	P	B
C <sub>60</sub> /MHA	Yes	P	B and P	P
MHA/MUAm	Yes	P	B	B
MHA/HSPyr	Yes	B	P	B
MHA/BZT	Yes	B and P <sup>c</sup>	P	P
MHA/MUO	Yes	B	B and P	

Pattern/backfill combinations were prepared as depicted in Figure 2 of the text; films were prepared and annealed as described in the Experimental Section. Fields left blank are for those cases where the results were ambiguous. <sup>a</sup>Patterned regions of the film; <sup>b</sup>Unpatterned regions of the film; <sup>c</sup>Both patterned and unpatterned regions show aggregation of material (or increased PCBM fluorescence), with clear influence from the surface patterning.



**Table S2** Summary of behaviors observed for P3HT:PCBM films.

<b>P3HT:PCBM films</b>	Patterning visible by Bright Field	Net Aggregation of Material (AFM)	Brighter PCBM Fluorescence	Higher PCBM Raman Signal Intensity	Formation of large PCBM crystallites
C <sub>60</sub> /MUAm	Yes		Unable to run fluorescence and Raman experiments on P3HT:PCBM samples due to interference from P3HT in the spectral regions of interest		N
C <sub>60</sub> /HSPyr	Yes	P			Y (P)
C <sub>60</sub> /BZT	Yes	B			Y (B)
C <sub>60</sub> /MUO	Yes	B (slight)			N
C <sub>60</sub> /MHA	No				N
MHA/MUAm	No				N
MHA/HSPyr	Yes	P			Y (P)
MHA/BZT	Yes	B			Y (B)
MHA/MUO	Yes	B			Y (B)

Pattern/backfill combinations were prepared as depicted in Figure 2 of the text; films were prepared and annealed as described in the Experimental Section. Fields left blank are for those cases where the results were ambiguous.

**Table S3** Summary of behaviors observed for F8BT:PCBM films.

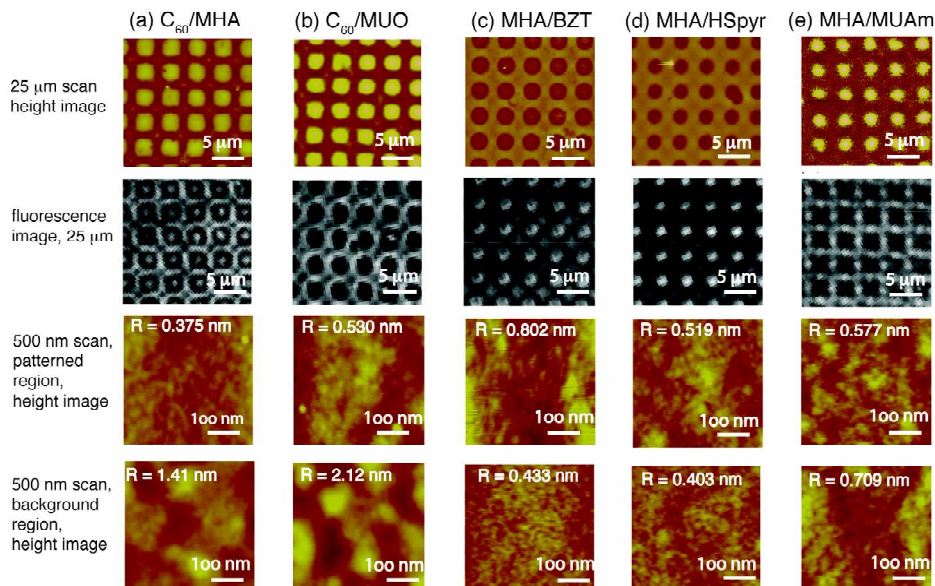
<b>F8BT:PCBM films</b>	Patterning visible by Bright Field	Net Aggregation of Material (AFM)	Brighter PCBM Fluorescence	Higher PCBM Raman Signal Intensity
C <sub>60</sub> /MUAm	Y	P (slight)		B (slight)
C <sub>60</sub> /HSPyr	Y			B
C <sub>60</sub> /BZT	Y	P	P	P
C <sub>60</sub> /MUO	Y			
C <sub>60</sub> /MHA	Y	P (slight)		
MHA/MUAm	Y	P (slight)		
MHA/HSPyr	Y		P	
MHA/BZT	Y	P	P	B
MHA/MUO	Y			

Pattern/backfill combinations were prepared as depicted in Figure 2 of the text; films were prepared and annealed as described in the Experimental Section. Fields left blank are for those cases where the results were ambiguous.

**Table S4** Summary of behaviors observed for PFB:PCBM films.

<b>PFB:PCBM films</b>	Patterning visible by Bright Field	Net Aggregation of Material (AFM)	Brighter PCBM Fluorescence	Higher PCBM Raman Signal Intensity
C <sub>60</sub> /MUAm	Y	P		
C <sub>60</sub> /HSPyr	Y			
C <sub>60</sub> /BZT	Y	B		
C <sub>60</sub> /MUO	N			
C <sub>60</sub> /MHA	N			
MHA/MUAm	Y	P (slight)		
MHA/HSPyr	Y, faint			
MHA/BZT	Y	P (slight)		
MHA/MUO	Y, faint	P (slight)		

Pattern/backfill combinations were prepared as depicted in Figure 2 of the text; films were prepared and annealed as described in the Experimental Section. Fields left blank are for those cases where the results were ambiguous.



**Figure S15** Row 1: Large area height images (intermittent mode) of MDMO-PPV:PCBM films on a variety of surface chemistries (the same as those in Figure 6). Vertical scale for (a), (b), (e) in Row 1 = 200 nm; vertical scale for (c) and (d) = 100 nm. Row 2: Fluorescence images for the same samples (as shown in Figure 6). Row 3: Height images (intermittent mode) of  $(500 \text{ nm})^2$  areas of the patterned regions (circles) of the samples in Row 1. Vertical scale for all images in Row 3 = 10 nm. Row 4: Height images (intermittent mode) of  $(500 \text{ nm})^2$  areas of the background regions of the samples in Row 1. Vertical scale for (a) and (b) in Row 4 = 25 nm; vertical scale for (c)-(e) = 10 nm. Values for surface roughness are shown for all the images in Rows 3 and 4.