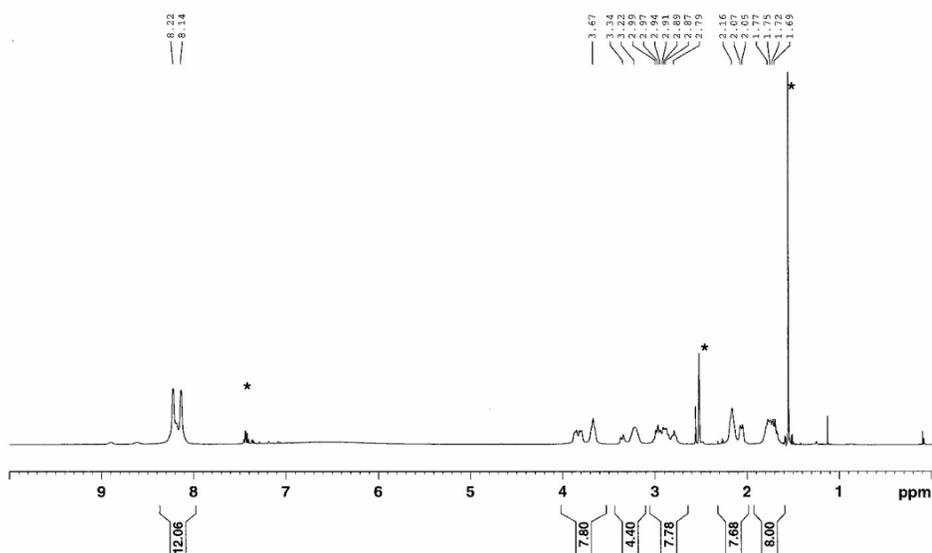
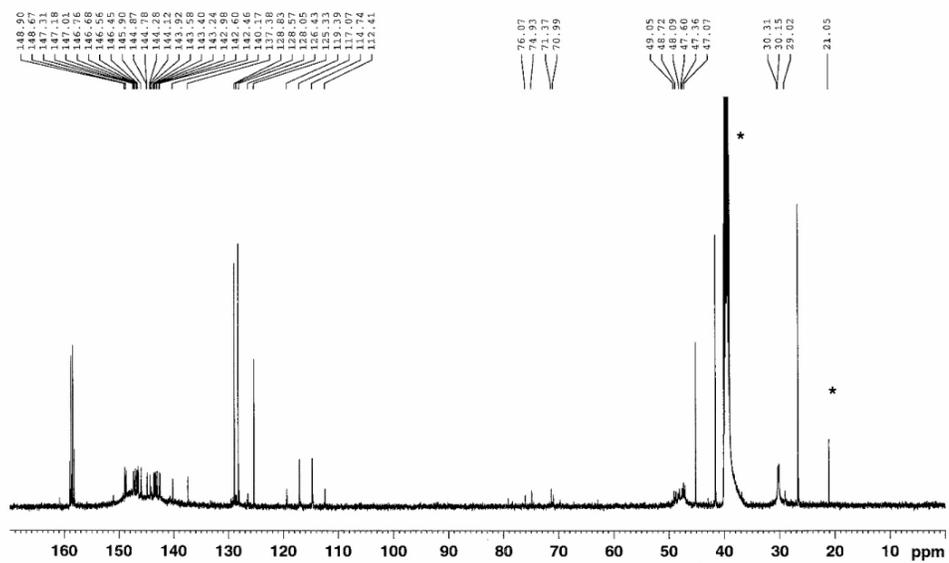


# Controlling Film Morphology in Conjugated Polymer:Fullerene Blends with Surface Patterning

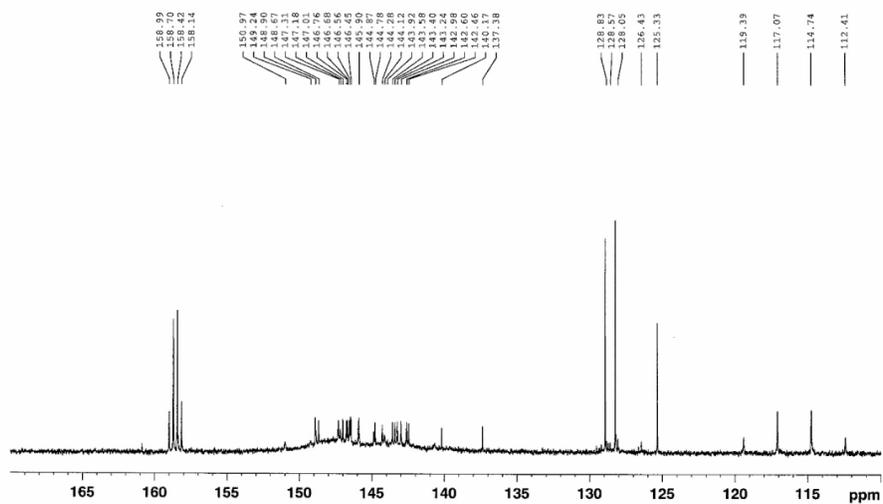
Lee Y. Park,<sup>\* ‡</sup> Andrea M. Munro,<sup>§</sup> David S. Ginger<sup>\* §</sup>



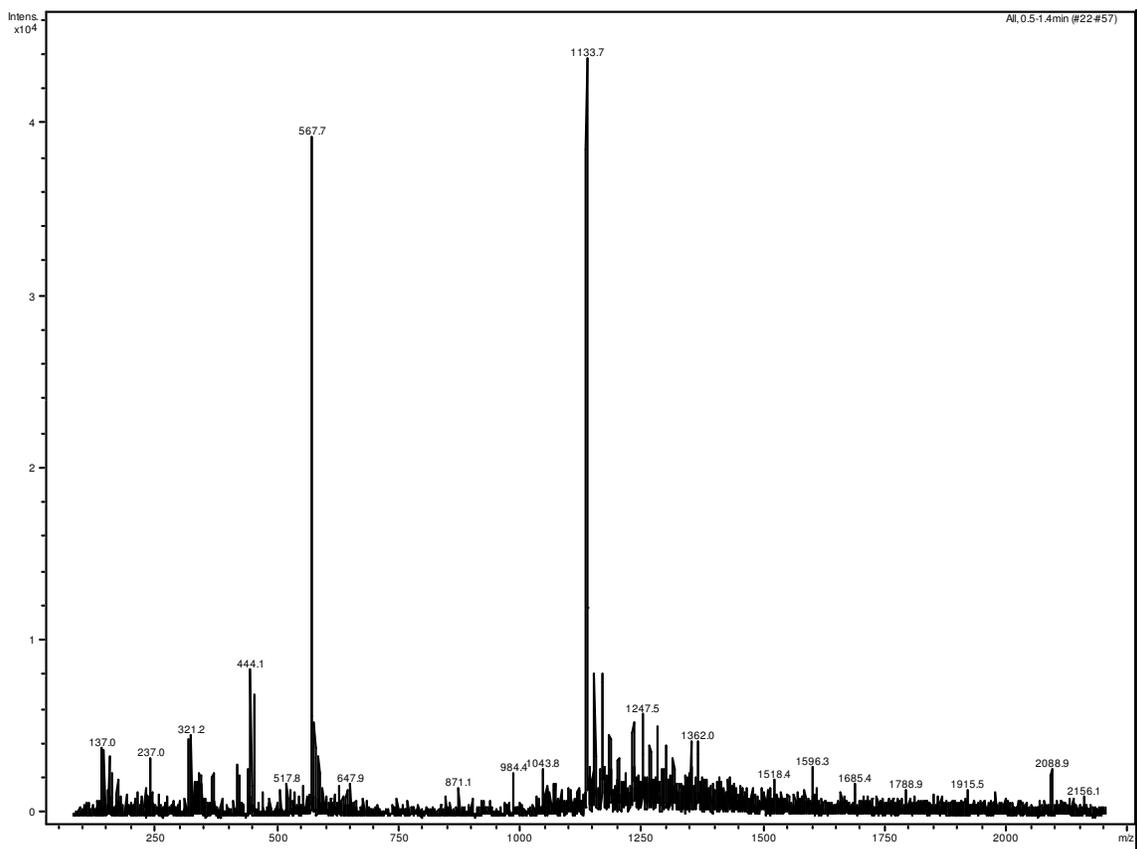
**Figure S1** <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 500 MHz) of **2** (collected on a Bruker 500 MHz Avance Spectrometer.) Residual solvent signals are marked with an asterisk.



**Figure S2**  $^{13}\text{C}$  NMR ( $d_6$ -DMSO, 500 MHz) of **2** (collected on a Bruker 500 MHz Avance Spectrometer.) Residual solvent signals are marked with an asterisk.

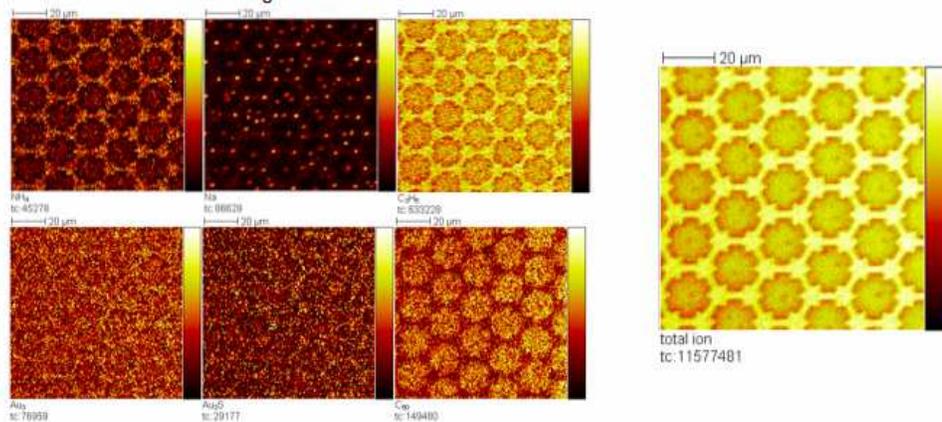


**Figure S3**  $^{13}\text{C}$  NMR ( $d_6$ -DMSO, 500 MHz) of **2**, expanded.

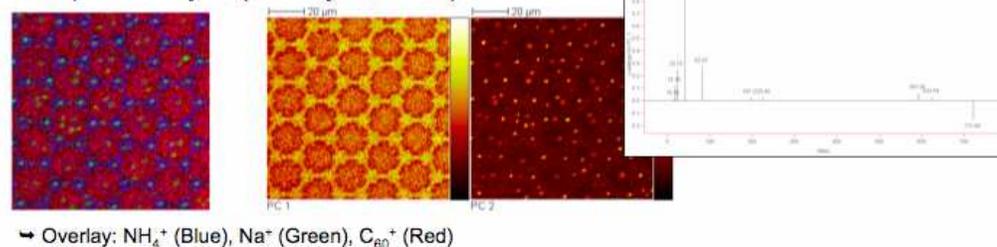


**Figure S4** ESI-MS of **2** obtained by direct infusion of the sample (from a solution in a mixture of DMSO and acetonitrile) on a Bruker Esquire LC ion trap mass spectrometer.

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



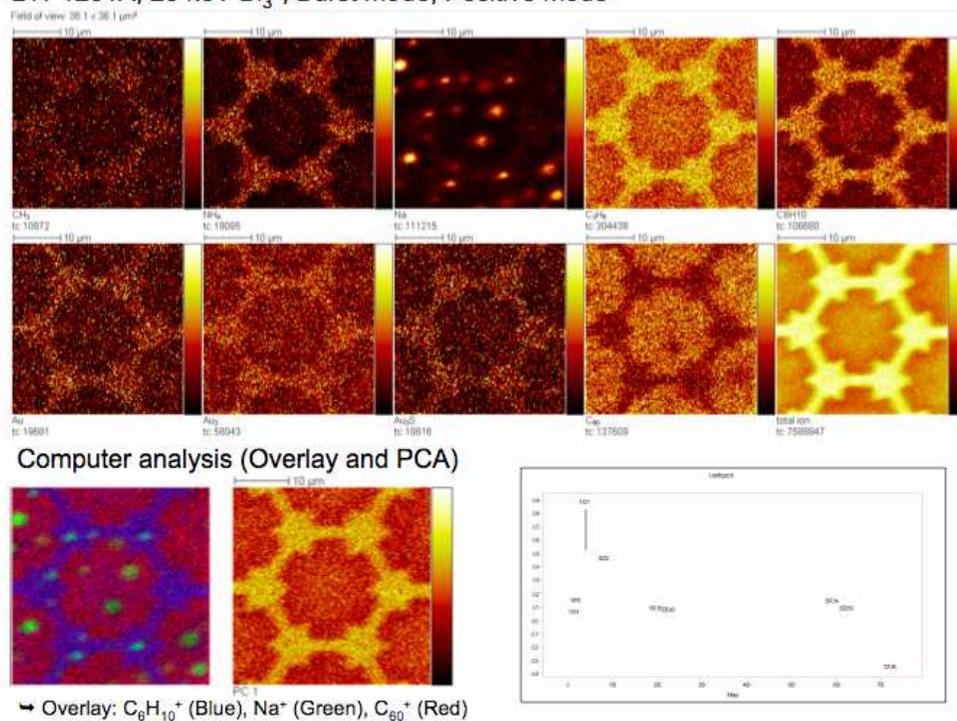
Computer analysis (Overlay and PCA)



→ Overlay: NH<sub>4</sub><sup>+</sup> (Blue), Na<sup>+</sup> (Green), C<sub>60</sub><sup>+</sup> (Red)

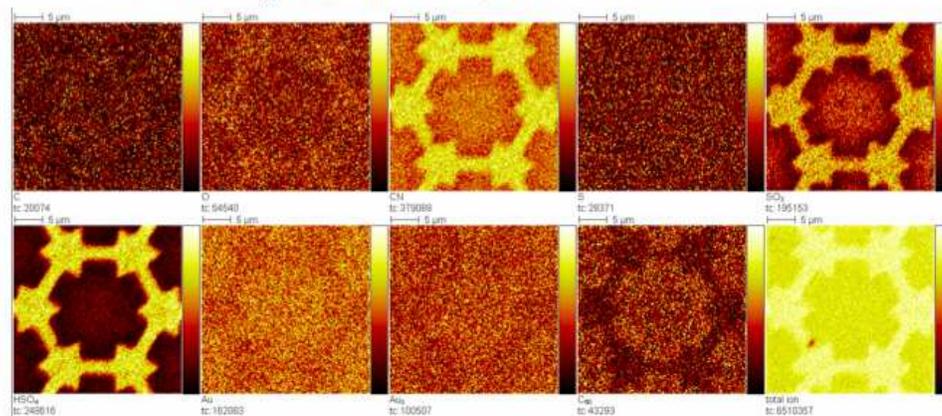
**Figures S5-S7** ToF-SIMS maps for Au surface patterned with fullerene as illustrated in Figure 2, backfilled with HSpyr. ToF-SIMS experiments were performed using an ToF-SIMS V from Ion-ToF GmbH (Munster, Germany). A 25 keV pulsed Bi<sub>3</sub><sup>+</sup> beam was raster-scanned across the target and secondary ion image of the micropatterned sample were obtained by plotting the intensity of the selected ions with respect to the coordinates of the beam on the target. The primary ion dose was kept under static conditions during all experiments ( $<10^{12}$  ions/cm<sup>2</sup>). The beam was operated in the high current unbunched mode (lateral resolution around 1 μm and unit mass resolution) and hit the target at an angle of 45°.

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

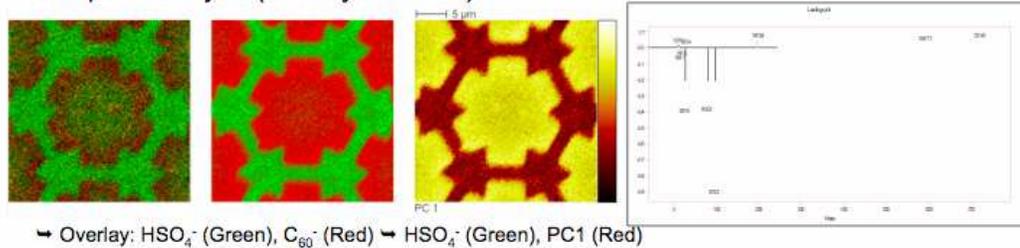


**Figure S6** ToF-SIMS maps for Au surface patterned with fullerene as illustrated in Figure 2, backfilled with HSpyr

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

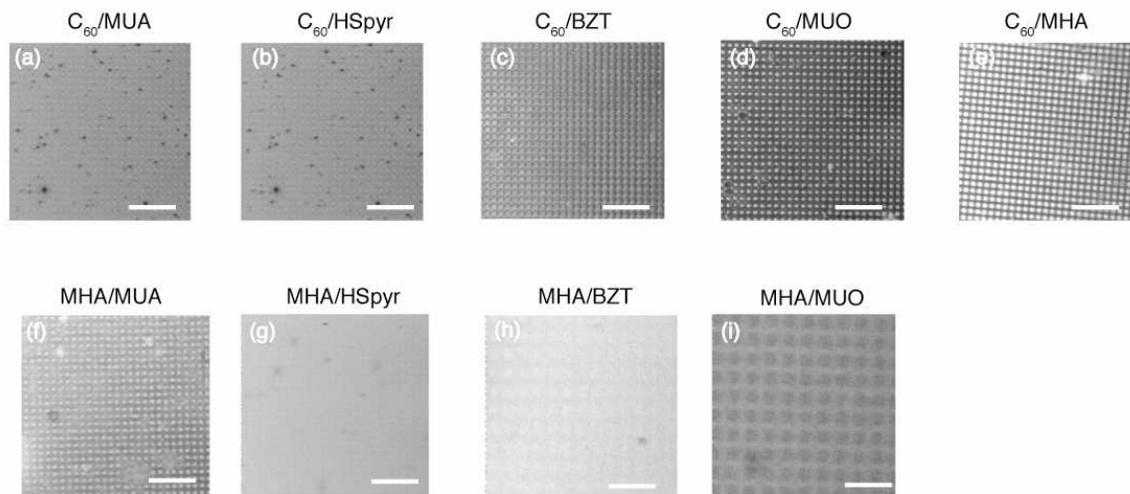


Computer analysis (Overlay and PCA)

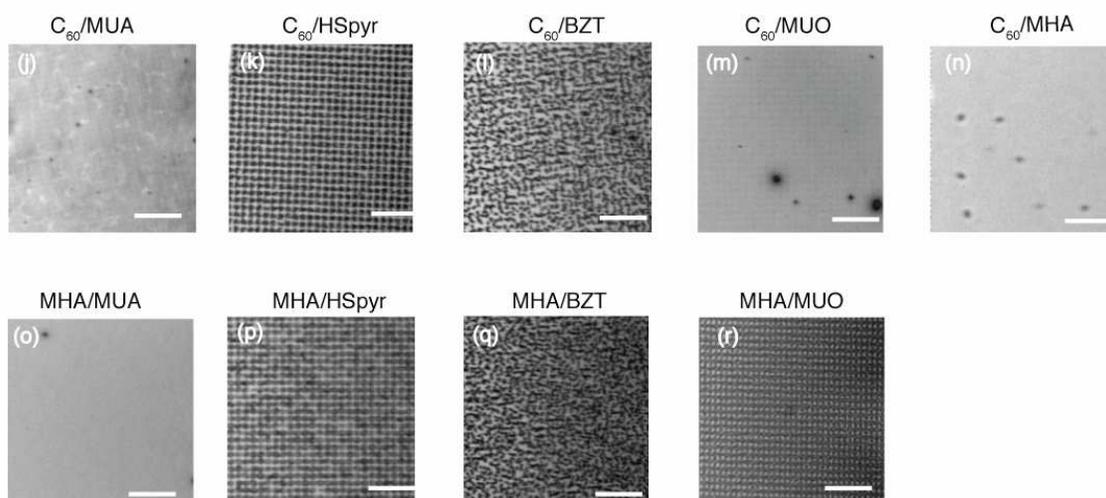


**Figure S7** ToF-SIMS maps for Au surface patterned with fullerene as illustrated in Figure 2, backfilled with HSpyr

MDMO-PPV:PCBM

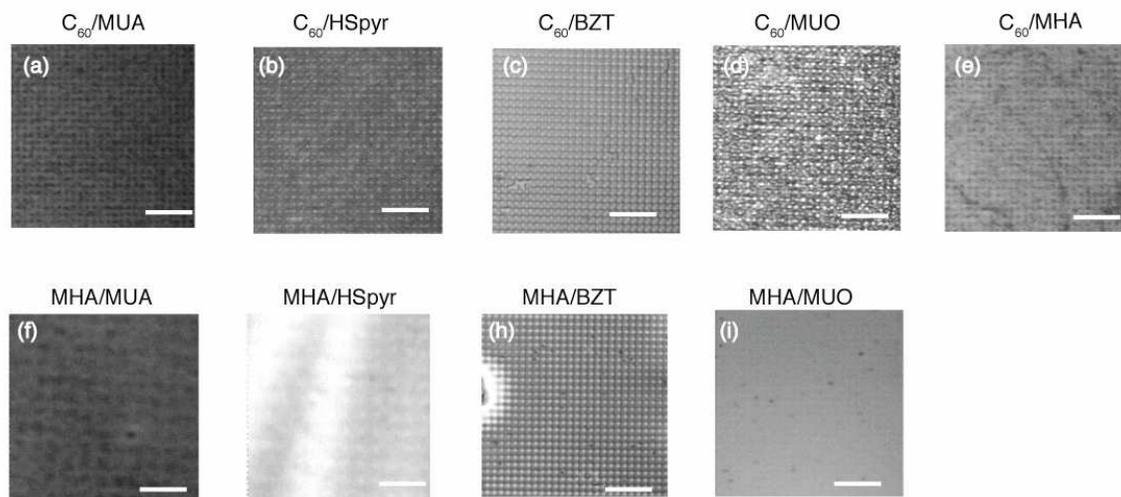


P3HT:PCBM

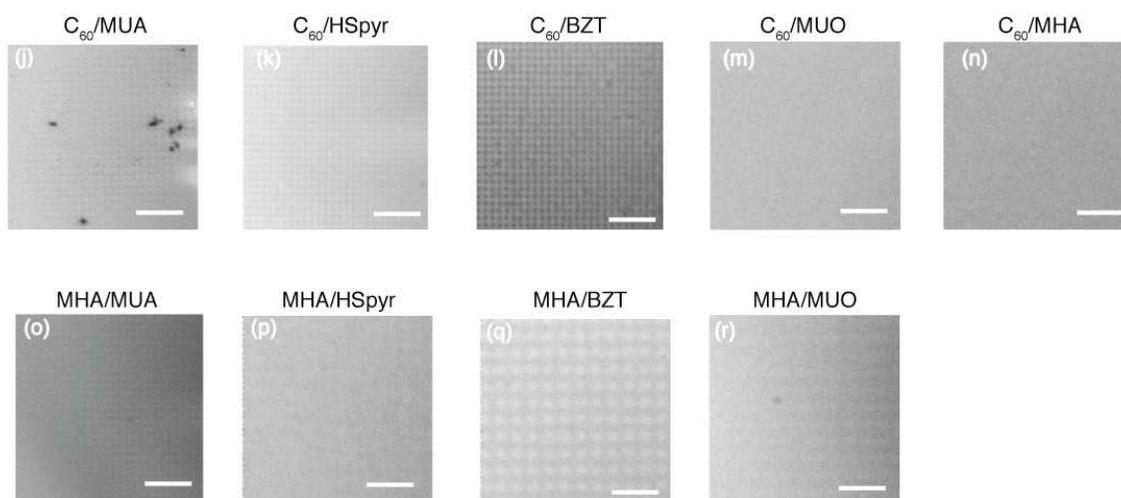


**Figure S8** Optical Microscopy Images of MDMO-PPV:PCBM and P3HT:PCBM films, cast onto patterned surfaces, after annealing. Scale bars in (a)-(g), (j)-(r) ~30  $\mu\text{m}$ ; in (h), (i) ~10  $\mu\text{m}$

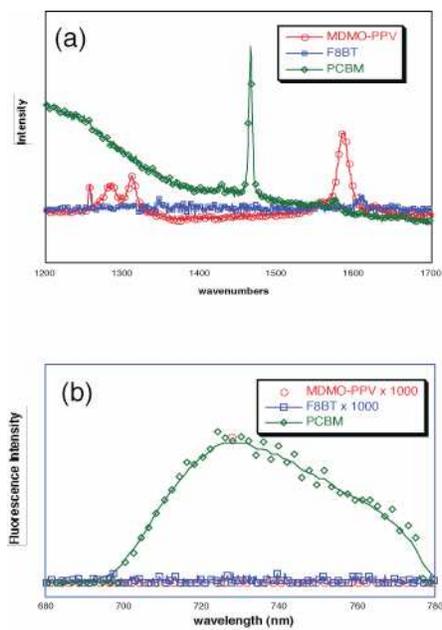
F8BT:PCBM



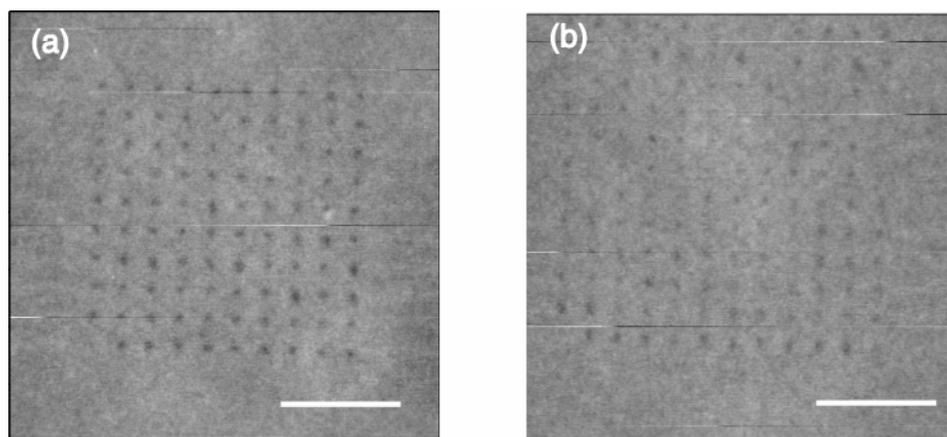
PFB:PCBM



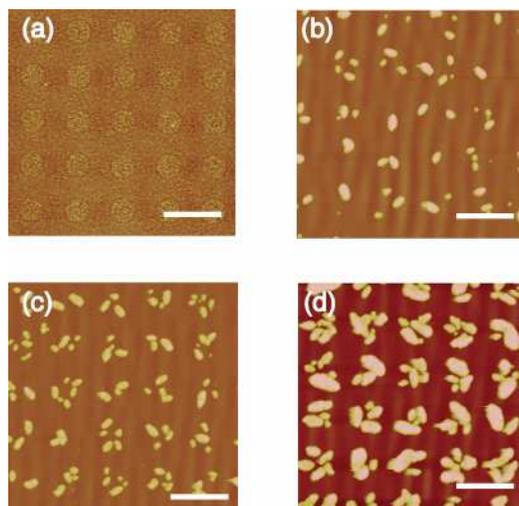
**Figure S9** Optical Microscopy Images of F8BT:PCBM and PFB:PCBM films cast onto patterned surfaces, after annealing. Scale bars in (a)-(e), (h)-(p) ~30  $\mu\text{m}$ ; in (f), (g), (q), (r) ~10  $\mu\text{m}$



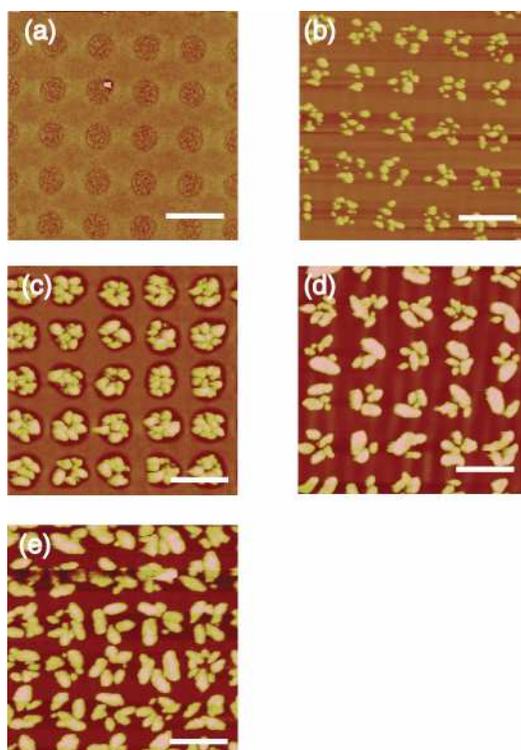
**Figure S10** (a) Raman spectra of MDMO-PPV, F8BT, and PCBM (b) Fluorescence spectra of MDMO-PPV, F8BT, and PCBM (excitation  $\lambda = 632$  nm)



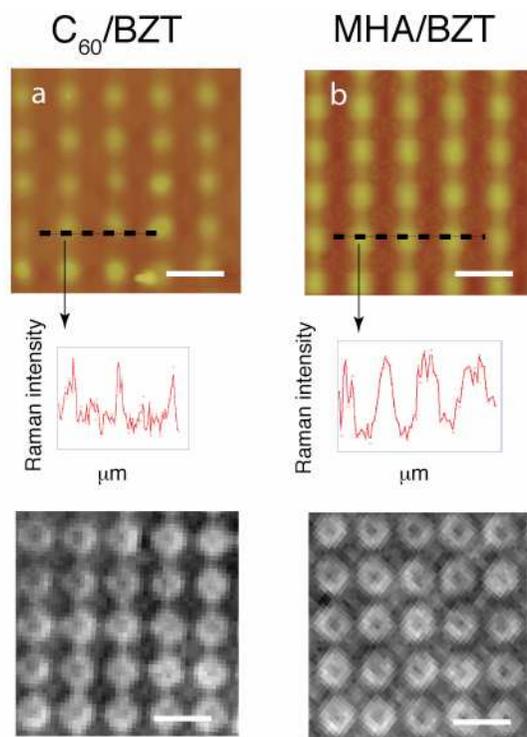
**Figure S11** AFM topography images (AC mode) of 200 nm thick MDMO-PPV:PCBM films on DPN-patterned surfaces (MHA/HSpyr) (a) DPN features ~200 nm in diameter (b) DPN features ~130 nm in diameter. Scale bars are 5  $\mu\text{m}$ .



**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 =  $5\ \mu m$ . Vertical scale = 200 nm for both samples.

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

<b>PPV:PCBM films</b>	<b>Patterning visible by Bright Field</b>	<b>Net Aggregation of Material (AFM)</b>	<b>Brighter PCBM Fluorescence</b>	<b>Higher PCBM Raman Signal Intensity</b>
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.

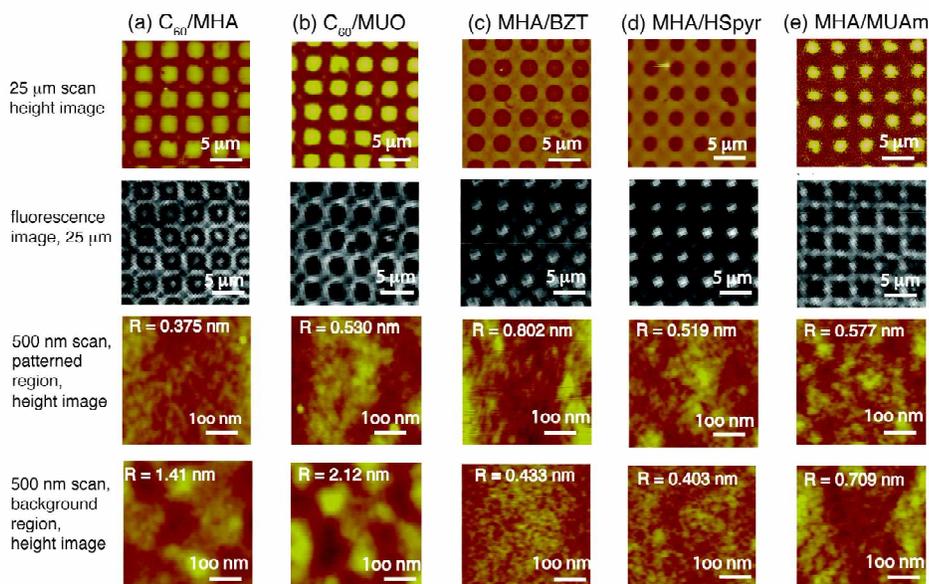
<b>F8BT:PCBM films</b>	Patterning visible by Bright Field	Net Aggregation of Material (AFM)	Brighter PCBM Fluorescence	Higher PCBM Raman Signal Intensity
C <sub>60</sub> /MUAm	Y	P (slight)		B (slight)
C <sub>60</sub> /HSPyr	Y			B
C <sub>60</sub> /BZT	Y	P	P	P
C <sub>60</sub> /MUO	Y			
C <sub>60</sub> /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>	<b>Patterning visible by Bright Field</b>	<b>Net Aggregation of Material (AFM)</b>	<b>Brighter PCBM Fluorescence</b>	<b>Higher PCBM Raman Signal Intensity</b>
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 the all the images in Rows 3 and 4.