

# Crystallization-Induced Energy Level Change of [6,6]-Phenyl-C<sub>61</sub>-Butyric Acid Methyl Ester (PCBM) Film: Impact of Electronic Polarization Energy

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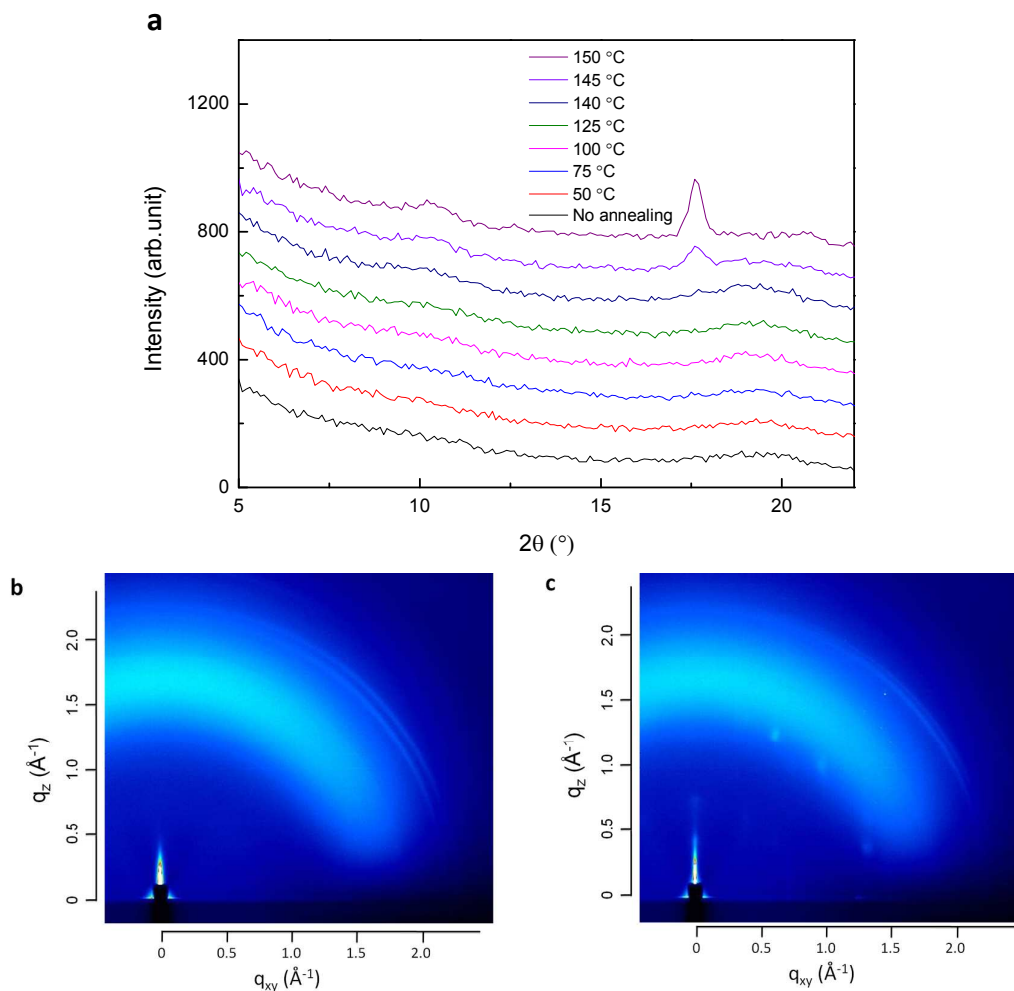
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Figure S1: 2D GIXRD patterns.

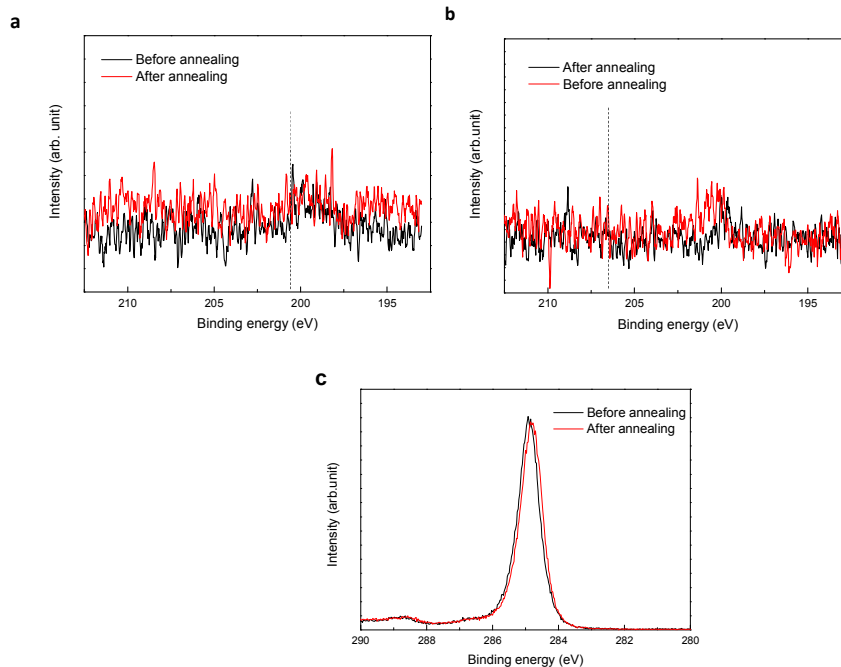
Figure S2: XPS spectra.

Figure S3: LEIPS spectra.

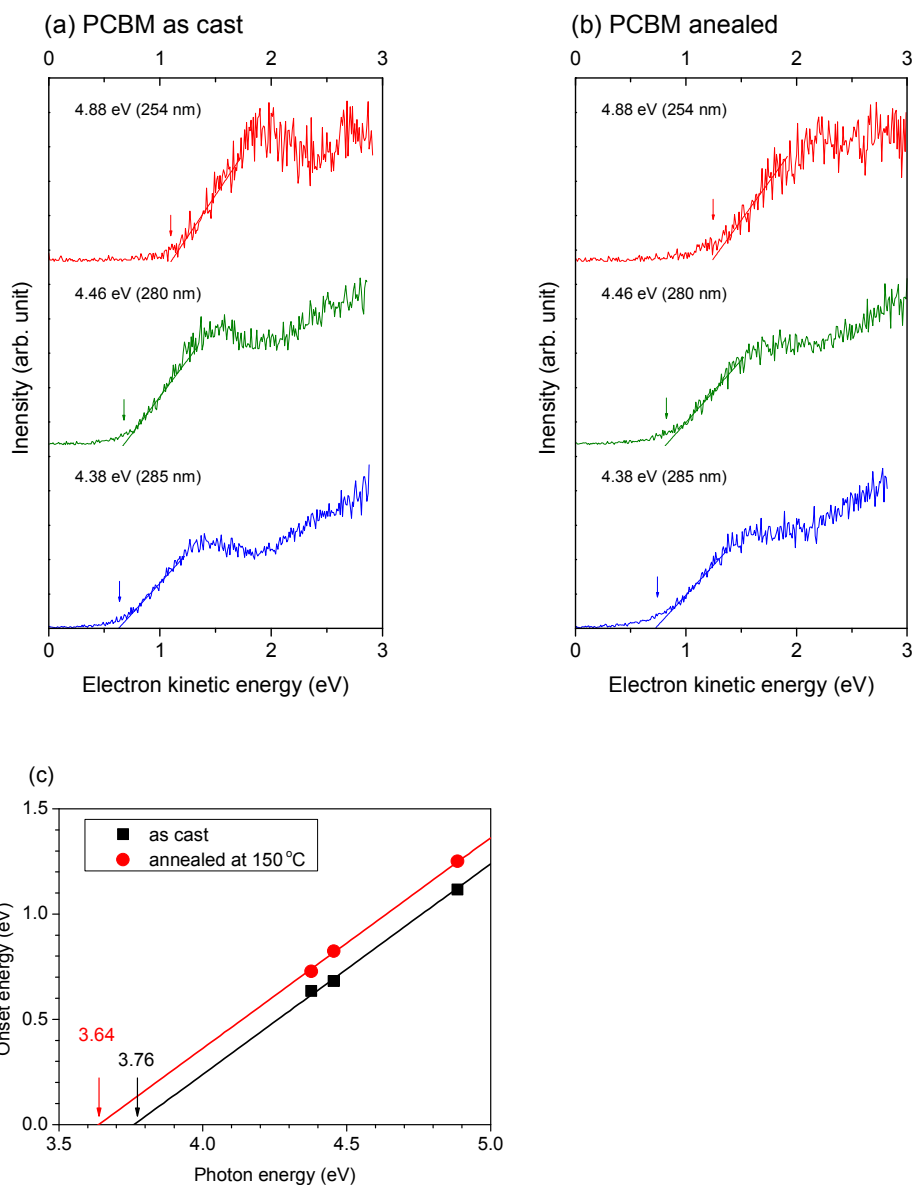
Figure S4: UV-Vis spectra.



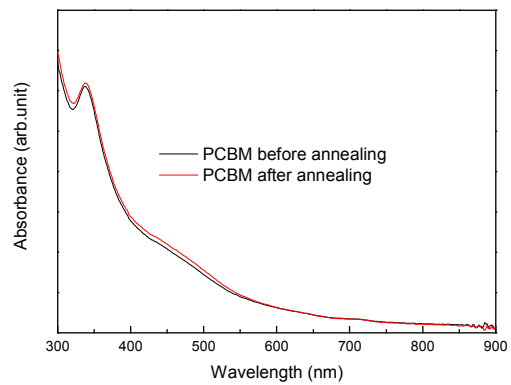
**Figure S1** a) In-plane GIXRD patterns of PCBM/TiO<sub>2</sub>/ITO at different annealing temperatures. Crystallization starts occurring at 140 °C and the peak at approximately 17.6° gradually increases in area at higher annealing temperature up to 150 °C. 2D GIXRD patterns of PCBM/ITO film b) before and c) after the annealing at 150 °C for 5 min. Only a broad ring was observed in the film before annealing, while clear diffractions are observed as spots after annealing.



**Figure S2.** XPS measurements of PCBM/ITO in the regions of a) Cl2p for PCBM spin-coated from chlorobenzene [binding energy of Cl in C<sub>6</sub>H<sub>5</sub>Cl (200.5 eV) is indicated by a dashed line], b) Cl2p for PCBM spin-coated from CHCl<sub>3</sub> [binding energy of Cl in CHCl<sub>3</sub> (206.8 eV) is indicated by a dashed line] and c) C1s peaks before and after annealing. No Cl2p peak was observed, indicating the absence of solvent residue in the PCBM film. The shift of the C1s peak was clearly observed after annealing. Peak maxima were obtained by Gaussian fitting for five different points from the same sample, which gives 284.97±0.04 eV and 284.79±0.04 eV for the PCBM film before and after annealing, respectively.



**Figure S3.** LEIPS profiles measured at different photon energies for the PCBM films a) before and b) after annealing at 150°C for 5 min. Arrows indicate the onsets of spectra. c) Plot of the onset energy as a function of photon energy for determining the electron affinities from the intersections with the  $x$ -axis.



**Figure S4.** Transmittance absorption spectra of PCBM film before and after annealing on quartz substrate.