## **Support Information**

## Ligand-free Rutile and Anatase TiO<sub>2</sub> Nanocrystals as Electron Extraction Layers for High Performance Inverted Polymer Solar Cells

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Fig. S1 The cross-sectional SEM images different kinds of  $TiO_2$  layer on ITO glass. a. anatase  $TiO_2$  layer; b. rutile  $TiO_2$  layer; c. amorphous  $TiO_2$ . The thicknesses of these three kinds of  $TiO_2$  layers are around 25 nm.



Fig. S2 The FTIR spectra of anatase and rutile TiO<sub>2</sub> nanocrystals.

Fourier-transform infrared spectra (FTIR) of the as-prepared  $TiO_2$  nanocrystals were measured to determine whether ligand chemically capped on the surface of the  $TiO_2$ nanocrystals (Fig. S2). Before FTIR test, the  $TiO_2$  nanocrystals were washed with ethanol for twice. From the FTIR spectra, two large bands centered at 3410 cm<sup>-1</sup> and 1640 cm<sup>-1</sup> are attributed to the stretching vibration of O-H and the bending vibration of H-O-H, respectively. The low frequency band in the range of 400-1000 cm<sup>-1</sup> is observed for the vibration of Ti-O-Ti mode in the TiO<sub>2</sub>. Also, the peaks located at 1046 cm<sup>-1</sup> and 1155 cm<sup>-1</sup> are attributed to the C-O stretches from ethanol during the synthesis and wash process.