Developing ternary organic solar cells (OSCs) is a promising strategy to improve the photovoltaic performance. The advanced characterization of photoactive layers allows a better understanding of morphology, and thereby more effective realization of high-performance solar cells. In this work, we integrated perylenediimide (PDI)-based non-fullerene material into OSCs as the third component to form the ternary OSCs. [1] Specifically, three-dimensional nanoscale morphology of ternary film was characterized in depth by photo-induced force microscopy (PiFM) coupled with infrared laser spectroscopy and the energy-filtered transmission electron microscopy (EFTEM), which qualitatively and quantitatively “view” the surface and cross-sectional morphology, and provide strong evidence that PDI-based material can suppress the aggregation of the fullerene molecules and generate the homogenous morphology with a higher-level of the molecularly mixed phase. In particular, the application of PiFM in this study enables the chemical imaging of all the three components at a high spatial resolution (~10 nm), unprecedented by all previous chemical imaging techniques. Thus, our work represents the first exploration of the morphology characterization in the real device setting with advanced characterization techniques.