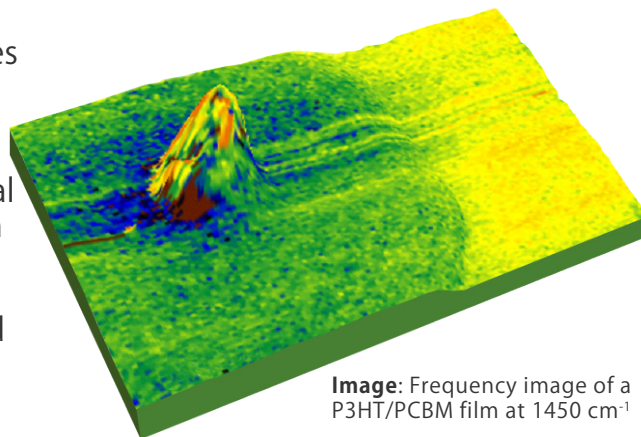


# Analyzing chemical variability of organic photovoltaic materials

- The nanoIR™ system provides nanoscale IR spectra of photovoltaic materials, and correlates to conventional IR spectral databases
- AFM-IR is able to detect phase separation in organic photovoltaic materials by correlating local chemical analysis with topographical information
- The relative material stiffness within a defected region of a material can be mapped and analyzed via IR chemical contrast imaging



**Image:** Frequency image of a P3HT/PCBM film at 1450 cm<sup>-1</sup>

## Abstract

This note describes the ability of the nanoIR™ system to obtain a set of high spatially resolved (~100 nm) chemical analyses of photovoltaic materials, namely P3HT (poly(3-hexylthiophene)) and PCBM ((6,6)-phenyl-C61-butyric acid methyl ester). Phase separation of the material is readily detected by comparing the spectrum of interest against pure component spectrum. By combining AFM with nanoIR spectroscopy into one platform, the topology of the samples and defects are linked directly. Spectral changes are observed within 100 nm when a spectral array is acquired across a flat area. The relative mechanical stiffness within a defect can then be evaluated in a contact stiffness image.

## Key words

AFM-IR | Nanoscale IR spectroscopy | Organic photovoltaics | Phase separation | Defect stiffness

## Introduction

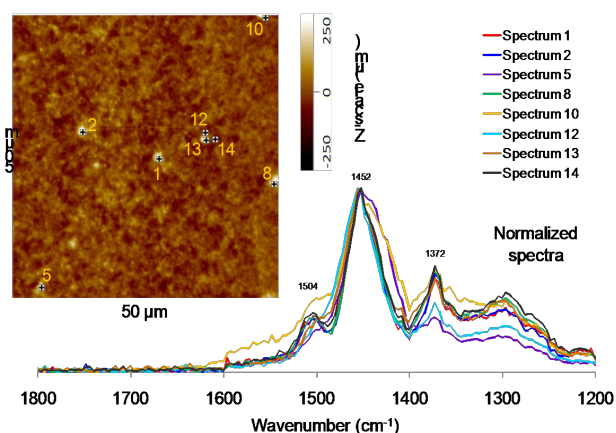
Organic photovoltaic (PV) materials are of great importance in harnessing solar power as an alternate energy source. In both private and academic sectors, there is a great challenge to prepare solar panels with the highest power conversion efficiency ( $\eta$ ) at the lowest possible cost. Polymer blends of poly(3-hexylthiophene), P3HT, and (6,6)-phenyl-C61-butyric acid methyl ester (PCBM) are a popular donor-acceptor (DA) bulk heterojunction (BHJ) that has been used for this purpose. Such material can be solution-processed before grafting onto surfaces and can be produced with high yield (>5%). In a typical organic

solar cell, P3HT and PCBM are immiscible, and eventually phase separated into microdomains<sup>[1]</sup>. This phase-separation is critical in the long-term stability and performance of the PV. Covalently linking PCBM to polymeric P3HT would yield small feature sizes, but the performance suffers as the P3HT backbone is believed to conduct charges poorly<sup>[2]</sup>. AFM and TEM have been used to characterize the morphology of the PV films at high-spatial resolution, but chemical information is not readily available at the nanoscale. In this application note, we will correlate topological features to local chemical spectroscopy on P3HT and PCBM-doped P3HT films using nanoscale IR spectroscopy on the nanoIR™ system.

## Measurements of drop-casted P3HT and PCBM-doped P3HT films

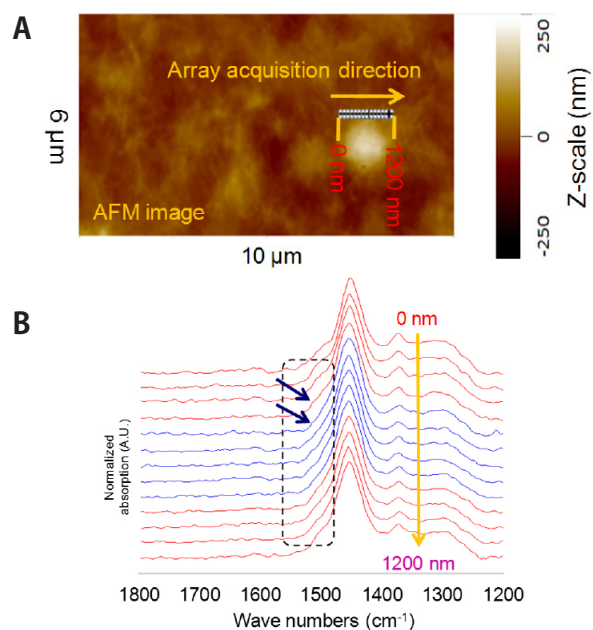
To illustrate how the AFM-IR technique is ideal for measuring polymeric samples in which there are local material variations, a conventional P3HT film was analyzed via AFM on the nanoIR system for nanoscale compositional variability.

In figure 1, it is evident that there is variability of topographical features in the AFM image, as small protrusions on the order of a few microns can be seen. AFM-IR spectral acquisition reveals that only some locations have slightly broadened absorption characteristics, i.e., a long absorption tail (Spectrum 10) and the shoulder near  $1500\text{ cm}^{-1}$  is less defined. The other locations yield spectra similar to bulk P3HT IR data. Near spectra 12 – 14, the broadened absorption implies distance from the height feature.



**Figure 1:** AFM height image and respective AFM-IR spectra (correlated with points on image).

To get a closer look at average compositional variability across the P3HT film, a spectral array was acquired (Figure 2B). Each spectrum is taken  $\sim 100\text{ nm}$  apart and spectral changes are seen within the same length scale (from second to third and from fifth to sixth spectra). As the shoulder around  $1500\text{ cm}^{-1}$  disappears and reappears (at the arrows), the signal near  $1380\text{ cm}^{-1}$  appears to broaden. With the nanoIR system, these IR spectral changes, and further, chemical composition changes, can be seen at high spatial resolutions.



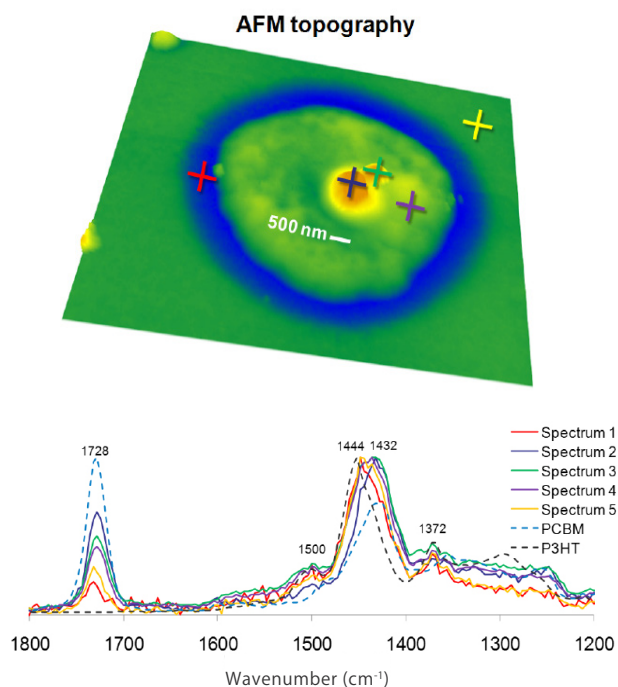
**Figure 2.** A spectral array acquisition shown in the AFM image (A) and the corresponding spectra (B) near spots 12-14 in figure 1; spacing between each marker is  $\sim 100\text{ nm}$ .

To show defectivity analysis capabilities on the nanoIR, a heat treated P3HT-PCBM sample was first analyzed via AFM. After an area of interest was identified, localized IR spectra pertinent to surface features were collected (Fig. 2b).

When the nanoIR spectra are compared against the spectra from the normal P3HT film, local variations are distinguished. The methylene bending modes at  $1444\text{ cm}^{-1}$  and  $1432\text{ cm}^{-1}$  corresponds to the P3HT and PCBM, respectively. The  $1444\text{ cm}^{-1}$  band also contains a contribution from an overlapping ring semicircle stretching mode. The corresponding spectrum for the yellow hash mark appears to have both components.

At the outer ring (red mark/spectrum 1), the peak at  $1732\text{ cm}^{-1}$  (PCBM) is small and the component at  $1444\text{ cm}^{-1}$  (P3HT) dominates. At both green and purple hash marks (spectra 3 and 4), the band near  $1432\text{ cm}^{-1}$  is mainly contributed by PCBM. Finally, the sharpness of the band at  $1432\text{ cm}^{-1}$  and a stronger  $1732\text{ cm}^{-1}$  signal suggest the lobe at the center is mostly PCBM. From the data, it can be concluded that there is local phase-separation of PCBM and P3HT within this surface defect.

The stiffness of the surface defect in the P3HT-PCBM blend can also be imaged using the



**Figure 3.** An IR chemical contrast image at  $1450\text{ cm}^{-1}$  of the heat-treated PCBM-doped P3HT sample.

**nanoIR.** Under the exposure of a continuously-pulsing IR laser radiation at  $1450\text{ cm}^{-1}$  (other overlapping wavenumbers for both materials can also be used), the contact frequency of the cantilever is traced continuously as the AFM tip moves across the sample (Fig. 3 & 4). Here the bulk material (yellow/orange) appears stiffer than most of the interior areas of the defect (green).

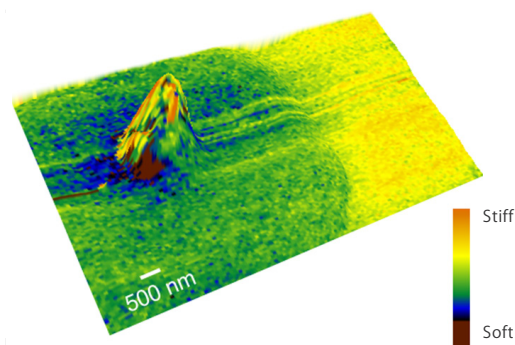
This application note is developed from the articles referenced.

Contact us today to see how nanoIR spectroscopy can benefit your research.

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**Figure 4.** Contact frequency image of a chemical defect mapped over the corresponding height image; the range of the frequency is approximately 30 kHz.

## Conclusions

This applications note has demonstrated the capabilities of the nanoIR in analyzing photovoltaic materials with high spatial resolution. Topological features of PH3T films, as well as heat treated P3HT/PCBM blends, can easily be linked to their corresponding chemical IR signatures. Local phase separation of materials can also be identified by comparing local AFM-IR spectra at defect sites with the bulk spectra of the pure components. Relative contact frequencies surrounding the defect are also mapped simultaneously with the corresponding topography. Using AFM-IR, topological information is readily correlated with the local chemical analysis, and shows great potential for failure analysis and defects at the nanoscale.

## References

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