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Nanoscale Chemical Mapping and Local Heterogeneity in PEPOT/SSp-PTh Polymer Blends via TERS

Understanding how the local molecular composition of polymer blends governs their functional properties requires characterization techniques capable of resolving chemical variations at the nanoscale. In this work, tip-enhanced Raman spectroscopy (TERS) mapping is used to probe the spatial distribution and local heterogeneity of poly(3,4-ethylenedioxythiophene) (PEPOT) and solid-state-polymerized polythiophene (SSp-PTh) blends with different compositions (1:5, 1:10, and 1:20).

The TERS response evolves systematically with blend composition, revealing changes in the position and linewidth of the main vibrational features together with the progressive emergence and attenuation of characteristic bands of the two polymer components. Beyond conventional spectral analysis, the intensity ratio between selected PEPOT and SSp-PTh TERS bands is exploited as a spectroscopic marker of local composition. Spatially resolved TERS maps provide a direct visualization of the molecular landscape of the blends, revealing an overall homogeneous distribution of the two components in the investigated areas, without evidence of large-scale phase segregation, while simultaneously highlighting local compositional fluctuations.

These results highlight the capability of TERS mapping not merely to identify the chemical fingerprints of polymer blends, but to resolve their local compositional landscape and uncover subtle heterogeneities that remain hidden in conventional ensemble-averaged measurements. The combination of nano-Raman imaging and scanning-probe characterization provides a powerful framework for linking molecular-scale organization to the electronic functionality of complex polymer systems.