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Chiral Discrimination by TERS

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Abstract

Tip-enhanced Raman scattering (TERS) using a silver tip that is chemically modified by an achiral para-mercaptopyridine (pMPY) probe molecule has been utilized for chiral discrimination. Differences in the relative intensities of the pMPY bands in the TERS spectra were used to monitor three pairs of enantiomers containing hydroxy (-OH) and/or amino (-NH₂) groups. The ND or N⁺-H functionality of the pMPY-modified tip is concerned with hydrogen-bond interactions with a particular molecular orientation of each chiral isomer. The asymmetric arrangement of silver atoms at the apex of the tip causes an asymmetric electric field, which makes the tip a chiral center. Variations in the charge-transfer (CT) states of the metal-achiral probe system in conjunction with the asymmetric electric field cause different enhancements in the Raman signals of the two enantiomers. The near-field effect of the asymmetric electric field induces further chiral discrimination.

Keywords: TERS, charge transfer, chirality, hydrogen bonding, Raman spectroscopy

Reference:

[1] Thanyada Sukmanee, Kanet Wongravee, Yasutaka Kitahama, Sanong Ekgasit, Tamitake Itoh, Prompong Pienpinijtham and Yukihiro Ozaki, *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.202005446