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Chiral Discrimination by TERS

Thanyada Sukmanee^{1,2}, Kanet Wongravee², Yasutaka Kitahama¹, Sanong Ekgasit²,
Tamtake Itoh³, Prompong Pienpinijtham² and Yukihiro Ozaki¹

¹*Department of Chemistry, School of Science and Technology, Kwansei Gakuin University
2-1 Gakuen, Sanda, Hyogo 669-1337 (Japan)*

²*Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University,
254 Phayathai Rd., Pathumwan, Bangkok 10330 (Thailand) And
National Nanotechnology Center of Advanced Structural and Functional Nanomaterials, Faculty of
Science, Chulalongkorn University,
254 Phayathai Rd., Pathumwan, Bangkok 10330 (Thailand)*

³*National Institute of Advanced Industrial Science and Technology (AIST), Takamatsu, Kagawa
761-0395 (Japan)*

E-mail: ozaki@kwansei.ac.jp

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, Tamtake Itoh, Prompong Pienpinijtham and Yukihiro Ozaki, *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.202005446