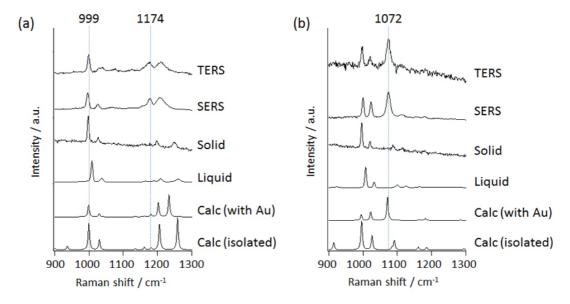
Supporting information

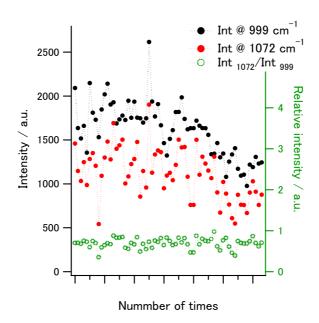
Nano-scale characterization of binary self-assembled monolayers under an ambient condition with STM and TERS

Noriko N. Horimoto, *a+ Shigeru Tomizawa, a Yasuhiko Fujita, a Shinji Kajimoto and Hiroshi Fukumura *a

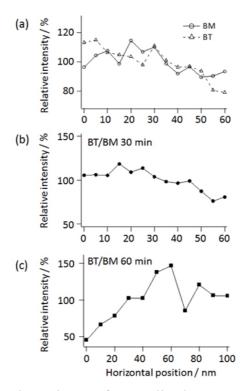
- ^a Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki Aoba, Sendai 980-8578, Japan. Fax: +81 22 795 6570; Tel: +81 22 795 6567; E-mail: fukumura@m.tohoku.ac.jp
- ⁺ Present address: Center for Emergent Matter Science, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan. Fax: +81 48 462 1554; Tel: +81 48 462 1111 ext. 6318; E-mail: horimotoatpc@gmail.com



Supplement 1. Comparison of Raman spectra of (a) BM and (b) BT, showing the chemisorption of BM and BT molecules onto gold surfaces. TERS spectra were taken at Au(111) surfaces by approaching gold tips, while SERS spectra were taken at rough gold surfaces after adsorption of nanoparticles on the surfaces. Note that the peaks at 1174 cm⁻¹ for BM and 1072 cm⁻¹ for BT adsorbed on gold surfaces were shifted from the original solid or liquid samples with the adsorption.



Supplement 2. A typical example showing temporal changes of TERS spectral lines measured on a BT/BM binary SAM (30 min immersion of a BM sample in BT solution). Both peaks at 999 cm⁻¹ (BM and BT) and 1072 cm⁻¹ (BT) gradually decayed with time, whereas the ratio of the two peaks remained nearly constant.



Supplement 3. Position dependence of normalized TERS peak relative intensity of SAMs on Au(111). TERS spectra were measured at different positions on a single sample surface, within a region of 60 x 60 nm for (a), (b) and 100 x 100 nm for (c). Intensity ratios between specific TERS peaks were calculated, and were normalized so that the average value will be "100%". (a) BM-SAM, I_{1174}/I_{1209} and BT-SAM, I_{999}/I_{1072} (b) BT/BM-binary-SAM (30min exchange with BT), $(I_{1174}+I_{1209})/I_{1072}$ (c) BT/BM-binary-SAM (60min exchange with BT), $(I_{1174}+I_{1209})/I_{1072}$.