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SERS and RAIR for Molecular Structure of Phenylazonaphthalene-terminated Self-Assembled Monolayer

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Abstract: The SAMs of 10-[4-(4-phenylazo)naphth-1-oxyl]-1-decanethiol (Compound **1**) on gold were prepared. Their molecular structures were determined by surface enhanced Raman spectroscopy (SERS) and reflection absorption infrared spectroscopy (RAIR).

Keywords: Self-assembled, SERS, RAIR.

Aromatic azo-based SAMs are attractive because of their possibilities for fabrication of data storage molecular devices[1-2]. The system of azobenzene-based alkylthiol on gold is one of the most intensive studies, which has a highly ordered and closely packed structure. The dense packing, however, limits the electroactivity of azobenzene. Therefore, another kind of aromatic azo molecule, phenylazonaphthalene, is considered as a substitute..

The SAMs of 10-[4-(4-phenylazo)naphth-1-oxyl]-1-decanethiol (compound **1**) on gold were prepared in this work. Their molecular structures were determined by surface enhanced Raman spectroscopy (SERS) and reflection absorption infrared spectroscopy (RAIR). All Spectra were recorded on Bruker IFS 55/FRA 106 spectrometer.

Figure 1a illustrates normal Raman spectrum of compound **1**. Several characteristic bands of the phenylazonaphthyl moiety at 1592, 1463 and1372 cm^{-1} are observed, which are assigned to ring stretching vibration of phenyl ring, N=N stretching vibration mode of azo, stretching vibration of naphthyl ring, respectively. A weak band near 2567 cm^{-1} is assigned to the S-H stretching vibration. From the SERS spectrum of compound **1**, as shown in **Figure 1b**, S-H band completely disappears while the band near 615 cm^{-1} due to stretching vibration of C-S band is clearly enhanced, confirming the self assemble of compound **1** on gold involves cleavage of the S-H bond and subsequent formation of S-C bond. Moreover, all the bands appearing in the SERS spectrum are originated from in-plane modes of phenylazonaphthyl moiety of compound **1**. According to SERS selection rules[3], aromatic rings are likely to be perpendicular to gold substrate.

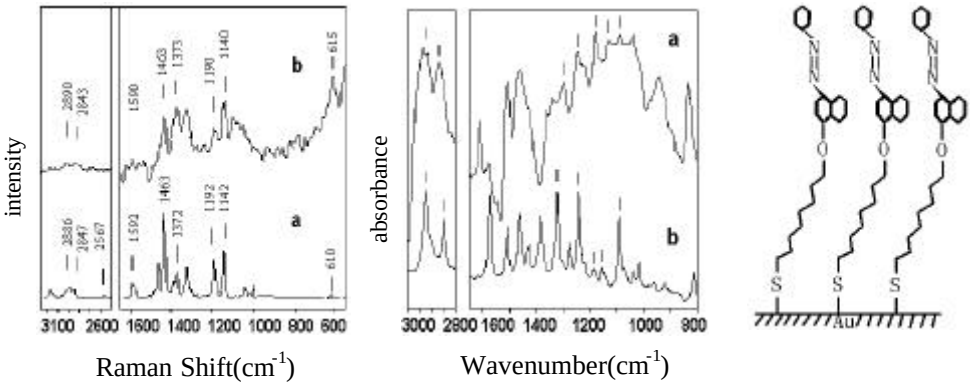
Furthermore, RAIR technique was used to measure the SAMs of compound **1** on a smooth gold film. **Figure 2a** displays p-polarized RAIR spectrum of compound **1** on gold. The absorbances of the stretching vibration mode of naphthalene-N at 1322 cm^{-1}, naphthalene-O at 1241 cm^{-1}, alkyl C-C at 1189 cm^{-1}, benzene-N near 1153cm^{-1} and C-O

at 1090 cm^{-1}, whose transition dipole moments are parallel to the molecular axis of compound **1**, appear in p-polarized RAIR spectrum. From the selection rule that only vibrational modes whose transition dipoles have a major component normal to surface are RAIR active, it is concluded that both phenylazonaphthyl moiety and alkyl backbone are arranged with their axes perpendicular to gold surface.

Figure 1 (a) Normal Raman spectrum of compound **1** (b) SERS spectrum of compound **1** on a gold island film

Figure 2 (a) RAIR spectrum of compound **1** assembled on a smooth gold film (b) IR spectrum of Compound **1**

Figure 3 A model of SAMS of compound **1** on gold



The *p*-polarized IRAS spectrum on gold shows two strong absorbances related to CH_2 symmetric and asymmetric vibrations at 2851 and 2933cm^{-1}, indicative of trans-extended CH_2 backbones in the SAMs. Compared to the absorption at 2922cm^{-1} in the transmission infrared spectrum of compound **1**, the absorption centered at 2933cm^{-1} in the SAMs is broader. The methyl group might be twisted and therefore more loose packing in the SAMs than in solid state. Based on the above analysis, a model in which the alkyl group with *trans*-extended chain upright on gold substrate and terminal functional group with aromatic rings perpendicular to the substrate is assumed in **Figure 3**.

Overall, SERS and *p*-polarized RAIR techniques are used to characterize molecular array of 10-[4-(4-phenylazo)naphth-1-oxyl]-1-decanethiols SAMs on gold. In the SAMs, alkyl chains are *trans*-extended, twisted and upright on the gold substrate.

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