

Electronic Supplementary Information

Surface-Enhanced Raman Scattering of 4,4'-Dimercaptoazobenzene Trapped in Au Nanogaps

Kwan Kim,^{*a} Dongha Shin,^a Kyung Lock Kim,^a and Kuan Soo Shin^{*b}

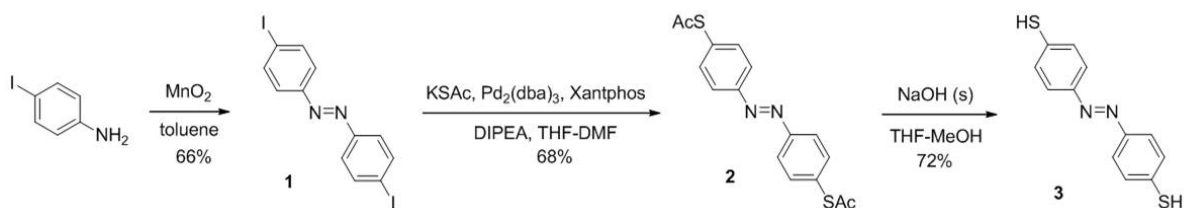
^a*Department of Chemistry, Seoul National University, Seoul 151-742, Korea. E-mail:*

kwankim@snu.ac.kr; Fax: +82 2 889 1568; Tel: +82 2 880 6651

^b*Department of Chemistry, Soongsil University, Seoul 156-743, Korea. E-mail:*

kshin@ssu.ac.kr; Fax: +82 2 824 4383; Tel: +82 2 820 0436

Figure S1. Synthesis of 4,4'-dimercaptoazobenzene (4,4'-DMAB)



Step 1: A 250 mL two-necked flask equipped with a stirrer and a reflux condenser was loaded with 4-iodoaniline (6.83 g, 31.2 mmol, 1.0 eq.), MnO_2 (10.8 g, 125 mmol, 4.0 eq.), and toluene (180 mL). The reaction mixture was boiled for 6 h, the precipitated was filtered off, the solvent was evaporated on a rotor evaporator, and the residue was recrystallized from heptanes to give the product **1** as an orange crystal (4.45 g, 10.2 mmol, 66%).

Step 2: 4,4'-Diiodo-azobenzene (**1**) (4.23 g, 9.76 mmol, 1.0 eq.), potassium thioacetate (6.69 g, 58.5 mmol, 6.0 eq.), $\text{Pd}_2(\text{dba})_3$ (893 mg, 0.976 mmol), xantphos (1.13 g, 1.95 mmol, 0.2 eq.), and DIPEA (14 mL, 78.0 mmol, 8.0 eq.) were suspended in an anhydrous mixture of DMF (30 mL) and THF (250 mL). The mixture was stirred at 100°C for 2 h and then cooled to ambient temperature. The reaction mixture was filtered through a celite pad. The filtrate was diluted with EtOAc and washed with water and brine. The organic layer was dried over MgSO_4 and evaporated to give a residue. The residue was purified by column chromatography (eluted with Hex:MC=2:1) to give the compound **2** (2.19 g, 6.62 mmol, 68%) as an orange solid.

Step 3: Sodium hydroxide (183 mg, 4.59 mmol, 3.0 eq.) was slowly added to a solution of compound **2** (505 mg, 1.53 mmol, 1.0 eq.) solved in MeOH (6 mL) and THF (24 mL). The mixture was stirred at room temperature for 30 min, concentrated, and then diluted with water (5 mL). After washing with EA, the aqueous phase was acidified to pH 2 with conc. HCl at 0°C . The precipitate was filtered to give the compound **3** (272 mg, 1.10 mmol, 72%) as a yellow solid.

Figure S2. Mass Spectra of 4,4'-DMAB (M.W. 246.35)

Liquid Chromatography Mass Spectrometer (Finnigan LCQ mass spectrometer, ThermoFinnigan, San Jose, CA)

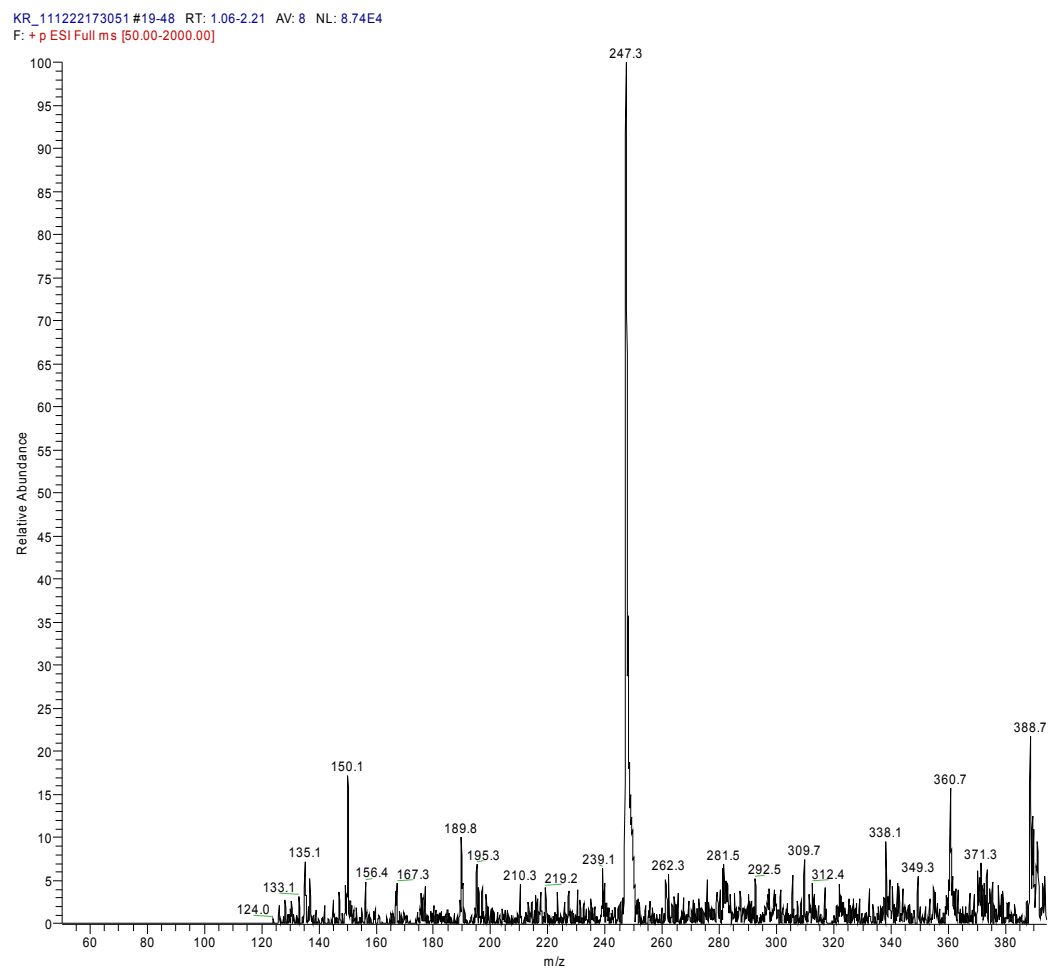


Figure S3. ¹H-NMR spectra of 4,4'-DMAB

¹H NMR (400 MHz, CDCl₃): δ. 7.8 (d, 4H), 7.4 (d, 4H), 3.6 (s, 2H).

