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nal group is well-tolerated in the boronic acid coupling partner (entries 6, 9, 10, 12). It is also well-tolerated in the halide coupling partner provided that the halogen atom is iodine (entries 7, 9, 10, 12). This coupling reaction could even be performed when both the boronic acid and the iodide coupling partners contain ortho tertiary benzamide groups (entries 9, 10, 11, 12). In this latter type of coupling, slightly lower yields were observed for the formation of quarterpheyls as compared to terphenyls. This is probably due to a buildup of steric congestion in these highly substituted oligomers.

The trimethylsily (TMS) group was successfully used as a protecting group for bromide or iodide owing to the stability of the TMS group under the Suzuki reaction conditions (entries 3, 4) and the ease with which aryl silanes undergo desilylation with bromine or iodine monochloride.[5] An example is shown in Scheme 1. Aryl diiodide 1 was mono-protected with a TMS group (2), and then transformed to boronic acid 3 in one pot. Boronic acid 3 was coupled with aryl dibromide 4 to give terphenyl 5 (entry 4) in 79.9% yield. Finally 5 was transformed to 6 by iododesilylation.

The representative heterogeneous coupling reaction for terphenyl 5 was performed as follows; Dibromide 4 (1.38 g, 5 mmol) and tetrakis (triphenyphosphine) palladium(0) (8.9 mg, 0.08 mol%) were dissolved in 20 ml of toluene. Boronic acid 3 (3.38 g, 12 mmol), 2 M sodium carbonate solution (10 ml), and ethyl alcohol (10 ml) were added. The mixture was refluxed for 24 hours and cooled to room temperature. The organic phase was separated and the aqueous phase was extracted with 20 ml of ether twice. The combined organic phases were dried with brine and then with anhydrous magnesium sulfate. The solvent was evaporated, and the crude mixture was purified by column chromatography (4× 30 cm, dichloromethane/hexane = 1/1). The pure product 5 was obtained in 79.7% yield (2.33 g) after crystallization from a mixture of dichloromethane and hexane.

In conclusion, good yields were usually obtained in Suzuki aryl-aryl coupling reactions, even when both coupling partners had a sterically hindered ortho substituent such as tertiary amide group.

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Roles of EDTA in Silver Sol-Fourier Transform Raman Spectroscopic Study Using Nd:YAG cw 1064 nm Excitation

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The silver colloidal suspension prepared by reduction of $AgNO_3$ with EDTA[1] has been used for surface-enhanced Raman scatting effects and surface adsorption behaviors of adsorbates. The silver colloids prepared with EDTA reduction procedures are significantly stable for additives, *e.g.*, acids, bases or adsorbates compared to colloids reduced with $NaBH_4$[2] or citrate[3]. It was reported[4] that they were stable for several hours even under pH = 4 condition. The intense yellow-brownish color developed during sol preparation with EDTA exhibited an absorption maximum at 414 nm. When colloids become aggregated to the larger size, they can turn color and develop another absorption band near the higher wavelength (in the range 500-700 nm). This requires understanding of the colloidal particle size. The average particle size of aqueous silver colloids determined by employing the proton correlation spectroscopy was about 20 nm in diameter[5]. The particle size was not much affected with time nor after addition of additives, such as pyridine, within experimental errors.

The excitation by cw 1064 nm of Nd:YAG laser has several advantages to the shorter wavelength exciation, *e.g.*, photodecomposition of photolabile compounds[6], non-resonant condition of chromophores[7,8], etc.. The excitation using 1064 nm is sufficiently far from surface plasmon absorption, from colloids absorption, or from the absorption of the possible charge-transfer complex between metal surface and adsorbates. Therefore this technique can provide well-defined non-resonant surface enhanced Raman spectra of adsorbed chromophores[7] of superior quality using Fourier transform advantages, coadding and multiplexing capabilities.[9] In this paper Fourier transform (FT) Raman spectroscopy using cw 1064 nm excitation is applied to elucidate the roles of EDTA which survived during silver sol preparation for the stability of EDTA-reduced silver colloids.

Figure 1 illustrates FT-Raman spectra of EDTA and EDTA-Ag$^+$ ion complex in various states between 800 and 1800 cm^{-1}. Figure 1(a) and 1(b) shows FT-Raman spectrum of disodium EDTA salt and tetrasodium EDTA salt in powder state, respectively. At a glance of above two spectra, the spectrum of tetrasodium EDTA is much simpler than that of disodium EDTA. It can mean better symmetry in the structure of tetraanion EDTA^{4-}. Two bands at 899 and 916 cm^{-1} in Figure 1(a) collapse into one broad band at 913 cm^{-1} in Figure 1(b). This band at 913 cm^{-1} is due primarily to the C-C stretching mode of C-CO$_2^-$ moiety of tetraanion EDTA. Splitting into two in the spectrum of dianion EDTA would indicate the nonequivalence of two C-C stretching modes between C-CO$_2$H and C-CO$_2^-$ moieties of disodium EDTA. Therefore two bands at 899 and 916 cm^{-1} in
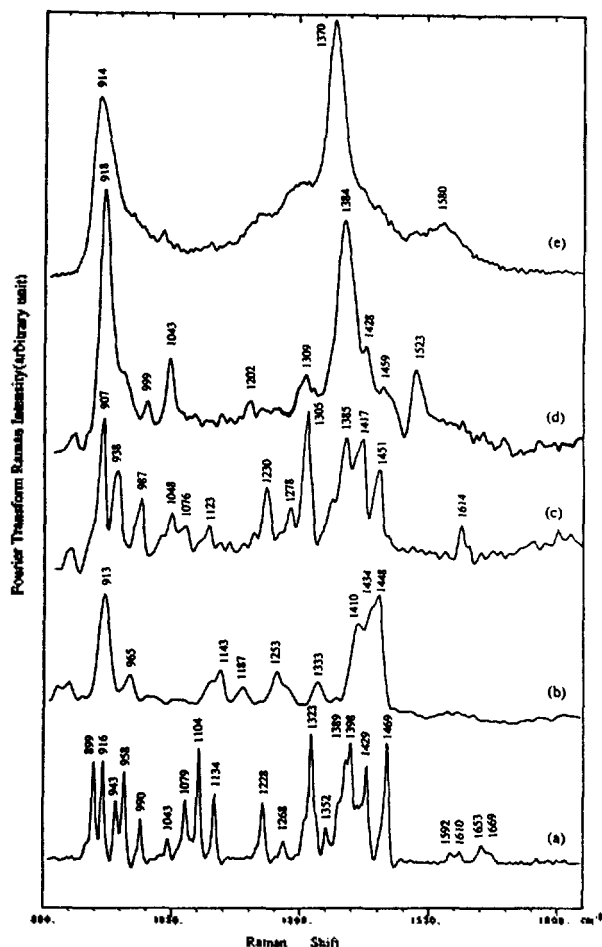
Figure 1. FT-Raman Spectra of (a) EDTA disodium salt in powder state (b) $4Na^+ : EDTA^{4-}$ salt in powder state (c) EDTA (2 $Na^+) : Ag^+$ 1 : 1 complex in powder state (d) EDTA $(2Na^+) : Ag^+$ 1 : 1 complex in 0.1 M aqueous solution (e) EDTA in aqueous silver colloids at pH=7.2 prepared by procedures in reference 4. Experimental Conditions : spectral resolution=10 cm^{-1}, coadding 1000 times. Powder samples (a), (b), and (c) were contained well packed in ordinary melting point capillary tube, and laser power was 0.1 watt at sample. Solution samples (d) and (e) were circulated with flow-rate 2 ml/min through a peristaltic pump in ordinary melting point capillary tube, and laser power was 0.8 watt at sample. Raman spectra were obtained employing Bomem DA3.002 spectrophotometer with liquid N_2 cooled InGaAS detector, cw 1064 nm excitation source from Quantronix Nd : YAG laser, quartz beam splitter, and back-scattering light collection optics.

Figure 1(a) can mean that there are equal numbers of protonated and ionized carboxylate groups. Similar observations had been reported from Raman spectra of EDTA at different pH values.[10] Further, Figure 1(a) has fair amounts of the C=O stretching intensities in the range 1640 to 1700 cm^{-1}. However there is only a trace intensity for those bands in Figure 1(b), FT-Raman spectrum of tetraanion EDTA. The antisymmetric stretching modes of carboxylate ions can be seen easily near 1600 cm^{-1} in Figure 1(a), but barely seen in Figure 1(b).

Figure 1(c) and 1(d) illustrate the FT-Raman spectrum

of disodium EDTA : Ag^+ 1 : 1 complex in powder state and in 0.1 M solution, respectively. These spectra have similar characteristics as observed in Figure 1(a) and 1(b). The symmetric stretching mode of carboxylate anions at 1384 cm^{-1} in Figure 1(d), Raman spectrum of silver complex with EDTA in solution, is unusually strong in intensity. The C-C stretching mode of $C-CO_2^-$ moiety at 918 cm^{-1} in Figure 1(d) also splits into two bands at 907 and 938 cm^{-1} in EDTA-silver ion complex. A band at 1043 cm^{-1} in Figure 1(c) can be assigned tentatively to the C-N stretching mode of EDTA. The frequency is a little lower than usual stretching frequency of the C-N stretching mode, partly because of the silver ion complexation to nitrogen. FT surface enhanced Raman spectrum of EDTA in silver colloid prepared with EDTA is illustrated in Figure 1(e). It has two strong bands at 914 and 1370 cm^{-1} due to the C-C stretching mode and the symmetric stretching mode of carboxylate anions, respectively.[11] The broad band near 1580 cm^{-1} is tentatively assigned to the C-O stretching mode[12] of $C-CO_2^-$ moiety. Though the mechanism is not yet clear enough for surface enhanced Raman scattering, the nears to surface can mean the higher enhancement under the non-resonant conditions according to electromagnetic effects. It can deduce that the carboxylate anions of EDTA are so close adsorbed on the metal surface to boost the intensities of Raman vibrational modes (in particular, symmetric stretching of CO_2^- and stretching of C-C) of $-C-CO_2^-$ moiety. But the antisymmetric stretching mode of carboxylate anions are not much active to Raman scattering as expected.[13] The negative charges of EDTA anions adsorbed on the silver metal surface become sufficiently even with the surface charges, mainly positive, of silver colloid. This may be responsible for silver sol not readily to aggregate further, and subsequently deteriorate by addition of additives and/or adsorbates or with time as previously observed.[4,5]

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