Abstract

SERS and SERRS (surface enhanced/resonance/Raman scattering) spectra of a dicationic Ru (II) bis(2,2’-bipyridine)(4,4’-dicarboxy-2,2’-bipyridine)/Ru(bpy)$_2$(dcbpy)/ complex in systems with aggregates of unmodified and/or chloride-modified Ag nanoparticles (NPs) were obtained and compared to those of dicationic Ru (II) tris(2,2’-bipyridine)/Ru(bpy)$_3$/ . The splitting of several bands and the appearance of a new band at 1367 cm$^{-1}$ observed solely in SERS and SERRS of Ru(bpy)$_2$(dcbpy) in the system with unmodified Ag NP aggregates was attributed to chemisorption of the complex onto Ag NP surface via two carboxylate groups. SERS/SERRS excitation profiles obtained for the spectral bands and attributed to the Ru-dcbpy unit of the chemisorbed Ru(bpy)$_2$(dcbpy)/ complex were found to maximize at 488 nm excitation, while those of the two Ru-bpy units peaked at 458 nm. Comparison of the profiles with the electronic absorption spectrum of free Ru(bpy)$_2$(dcbpy) has revealed that chemisorption of the complex causes a red-shift of the Ru→dcbpy charge transfer transition band. The observed decrease of the energy of the Ru→dcbpy charge transfer is explained by an increase of the electron-withdrawing ability of the two COO$^-$ groups upon their chemisorption on AgNP surface. Concentration value of SERRS spectral detection limits of complexes in systems with unified morphologies of AgNPs were compared at $\lambda_{exc} = 441.6$ nm. Detection limit of chemisorbed Ru(bpy)$_2$(dcbpy) is $1\cdot10^{-9}$ M and that of electrostatically bonded Ru(bpy)$_3$ $1\cdot10^{-12}$ M. The main contribution to the increase in Ru(bpy)$_2$(dcbpy) detection limit in comparison with Ru(bpy)$_3$ detection limit belongs to the stronger molecular resonance damping (roughly 500 times) which is caused by the direct adsorption of this complex on AgNP surface.