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 morfologies of AgNPs were compared at λ_{exc} = 441,6 nm. Detection limit of chemisorbed $Ru(bpy)_2(dcbpy)$ is $1 \cdot 10^{-9}$ M and that of electrostatically bonded $Ru(bpy)_3$ $1 \cdot 10^{-12}$ 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.

Key words: Ru (II) bis(2,2'-bipyridine)(4,4-dicarboxy-2, 2'-bipyridine), Ru (II) tris(2,2'-bipyridine), surface-enhanced (resonance) Raman scattering /SE(R)RS/, SE(R)RS excitation profile, SE(R)RS spectral detection limit, fractal aggregates of silver nanoparticles