

## Abstract

The work is focused on preparation and characterization of octahedral Fe(II) complexes of 2,2':6',2''-terpyridine (tpy) substituted in 4' position by various groups: Cl (tpyCl), chlorophenyl (tpyPhCl) and 2-thienyl (Ttpy).

Formation and stability of prepared complexes were studied by UV/vis spectroscopy on the basis of titration of tpy ligands by Fe(II) ions. The molar absorption coefficient of the metal-to-ligand charge transfer (MLCT) band was found to increase in the order: tpy < tpyCl < tpyPhCl < Ttpy. The MLCT band position increases in the same order, starting from 551 nm for  $[\text{Fe}(\text{tpy})_2]^{2+}$  to 576 nm for  $[\text{Fe}(\text{Ttpy})_2]^{2+}$ . Raman scattering (RS) spectra of tpy ligands were obtained upon non-resonance 780 nm excitation. Four excitation wavelengths (445, 532, 633 a 780 nm) were used for measurement Fe(II) complexes. The excitation profiles of both Raman scattering and surface-enhanced Raman scattering (SERS) spectra were constructed for  $[\text{Fe}(\text{tpyCl})_2]^{2+}$  complex. On the basis of DFT calculations performed for this complex, the Raman active modes have been assigned to the symmetry species of the  $D_{2d}$  point group. Similarly as for the previously studied  $[\text{Fe}(\text{tpy})_2]^{2+}$  complex, activation of E modes in the region of MLCT band suggests contribution of Herzberg-Teller mechanism to the overall molecular resonance enhancement. The maximal enhancement of all Raman active bands in RS spectra was observed at excitation 532 nm. On the other hand, several bands with maximal enhancement at 633 nm excitation were found. Comparison with the spectrum obtained by DFT calculation and graphical display of the vibration modes showed these bands to be mainly in-plane vibrations of side pyridine rings of tpy unit. Therefore, some changes in molecular geometry in the excited state of the complex at this excitation occur if the complex is adsorbed on the Ag nanoparticle (AgNP) surface. The reason for it seems to be interaction of Cl atom in the 4' position of tpy with AgNP surface. Moreover, beyond the study, time evolution of SERS signal of the AgNP/  $[\text{Fe}(\text{tpyCl})_2]^{2+}$  system after addition of ethanol has been followed. Treatment of the spectral series by factor analysis enabled to obtain information about changes in surface-plasmon extinction spectra, about the aggregation stage of the system directly from the SERS spectra.

**Keywords:** 2,2':6',2''-terpyridin,  $[\text{Fe}(\text{tpyCl})_2]^{2+}$  complex, vibration spectroscopy, Raman scattering, resonance Raman scattering, surface-enhanced Raman scattering, surface plasmon extinction spectra, excitation profile