

Abstract

$[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) and its dicarboxybipyridine derivatives, namely $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$ (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) and $[\text{Ru}(\text{dcbpy})_3]^{2+}$, were employed as model molecular ions for investigation of the mechanism of surface-modified luminescence, of light-induced surface reactivity of adsorbates in systems with Ag nanoparticles (NPs), and as prospective photoexcited reductants of Ag^+ ions capable of in-situ generation of Ag NPs. The steady state and the nanosecond time resolved luminescence (namely, $^3\text{MLCT}$ phosphorescence) of the $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$ chemisorbed onto the non-aggregated Ag NPs has been investigated and compared to those of the electrostatically bonded $[\text{Ru}(\text{bpy})_3]^{2+}$. The intensity decrease of the emission and the excitation spectra observed for both complexes upon their attachment to Ag NPs has been attributed to the overlap of the excitation spectra with the surface plasmon extinction (SPE) of Ag NPs. This overlap enabled energy transfer from $^3\text{MLCT}$ excited state of the complexes to the excited surface plasmon state of Ag NPs. Additionally, it was proved that the chemisorption of the complexes manifests itself by at least one order of magnitude shorter $^3\text{MLCT}$ excited state lifetime than the electrostatic interaction. Furthermore, by the newly developed strategy based on targeted SERRS and SERS (surface-enhanced (resonance) Raman scattering) spectral probing and monitoring supported by factor analysis, UV/vis spectral measurements and TEM imaging, $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$ and $[\text{Ru}(\text{dcbpy})_3]^{2+}$ were shown to undergo a plasmon catalysed decarboxylation reaction in systems with Ag NPs containing Ag(0) adsorption sites. The mechanism of charge carrier generation has been established as the most probable mechanism of these reactions. The presence of Ag(0) adsorption sites on Ag NP surfaces has been determined as the necessary condition of the reaction progress. These sites create the interface required for the transport of hot electrons (e^-) to H^+ co-reactants complementing thus the C–C bond breaking and CO_2 formation caused by hot holes (h^+). Finally, introduction of two or six strongly electron withdrawing carboxylate groups into the structure of parent $[\text{Ru}(\text{bpy})_3]^{2+}$ was found to selectively affect the ability of the resulting complex to act as a photoexcited reductant of Ag^+ ions and to generate Ag NPs in situ. For $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$, generation of Ag NPs was detected by the increase of the RRS signal of the complex into the SERRS one and by obtaining the TEM images of the in situ formed Ag NP. By contrast, for $[\text{Ru}(\text{dcbpy})_3]^{2+}$, the presence of six carboxylate groups in the complex structure lead to the lost of this ability of the photoexcited complex.