

Excited state reaction of [(2-carboxypyridinato)bis(2,2'-bipyridine)ruthenium(II)] ion with phenolate ions

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Photoinduced electron transfer (PET) reaction of homoleptic *tris*-chelated polypyridine ruthenium(II) complexes with phenolate ions is sensitive to the structure of the ligand of the Ru(II) complex as well as of the phenolate ions¹. In recent years² the photophysical and photochemical properties of Ru(II) complexes based on ligands that include coordinating atoms other than nitrogen have been generally explored. When picolinic acid (PA) is used as the ligand, it is coordinated to the metal via the carboxylate ion and the nitrogen atom. In the present study we have synthesised [(2-carboxypyridinato)bis(2,2'-bipyridine)ruthenium(II)] ion $[\text{Ru}^{\text{II}}(\text{PA})(\text{bpy})_2]^+$ and studied the photophysics and PET reaction of *tris*-chelated heteroleptic ruthenium(II) complex with several phenolate ions and compared the results with those observed for the parent complex, $\text{Ru}(\text{bpy})_3^{2+}$.

The wavelength (λ_{max}) of absorption (477 nm) and emission (645 nm) maxima of $[\text{Ru}^{\text{II}}(\text{PA})(\text{bpy})_2]^+$ are red-shifted compared to $\text{Ru}(\text{bpy})_3^{2+}$ and emission lifetime (τ) is less (120 ns) at room temperature. Phenolate ions containing electron-releasing groups form a ground-state complex with $[\text{Ru}^{\text{II}}(\text{PA})(\text{bpy})_2]^+$ but quench the emission by electron transfer mechanism. The luminescence quenching of $^*[\text{Ru}^{\text{II}}(\text{PA})(\text{bpy})_2]^+$ with ArO^- is less efficient compared to that of $^*\text{Ru}(\text{bpy})_3^{2+}$. The excited-state reduction potentials of $[\text{Ru}^{\text{II}}(\text{PA})(\text{bpy})_2]^+$ and $\text{Ru}(\text{bpy})_3^{2+}$ are 0.57 V and 0.80 V respectively. The excited state reaction of $[\text{Ru}^{\text{II}}(\text{PA})(\text{bpy})_2]^+$ with ArO^- is explained using a scheme involving complex formation between the reactants in the ground state.

References

1. Rajagopal S *et al* 1998 *J. Chem. Soc., Faraday Trans.* **94** 3339
2. Norrby T *et al* 1997 *Inorg. Chem.* **36** 5850