

## Dinuclear ruthenium(II) and/or osmium(II) complexes of bipyridyl ligands bridged by rigid spacers: Synthesis, electrochemical behaviour, absorption spectra and luminescence properties

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Supramolecular Ru(II) and Os(II) polypyridyl chemistry gained considerable interest due to their rich electrochemical and photophysical properties and potential use in a variety of energy/electron transfer processes. Such systems can be developed by covalent linking of prefabricated molecular components (building blocks) with spacers having bidentate donor sets. Suitable choice of the building blocks and appropriate designing of the structure can, in fact, allow the occurrence of energy/electron transfer along the supramolecular array. With a view to develop such systems, new bridging ligands, 1,4-*bis*[4-(4-methyl)-2,2-bipyridyl]imine]benzene (BL1) and 4,4-*bis*[4-(4-methyl)-2,2-bipyridyl]imine]benzene (BL2) and their dinuclear complexes of the type [(bpy)<sub>2</sub>Ru-BL1/BL2-Ru(bpy)<sub>2</sub>]<sup>4+</sup>, [(bpy)<sub>2</sub>Os-BL1/BL2-Os(bpy)<sub>2</sub>]<sup>4+</sup> and [(bpy)<sub>2</sub>Ru-BL1/BL2-Os(bpy)<sub>2</sub>]<sup>4+</sup> have been synthesized. For the synthesis of heterodinuclear complexes a new strategy has been adopted, which eliminates the possibility of the presence of homodinuclear complexes as impurity. Mononuclear model complexes [(bpy)<sub>2</sub>RuL1]<sup>2+</sup>, [(bpy)<sub>2</sub>OsL1]<sup>2+</sup> and [(bpy)<sub>2</sub>RuL2]<sup>2+</sup>, where L1 = [4-(4-methyl)-2,2-bipyridyl]imine]-4-aminobenzene and L2 = [4-(4-methyl)-2,2-bipyridyl]imine]-4-aminodiphenylene, have been prepared. Ligands and metal complexes were characterized on the basis of elemental analysis, FAB mass, IR, and <sup>1</sup>H NMR data. All metal complexes exhibit characteristic MLCT absorption bands in the visible region. They also show luminescence bands at room temperature. Cyclic and square wave voltammograms of all complexes exhibit metal-based oxidations (M(II)/(III)) in the potential ranges +1.20 to +1.23 V for Ru(II) and +0.75 to +0.82 V for Os(II). Ligand-based reductions occurred in the potential range -1.28 to -1.90 V. Mixed-valence species of the dinuclear complexes were generated by the addition of standard solution of ammonium cerium(IV) nitrate, and the properties of the mixed valence species have been studied. The emission state lifetimes of all complexes were measured at room temperature. The homodinuclear complexes exhibit significantly long lifetimes due to delocalization of the excited electron on the conjugated bridging unit. In heterodinuclear complexes the Ru-based emission lifetimes decreased significantly due to energy transfer from the Ru-unit to the Os-based unit.