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Synthesis, characterization and photophysical studies of supramolecular metal complexes of ruthenium(II)

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A unique combination of chemical stability, redox properties, luminescence emission and excited state reactivity made $Ru(bp)_2^{2+}$ ion (bp = 2,2′ bipyridyl) and its derivatives attractive candidates for designing polynuclear (supramolecular) complexes capable of performing useful light induced functions like light harvesting and conversion of light energy into chemical/electrical energy. To achieve these specific objectives we have synthesised three new polynucleating ligands; L_1 (having two similar 2,2′-bp derivatives covalently linked to a dissimilar bridging 2,2′-bp), L_2 and L_3 (having four 1,10-phenanthroline derivatives covalently linked by aliphatic/aromatic moieties respectively). Reactions of $Ru(2,2'\text{-bp})_2Cl_2$ with L_1 afforded a new asymmetric A_2B type trinuclear complex C_1, while reactions with L_2 and L_3 yielded two new symmetrical tetranuclear complexes (C_2 and C_3). All the ligands and their corresponding polynuclear complexes are characterised. Cyclic voltammetric and square wave voltammetric studies show weak ground state interaction ($\sim$ 130 mV; for $Ru^{II/III}$ couple) between the two dissimilar Ru-centres in C_1, whereas $Ru^{II/III}$ couple for tetranuclear complexes, C_2 and C_3, occurs at the same potential. Excitation of all these complexes at their LMCT band (455–460 nm) generated ^{3}MLCT excited state. $\tau_{1/2}$ for the respective complexes are 360 ns for C_1, 250–300 ns for C_2 and C_3. Results of the photophysical studies relating to the photoinduced energy electron transfer pathways in the supramolecular pathway energy-electron will be presented.

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