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Inorganic Chemistry Communications 10 (2007) 307–312
INORGANIC CHEMISTRY COMMUNICATIONS
www.elsevier.com/locate/inoche

A structurally diverse mixed-metal complex with mixed bridging ligands $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$: Modulating orbital energetics within a supramolecular architecture

Ran Miao, Karen J. Brewer *

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212, United States

Received 20 August 2006; accepted 5 October 2006
Available online 28 October 2006

Abstract

A structurally diverse supramolecular complex, $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$, has been prepared (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, and dpq = 2,3-bis(2-pyridyl)quinoxaline). The supramolecular assembly contains four light absorbing osmium metal centers coupled to two ruthenium metal centers linked by two different bridging ligands (BL) capped by bpy terminal ligands. This supramolecule possesses a lowest unoccupied molecular orbital (LUMO) localized on the central μ-dpq bridging ligand (BL) and a highest occupied molecular orbital (HOMO) localized on the terminal Os centers, providing significant spatial separation of these donor and acceptor orbitals. This hexametallic complex absorbs throughout the visible region due to overlapping singlet metal-to-ligand charge transfer (MLCT) transitions from the Os and Ru chromophores to each π-acceptor ligand. The Os based ^{3}MLCT bands extend into the near-infrared. The light absorbing and redox properties for this hexametallic complex have been elucidated using smaller model fragments and spectroelectrochemistry.

Keywords: Supramolecular; Ruthenium complexes; Osmium complexes; Bridging ligand; Electrochemical properties; Spectroscopy; Spectroelectrochemistry

The synthesis and study of ruthenium and osmium polyazine complexes is an area of great interest [1–3]. These complexes are efficient light absorbers with tunable properties and highly-studied metal-to-ligand charge transfer (MLCT) excited states. Interest in supramolecular assemblies of Ru and Os explores their promise as photochemical molecular devices for a wide variety of applications [2,4]. Developing synthetic methods and understanding properties of supramolecular complexes with widely varied building blocks will aid in the development of the complicated systems needed for many applications [2,5–8]. Within this framework we have designed a mixed-bridging-ligand, mixed-metal hexametallic assembly $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, and dpq = 2,3-bis (2-pyridyl)quinoxaline) (Fig. 1).

The title supramolecular complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ has an extended structure with four terminal $(bpy)_2Os^{II}$ centers bridged by four μ-dpp ligands to two Ru centers connected to one central μ-dpq bridging ligand. Reported herein is the application of a building block strategy to assemble this hexametallic complex and related trimetallic $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ systems with characterization by MALDI-TOF and FAB MS, elemental analysis, electronic absorption spectroscopy, square wave voltammetry and spectroelectrochemistry.

Mixed-metal, mixed-ligand supramolecular complexes can be assembled in high yield, ca. 90%, using a building block synthetic method. Typically, terminal ligands like

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* Corresponding author. Tel.: +1 540 231 6579; fax: +1 540 231 3255.
E-mail address: kbrewer@vt.edu (K.J. Brewer).

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doi:10.1016/j.inoche.2006.10.016

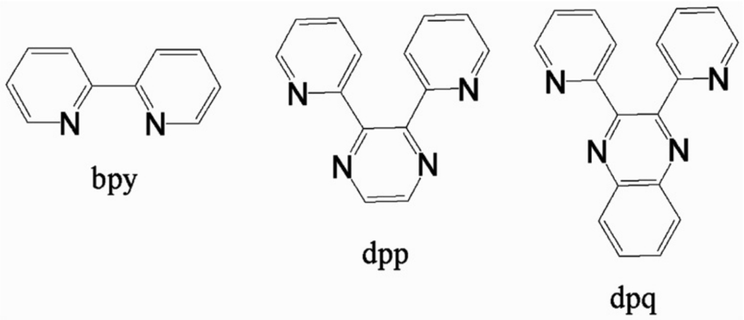

Fig. 1. Structures of the polyazine ligands bpy, dpp and dpq (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline).

bpy are bound to metals first, followed by bridging ligand incorporation and supramolecular assembly (Fig. 2).

$[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ was synthesized by modification of the published building block methodology. $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ was synthesized by a

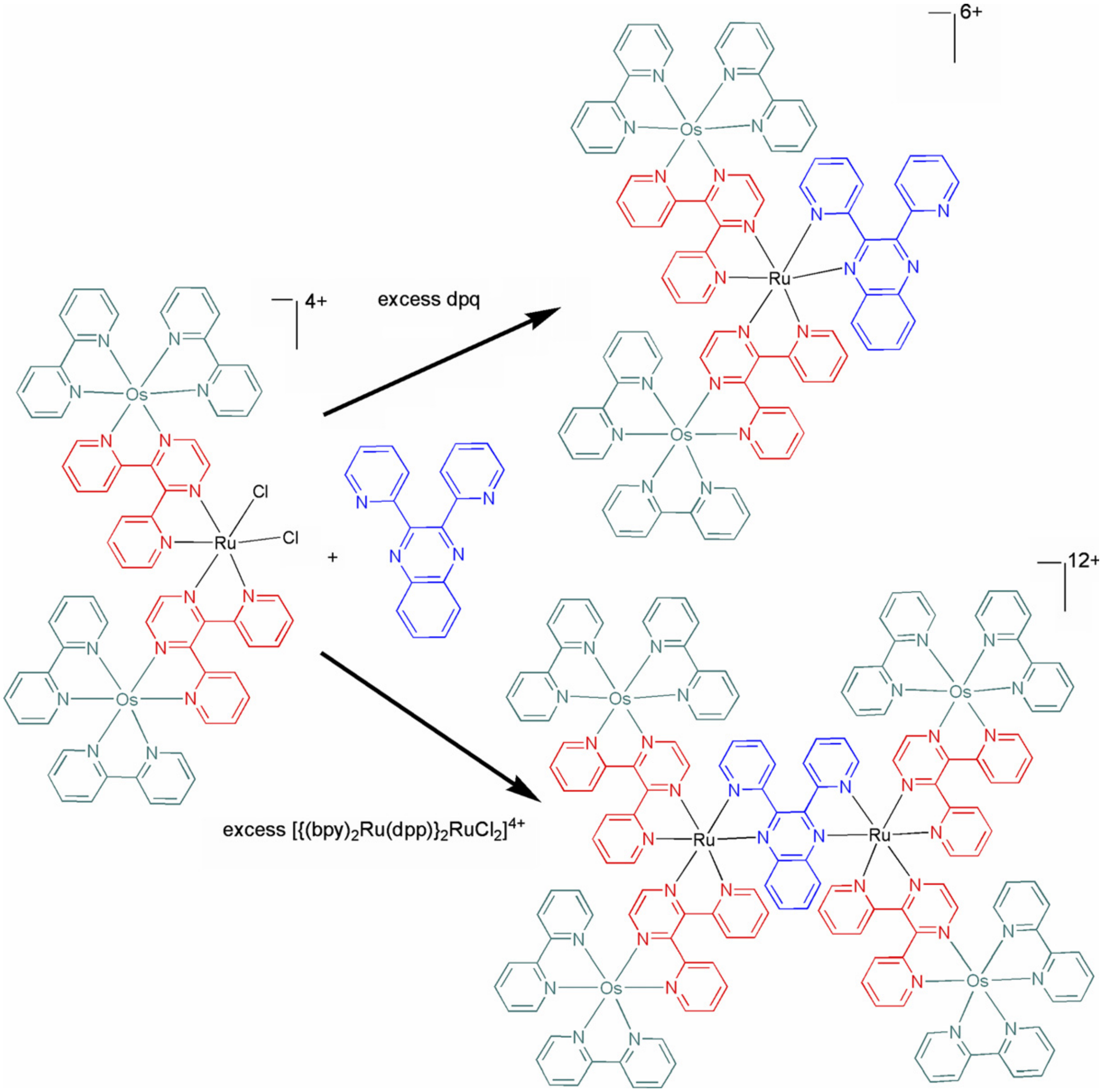

Fig. 2. Stoichiometric control of supramolecular synthesis producing preferentially a trimetallic $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ or hexametallic assembly $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline).