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Inorganic Chemistry Communications 10 (2007) 307–312
INORGANIC CHEMISTRY COMMUNICATIONS
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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

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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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doi:10.1016/j.inoche.2006.10.016

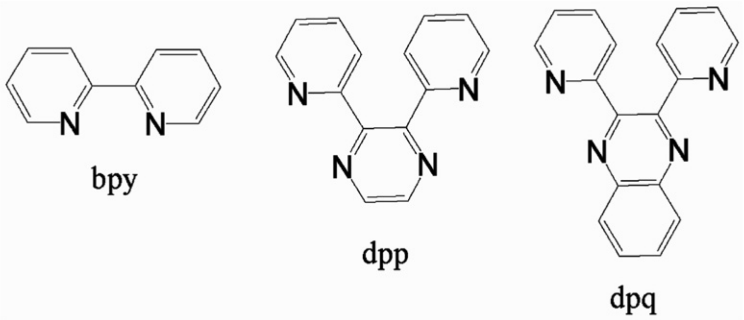

Fig. 1. Structures of the polyazine ligands bpy, dpp and dpq (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline).

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

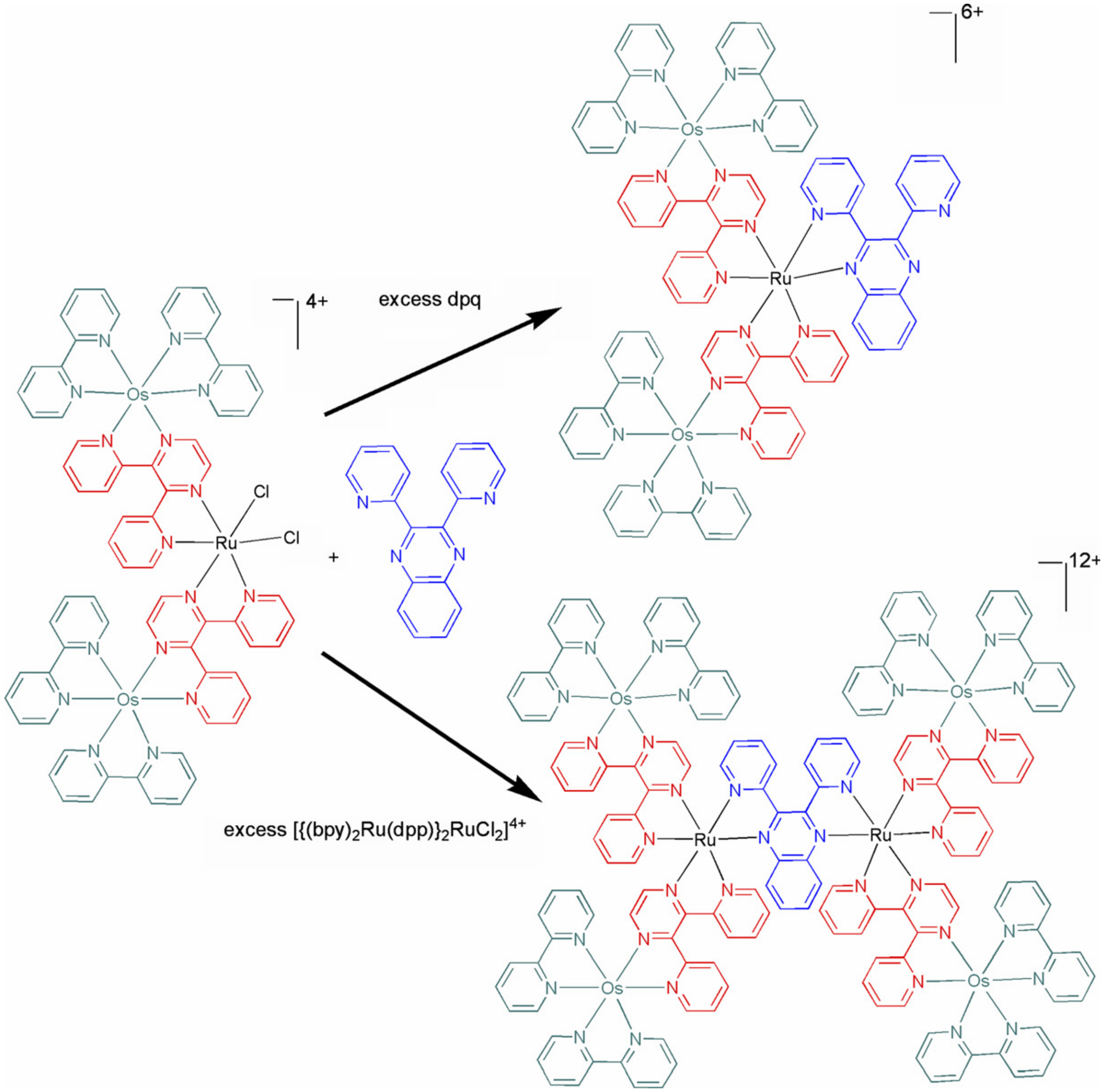

Fig. 2. Stoichiometric control of supramolecular synthesis producing preferentially a trimetallic $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ or hexametallic assembly $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline).

building block method. The complex $[(bpy)_2OsCl_2]$ is assembled first by reaction of bpy with $OsCl_3 \cdot 3H_2O$, then $[(bpy)_2OsCl_2]$ is combined with the dpp bridging ligand to yield $[(bpy)_2Os(dpp)]^{2+}$. This light absorbing building block $[(bpy)_2Os(dpp)](PF_6)_2$ is coupled to a central Ru to yield $[\{(bpy)_2Os(dpp)\}_2RuCl_2](PF_6)_4$ which is coupled to dpq to produce the title $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$.[1] The modified preparation of trimetallic compound $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ [5] enhances yield and simplifies purification by the sequential addition of the dichloro metal complex precursor into refluxing dpq solution. This method provides an excess of dpq in solution, available to bind to the dichloro precursor $[\{(bpy)_2Os(dpp)\}_2RuCl_2](PF_6)_4$ immediately upon chloride loss. Conversely, the slow addition of the dpq ligand, into a refluxing solution of the dichloro precursor, $[\{(bpy)_2Os(dpp)\}_2RuCl_2](PF_6)_4$, maintains a limited amount of available dpq ligand and produces the desired hexametallic compound in good yield. In both cases, Ag^+ was added to scavenge free chloride.

The electrochemical properties of the title hexametallic complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ and trimetallic complex $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ are summarized in Table 1 with reductive square wave voltammograms shown in Fig. 3 [5].

One reversible couple is observed by CV in the oxidative region, corresponding to the simultaneous oxidation of the four peripheral Os centers, $4Os^{II/III}$, indicative of a lack of electronic coupling of these spatially separated chromophoric metals. Several overlapping redox couples are observed in the reduction region for $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ and $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$. Given the supramolecular nature of the hexametallic complex, the reductive electrochemistry is expected to be complicated. The hexametallic $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ and the trimetallic $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ have similar electroactive units except the hexametallic complexes possesses a μ-dpq ligand instead of the terminal dpq in the trimetallic. The trimetallic complex $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ displays two μ-$dpp^{0/-}$ couples prior to the terminal $dpq^{0/-}$ couple, consistent with a bridging dpp and terminal dpq ligand. The separate dpp couples illustrate the two dpp ligands are electronically coupled in this structural motif. The redox properties of the hexametallic complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ are consistent with its formulation. The first reduction of dpq occurs at −0.48 V for the hexametallic complex, consistent with a bridging dpq. The μ-$dpq^{0/-}$ couple is followed closely by a set of two μ-$dpp^{0/-}$ couples at −0.66 and −0.84 V, representing the simultaneous reduction of one and then the second dpp bound to each Ru center. The second reduction of dpq and each dpp is followed by terminal bpy reduction (Fig. 4).

Table 1
Electrochemical properties of the hexametallic $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$, trimetallic $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ and related model supramolecular assemblies[a] (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline)

Complex	$E_{1/2}$(V)	Assignment
$[(bpy)_2Ru(dpp)Os(bpy)_2]\ (PF_6)_4$[b]	1.56	$Ru^{II/III}$
	1.01	$Os^{II/III}$
	−0.62	μ-$dpp^{0/-}$
	−1.03	μ-$dpp^{-/2-}$
$[(bpy)_2Ru(dpq)Ru(bpy)_2](PF_6)_4$[c]	1.57	$Ru^{II/III}$
	1.42	$Ru^{II/III}$
	−0.42	μ-$dpq^{0/-}$
	−1.15	μ-$dpq^{-/2-}$
$[(bpy)_2Ru(dpq)](PF_6)_2$[c]	1.36	$Ru^{II/III}$
	−0.83	$dpq^{0/-}$
	−1.46	$bpy^{0/-}$
$[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$	1.17	$4Os^{II/III}$
	−0.48	μ-$dpq^{0/-}$
	−0.66	2μ-$dpp^{0/-}$
	−0.84	2μ-$dpp^{0/-}$
	−1.2	μ-$dpq^{-/2-}$, 2μ-$dpp^{-/2-}$
	−1.4	2μ-$dpp^{-/2-}$
		$4bpy^{0/-}$
	−1.8	$4bpy^{0/-}$
$[(\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$	1.07	$2Os^{II/III}$
	−0.56	μ-$dpp^{0/-}$
	−0.71	μ-$dpp^{0/-}$
	−0.88	$dpq^{0/-}$
	−1.2	2μ-$dpp^{-/2-}$
	−1.4	$2bpy^{0/-}$, $dpq^{-/2-}$
	−1.8	$2bpy^{0/-}$

[a] Square wave voltammetry is measured in 0.1 M Bu_4NPF_6 CH_3CN solution at room temperature at a scan rate 200 mV/s (potential reported vs. Ag/AgCl, 0.286 V vs. NHE), except for other specified experimental conditions.

[b] Data is measured from experiments performed in 0.1 M Bu_4NPF_6 DMF solution at room temperature at a scan rate 200 mV/s (potential reported vs. Ag/AgCl). Ref. [9].

[c] Data is converted to the value vs. Ag/AgCl electrode. The experiment is performed in 0.1 M Et_4NClO_4 CH_3CN solution at room temperature vs. saturated sodium calomel electrode (SSCE). Ref. [10].

The electrochemical data of $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ and $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ demonstrates the peripheral Os(dπ) based nature of highest-occupied molecular orbital (HOMO) and the μ-dpq (π*) nature of the lowest-unoccupied molecular orbital (LUMO) for the hexametallic complex vs. the μ-dpp (π*) LUMO in the trimetallic system. These orbital energetics illustrates the thermodynamic possibility of generating a charge separated excited state for the title hexametallic

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[1] Elemental analysis: Calc. for $Os_4Ru_2C_{170}H_{148}N_{44}O_4\ P_{12}F_{72}$: C, 36.63; H, 2.68; N, 11.06. Found: C, 37.14; H, 2.71; N, 10.64. FAB-MS: *m/z* [relatively abundance, ion]: 3326 [32, $(M\text{-}4PF_6\text{-}8bpy\text{-}F+H)^+$]; 3181 [100, $(M\text{-}5PF_6\text{-}8bpy\text{-}F+H)^+$]; 2439 [67, $(M\text{-}8PF_6\text{-}\{(bpy)_2Os(dpp)\}_2Ru)^+$]; MALDI-TOF MS: *m/z* [relatively abundance, ion]: 4529 [11, $(M\text{-}(bpy)_2Os\text{-}PF_6+3H)^+$]; 4390 [14, $(M\text{-}(bpy)_2Os\text{-}2PF_6+9H)^+$]; 3044 [42, $(M\text{-}6PF_6\text{-}8bpy\text{-}F+9H)^+$]; 2895 [100, $(M\text{-}7PF_6\text{-}8bpy\text{-}F+5H)^+$]; 2297 [32, $(M\text{-}9PF_6\text{-}\{(bpy)_2Os(dpp)\}_2Ru+3H)^+$].

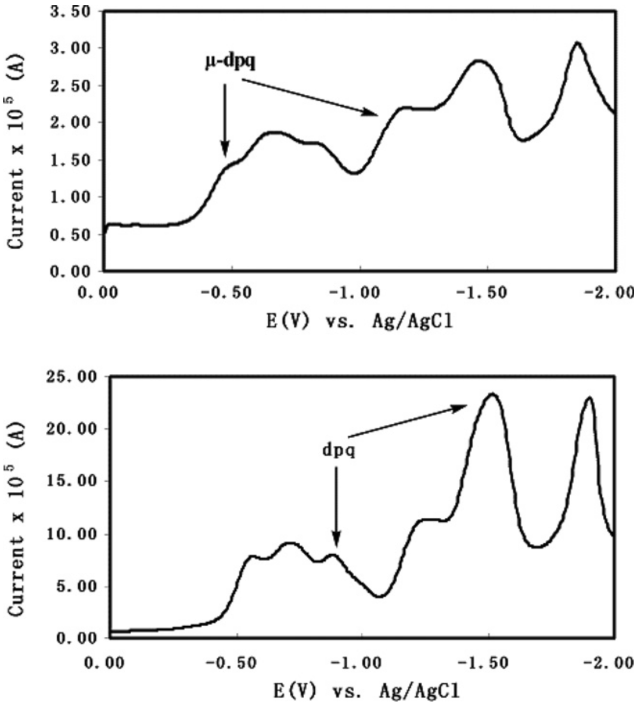

Fig. 3. Square wave voltammetry of the hexametallic complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ (a) and the trimetallic complex $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ (b) measured in 0.1 M Bu_4NPF_6 CH_3CN solution at room temperature at a scan rate 200 mV/s (potential reported vs. Ag/AgCl, bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline).

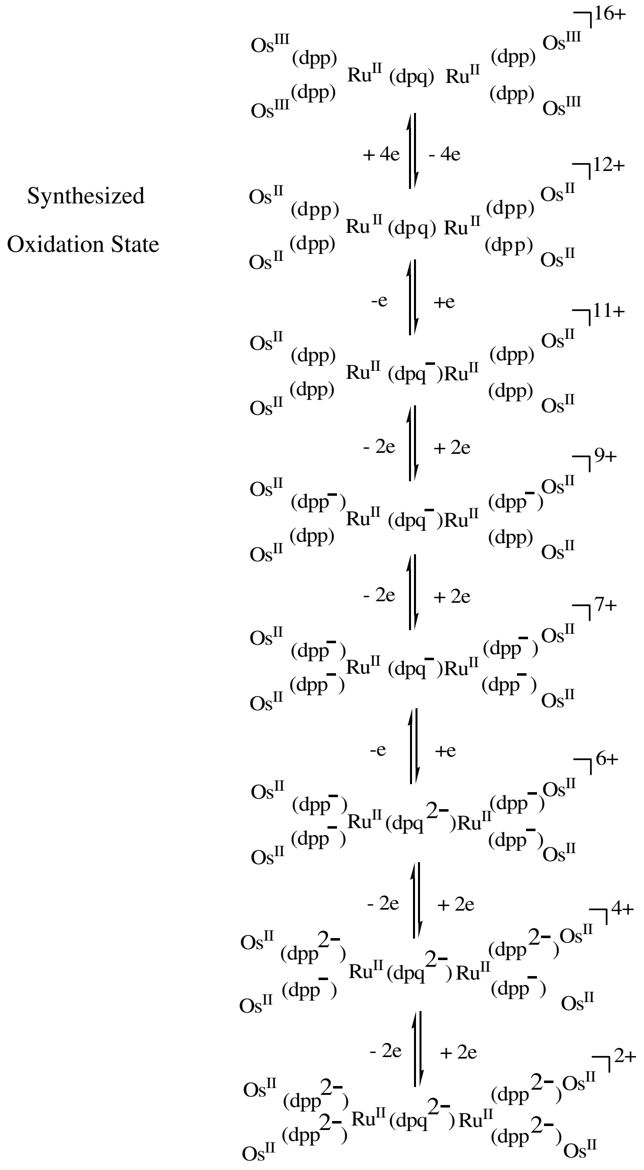

Fig. 4. Electrochemical mechanism for $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ with the bpy ligands omitted for clarity (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline).

complex between the terminal Os and central dpq, separated by the intervening Ru metal center. This large spatial separation between the site of localization of the HOMO and LUMO in this $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ complex makes this structural motif of interest to probe factors governing light initiated charge separation and charge recombination within a metal base framework [11].

The electronic absorption spectra of $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ and $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ are shown in Fig. 5 and summarized in Table 2 [5].

Both complexes show similar spectroscopy owing to their similar chromophoric units. The hexametallic $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ and related trimetallic $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ are efficient light absorbers, absorbing light throughout the UV and visible region. These complexes display bpy, dpp and dpq $\pi \rightarrow \pi^*$ transitions in the UV with MLCT transitions in the visible. The extinction coefficient of the hexametallic complex is roughly twice that of the trimetallic, showing the additivity of the absorbance. These complexes display intense transitions in the visible region with Os → bpy, Os → dpp, Ru → dpp and Ru → dpq CT transitions all occurring in this region.

The careful analysis of the spectrum of the $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ vs. $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ is possible through spectral subtraction. (Supplementary material). This analysis shows a peak at ca. 510 nm in the trimetallic complex $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ that has shifted to ca. 590 nm in the hexametallic complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ consistent with a terminal dpq in the trimetallic becoming bridging in the hexametallic complex. This peak at 590 nm in $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ corresponds to the $Ru(d\pi) \rightarrow \mu\text{-}dpq(\pi^*)$ charge transfer transition, consistent with the previously reported 605 nm $Ru(d\pi) \rightarrow \mu\text{-}dpq(\pi^*)$ CT band in $[(bpy)_2Ru(dpq)Ru(bpy)_2](PF_6)_4$ [10]. This electronic absorption spectral analysis again illustrates the $dpq(\pi^*)$ nature of the lowest acceptor orbital in the hexametallic complex, $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$.

The nature of the complicated spectroscopy and redox chemistry of these assemblies can be further clarified

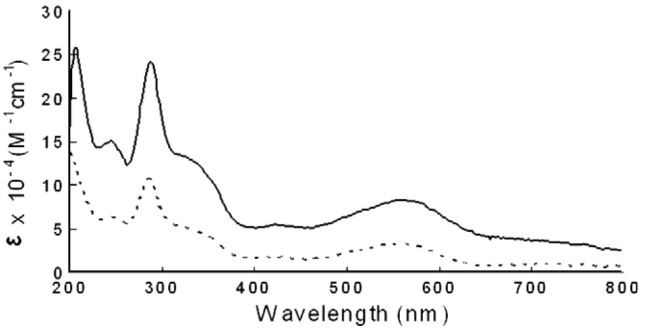

Fig. 5. Electronic absorption spectroscopy of hexametallic complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$(—-) and trimetallic complex $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$(----), measured in CH_3CN solvent at room temperature (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline).

through the use of spectroelectrochemistry. The title hexametallic $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ and model trimetallic $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ can be reversibly oxidized and their spectroscopy studied (Supporting Information). Oxidation at 1.30 V vs. Ag/AgCl, positive of the $Os^{II/III}$ couple, leads to generation of the Os^{III} form of these complexes. Oxidation leads to a shift out of the visible region of the osmium based MLCT transitions including the Os(dπ) → μ-dpp(π*) CT transition at 552 nm and the Os(dπ) → bpy(π*) at 432 nm. This uncovers the Ru based MLCT transitions in this region. The Ru(dπ) → μ-dpp(π*) CT band occurs at 515 nm for the oxidized trimetallic $[\{(bpy)_2Os^{III}(dpp)\}_2Ru^{II}(dpq)]^{8+}$ and 523 nm for oxidized hexametallic $[(\{(bpy)_2Os^{III}(dpp)\}_2Ru^{II})_2(dpq)]^{16+}$, consistent with the 525 nm Ru(dπ) → μ-dpp(π*) CT transition for the symmetric $[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_2$ system [2,16]. It was also noteworthy that the low energy tails from 650 nm to 800 nm are lost upon oxidation of osmium centers, consistent with their Os based ^{3}MLCT assignment [5,17]. Comparison of the spectroscopy of the Os^{III} forms of the trimetallic and hexametallic compounds by spectral subtraction uncovers an additional peak at 570 nm for the hexametallic $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ in Fig. 6. This 570 nm peak corresponds to the Ru(dπ) → μ-dpq(π*) CT for the hexametallic complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$.

Utilizing a building block synthetic method, a large supramolecular complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ containing four osmium atoms and two ruthenium atoms connected by mixed polyazine bridging ligands can be prepared. This hexametallic complex has a high molecular weight 5173 g/mol with large extinction coefficients of 8.3×10^5 M^{-1} cm^{-1} at 560 nm, making it an efficient MLCT

Table 2
Electronic absorption spectroscopy for hexametallic $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$, trimetallic $[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$ and related model supramolecular assemblies (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline)[a]

Complex	Wavelength (nm)	$\varepsilon \times 10^{-4}$ (M^{-1} cm^{-1})	Assignments
$[(bpy)_2Ru(dpp)Ru(bpy)_2](PF_6)_4$[b]	425	1.7	Ru(dπ) → bpy(π*) CT
	525	2.1	Ru(dπ) → μ-dpp(π*) CT
$[(bpy)_2Os(dpp)Os(bpy)_2](PF_6)_4$[c]	432	2.0	Os(dπ) → bpy(π*) CT
	552	2.5	Os(dπ) → μ-dpp(π*) CT
$[(bpy)_2Ru(dpp)Os(bpy)_2](PF_6)_4$[d]	430	2.2	Ru(dπ) → bpy(π*) CT Os(dπ) → bpy(π*) CT
	542	2.9	Os(dπ) → μ-dpp(π*) CT Ru(dπ) → μ-dpp(π*) CT
$[(bpy)_2Ru(dpq)Ru(bpy)_2](PF_6)_4$[e]	423	–[f]	Ru(dπ) → bpy(π*) CT
	605	0.98	Ru(dπ) → μ-dpq(π*) CT
$[(bpy)_2Ru(dpq)](PF_6)_2$[e]	515	0.81	Ru(dπ) → dpq(π*) CT
$[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$	430	5.4	Ru(dπ) → bpy(π*) CT Os(dπ) → bpy(π*) CT
	560	8.3	Os(dπ) → μ-dpp(π*) CT Ru(dπ) → μ-dpp(π*) CT
	720	3.5	^{3}Os(dπ) → μ-dpp(π*) CT
$[\{(bpy)_2Os(dpp)\}_2Ru(dpq)](PF_6)_6$	430	1.8	Ru(dπ) → bpy(π*) CT Os(dπ) → bpy(π*) CT
	560	3.3	Os(dπ) → μ-dpp(π*) CT Ru(dπ) → μ-dpp(π*) CT
	720	0.89	^{3}Os(dπ) → μ-dpp(π*) CT

[a] Electronic absorption spectroscopy measured in CH_3CN solvent at room temperature.
[b] Ref. [12] and the references therein.
[c] Refs. [13,14].
[d] Ref. [9].
[e] Refs. [10,15].
[f] Extinction coefficient not provided in Ref. [10].

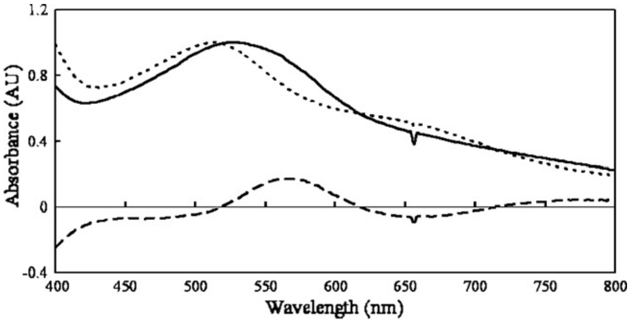

Fig. 6. Difference spectrum of the Os^{III} forms of the hexametallic complex $[(\{(bpy)_2Os^{III}(dpp)\}_2Ru^{II})_2(dpq)]^{16+}$ (—), trimetallic complex $[\{(bpy)_2Os^{III}(dpp)\}_2Ru^{II}(dpq)]^{8+}$ (···) and subtraction of oxidized trimetallic spectrum from oxidized hexametallic spectrum (---), measured in CH_3CN solution at room temperature with 0.1 M Bu_4NPF_6 present (bpy = 2,2′-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis-(2-pyridyl)quinoxaline).

light absorber. The structural diversity of this system with Os and Ru metals bound to bpy, dpp and dpq ligands makes this system of interest in understanding the properties of complex assemblies. Comparison of the spectroscopy and spectroeletrochemistry of the hexametallic vs. trimetallic complex allows the observation of the low energy Ru(dπ) → μ-dpq(π*) CT band at 590 nm. The title hexametallic complex $[\{[(bpy)_2Os(dpp)]_2Ru\}_2(dpq)](PF_6)_{12}$ has a HOMO that is localized on the peripheral Os centers and a LUMO localized on the central dpq bridging ligand, spatially separated by the Ru centers. The study of this and related supramolecular assemblies coupling central acceptors and terminal donors is of significant current interest [11].

Acknowledgements

Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for their generous partial support of this research. Acknowledgement is made to the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy for their generous partial support of this research.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.10.016.

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