

Synthesis and characterization of osmium(II) complexes incorporating polypyridyl bridging ligands

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Abstract

A series of osmium(II) compounds have been prepared which contain the polypyridyl bridging ligands 2,3-bis(2'-pyridyl)pyrazine (dpp), 2,3-bis(2'-pyridyl)quinoxaline (dpq) and 2,3-bis(2'-pyridyl)-benzoquinoxaline (dqb). The compounds $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$, $[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$ and $[\text{Os}(\text{bpy})_2(\text{dqb})](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine) have been synthesized and their electrochemical and spectroscopic properties have been studied and are reported herein. The complexes show absorbances throughout the visible region of the spectrum. The potential of the first electrochemical reduction as well as the energy of the lowest energy metal to ligand charge transfer excited state (MLCT) are found to be dependent upon the nature of the bridging polypyridyl ligand. This combined with the fact that the bridging ligands are more easily reduced than bipyridine support the assignment of the lowest unoccupied molecular orbital (LUMO) as arising from a bridging ligand based π^* orbital.

Introduction

While the chemistry associated with ruthenium polypyridyl complexes has flourished and grown in the past twenty years, due in part to the efficiency of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) as a visible photosensitizer, the chemistry associated with osmium polypyridyl complexes has received much less attention. This is surprising since osmium is quite similar to ruthenium with the observed differences generally being associated with electronic factors [1]. In many instances osmium would appear to be the metal of choice since the excited state chemistry of ruthenium is strongly affected by low-lying dd states which complicate the interpretation of the photophysical and photochemical properties and lead to photodecomposition [2]. However, since the value of $10Dq$ in osmium complexes is much higher than that of analogous ruthenium systems many of the problems associated with ruthenium can be bypassed or avoided [1].

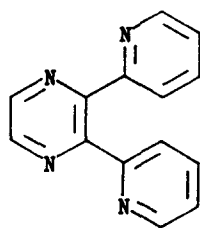
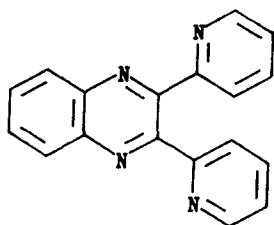
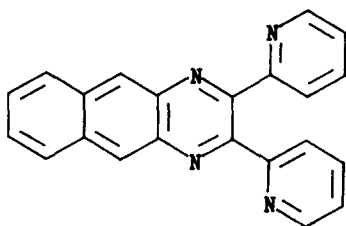
Meyer and co-workers have shown that the photophysical and redox properties of Os(II) complexes are 'tunable' by varying the attendant chromophoric and non-chromophoric ligands [1–3]. Their work has

shown that synthetic control of excited states is readily obtainable and offers attractive new routes to their systematic control. Os(II) polypyridine compounds have been shown to undergo facile photoinitiated electron transfer [4], oxidative and reductive quenching [2b] and are capable of functioning as electron-transfer photocatalysts [2]. All of these features make them likely candidates for incorporation into solar energy conversion schemes.

While the short lifetime of $\text{Os}(\text{bpy})_3^{2+}$ (60 ns) compared to $\text{Ru}(\text{bpy})_3^{2+}$ (600 ns) makes solar energy conversion schemes more difficult to implement our systems are designed to take advantage of the photostability of Os. The difficulties presented by the short lifetime of the osmium excited state can be avoided by covalent coupling of the osmium complex to another metal complex via the remote nitrogens on the bridging ligand, opening up the possibility of using these compounds in intramolecular solar energy conversion schemes.

Within this framework we have synthesized compounds with the general form $[\text{Os}(\text{bpy})_2(\text{BL})](\text{PF}_6)_2$, where BL = bridging ligand. The bridging ligands used are 2,3-bis(2'-pyridyl)pyrazine (dpp), 2,3-bis(2'-pyridyl)quinoxaline (dpq) and 2,3-bis(2'-pyridyl)-benzoquinoxaline (dqb), see below.

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**dpp****dpq****dpb**

These ligands are similar to bpy but have the added ability to coordinate additional metal centers through the remote nitrogens, making possible the development of polymetallic systems. This series differs only by the addition of electron-withdrawing aromatic rings fused to the side of the pyrazine ring. Each additional ring results in an increase in the electronegativity of the bridging ligand.

This series of complexes clearly demonstrates the trends in osmium bridging ligand complexes as a function of ligand electronegativity and has enabled us to show that both the redox properties and MLCT excited state properties are dependent upon the character of the bridging polypyridyl ligand. The effect of this variation on both electrochemical and spectroscopic properties has been explored.

Experimental

Materials

The materials were reagent grade and used without further purification. Potassium hexachloroosmate(IV) was purchased from Johnson Matthey. 2,3-Bis(2'-pyridyl)pyrazine (dpp) was purchased from Aldrich Chemical Company. 2,3-Bis(2'-pyridyl)quinoxaline (dpq) was synthesized according to the method of Goodwin and Lions by the reaction of *o*-phenylenediamine and 2,2'-pyridyl in ethanol [5]. The ligand dpb [6] was prepared by an extension of the method of Goodwin and Lions [5] involving a Schiff base condensation between 2,2'-pyridyl and 2,3-diaminonaphthalene in ethanol. Both dpq and dpb must be recrystallized several times from hot

ethanol. The supporting electrolyte used in the electrochemical studies was electrochemical grade tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , Bioanalytical Systems), and was stored in a vacuum desiccator. All other chemicals were Fisher Scientific reagent grade and used without further purification.

Syntheses

Dichlorobis(bipyridine)osmium(II), $[\text{Os}(\text{bpy})_2\text{Cl}_2]$, was synthesized by a modification of the procedure of Buckingham *et al.* [7]. K_2OsCl_6 (1.90 g, 3.95 mmol) and 2,2'-bipyridine (1.30 g, 8.32 mmol) were heated at reflux in 20 ml of dimethylformamide. After approximately one hour, the heat was removed and the solution allowed to cool. KCl precipitate was removed by vacuum filtration and 10 ml of methanol was added to the filtrate. Next, a solution of 0.116 g (0.656 mmol) of sodium dithionite (sodium hydrosulfite, Fisher Scientific) in 100 ml of deionized water was added and the solution placed in an ice bath. Upon cooling, a reddish-purple microcrystalline product precipitated and was collected by vacuum filtration on a sintered glass filter frit. The product was washed with 25 ml of deionized water and 25 ml of diethyl ether. Sodium dithionite addition was repeated three times and the product stored in a vacuum desiccator. Typical yields were 70%.

$[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ was prepared by a modification of the procedure of Kalyanasundaram and Nazeeruddin [8] by reacting 1.5 equiv. of the bridging ligand (0.704 g, 3.03 mmol) with $[\text{Os}(\text{bpy})_2\text{Cl}_2]$ (0.844 g, 2.02 mmol) in ethylene glycol (30 ml). The solution was heated at reflux and the reaction monitored by UV-Vis spectroscopy. The reaction appeared to be complete after 1 h with no further change observed in the visible spectra. The flask was then removed from the heat and a saturated solution of aqueous KPF_6 (30 ml) was added with stirring. The precipitate was collected by vacuum filtration. The product was purified by column chromatography on neutral alumina using a 2:1 (vol./vol.) toluene/acetonitrile eluent. The dark brown product was the first band to elute. It was collected, concentrated by rotary evaporation, and precipitated by addition to a stirred solution of diethyl ether (200 ml). The precipitate was separated from the supernatant by vacuum filtration, washed with diethyl ether, and dried under vacuum. The chromatographic procedure was repeated once to insure product purity as judged by thin layer chromatography (TLC). A typical yield was 85%. *Anal.* Calc.: C, 39.16; H, 2.61; N, 10.75. Found: C, 39.21; H, 2.60; N, 10.75%.

$[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$ was prepared as above substituting the ligand dpq (0.862 g, 3.03 mmol) for the ligand dpp. Again, the product eluted first and was

a red–purple color. The chromatographic procedure was repeated three times to insure product purity as judged by TLC. A typical yield for this reaction was 80%. *Anal. Calc.*: C, 42.40; H, 2.62; N, 10.41. *Found*: C, 42.99; H, 2.86; N, 10.65%.

$[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$ was also prepared as above by substituting the ligand dpp (1.02 g, 3.03 mmol) for the ligand dpq. A 1:1 (vol./vol.) toluene/acetonitrile eluent was used and the product band eluted was dark purple. The chromatographic procedure was repeated four times to insure product purity as judged by TLC. A typical yield for this reaction was 75%. *Anal. Calc.*: C, 44.68; H, 2.85; N, 9.93. *Found*: C, 44.74; H, 2.88; N, 9.87%.

$[\text{Os}(\text{bpy})_3]^{2+}$ as first reported by Burstall *et al.* [9] was prepared as above by the reaction of $[\text{Os}(\text{bpy})_2\text{Cl}_2]$ with two equivalents of 2,2'-bipyridine in ethylene glycol. A 2:1 (vol./vol.) toluene/acetonitrile eluent was used and the product band eluted was dark green. It was only necessary to perform the chromatographic procedure once to insure product purity as judged by TLC. Recrystallization using the technique of vapor diffusion [10], with the compound dissolved in acetonitrile and using ether as the more volatile solvent, gave X-ray quality crystals. The structure is reported elsewhere [11].

Spectroscopy

Absorption spectra were recorded on a Hewlett Packard 8452 diode array spectrophotometer interfaced to a Hewlett Packard Vectra ES computer. The spectra were measured in acetonitrile solution at room temperature.

Electrochemistry

Cyclic voltammograms and Osteryoung square wave voltammetry were recorded on a BioAnalytical Systems 100A electrochemical analyzer equipped with a Houston Instruments DMP-40 digital plotter. Three electrodes were utilized in this system, a glassy carbon disk working electrode, a platinum wire auxiliary electrode, and a silver/silver chloride gel reference electrode (0.268 V versus SHE). The glassy carbon disk working electrode was manually cleaned prior to each scan. The solvent used was Burdick and Jackson high purity acetonitrile dried over activated molecular sieves. The supporting electrolyte was 0.1 M Bu_4NPF_6 . The solutions were deoxygenated by bubbling with argon for 20 min prior to each scan and blanketed with argon during each scan.

Results and discussion

Absorption spectra

The ligands used in this study have been characterized in detail elsewhere [6, 12]. The free ligand

spectra are shown in Fig. 1. The spectra show bands at high energies which are typical of $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ transitions and, as expected, the lowest energy $\pi\text{--}\pi^*$ transition shifts to higher wavelength as the electronegativity of the BL increases from dpp to dpq to dpb [6].

The UV–Vis electronic spectral data for each of the osmium bridging ligand compounds is summarized in Table 1 and shown in Fig. 2 (with the previously studied $[\text{Os}(\text{bpy})_3]^{2+}$ included in the Figure for comparative purposes [4]). The electronic spectra of $[\text{Os}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$ have been reported previously in H_2O and DMF, respectively [4, 8]. The values reported in the Table (for

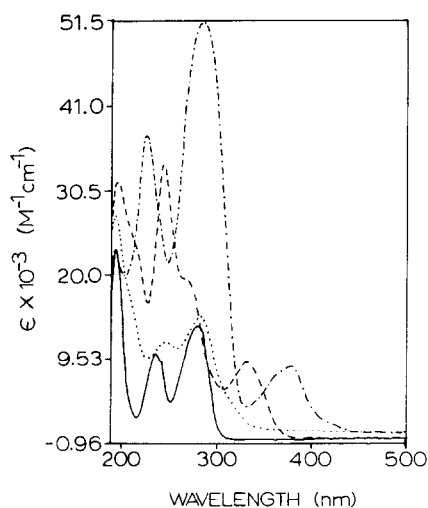


Fig. 1. Electronic absorption spectra of bpy (—), dpp (·····), dpq (---) and dpb (- · -). Spectra were recorded in CH_3CN .

TABLE 1. Electronic spectral data for a series of osmium(II) complexes containing polypyridyl bridging ligands^a

Complex	Absorption λ_{max} (nm)	$\epsilon \times 10^{-3}$ ($\text{M}^{-1} \text{cm}^{-1}$)	Assignment
$[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$	290	67.3	$\pi\text{--}\pi^*$
	432 (sh)	11.0	$^1\text{MLCT}$ (bpy)
	486	12.7	$^1\text{MLCT}$ (dpp)
$[\text{Os}(\text{bpy})_2(\text{dpq})]^{2+}$	286	73.2	$\pi\text{--}\pi^*$
	346	25.1	$^1\text{MLCT}$ (bpy)
	428	11.0	$^1\text{MLCT}$ (bpy)
	536	13.4	$^1\text{MLCT}$ (dpq)
$[\text{Os}(\text{bpy})_2(\text{dpb})]^{2+}$	290	70.0	$\pi\text{--}\pi^*$
	366 (sh)	24.4	
	408 (sh)	17.3	$^1\text{MLCT}$ (bpy)
	446 (sh)	12.8	$^1\text{MLCT}$ (bpy)
	570	13.8	$^1\text{MLCT}$ (dpb)

^aSpectra were recorded in CH_3CN at room temperature.

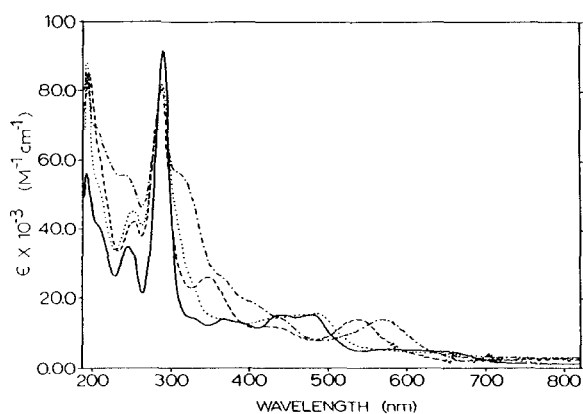


Fig. 2. Electronic absorption spectra for a series of Os(II) polypyridyl complexes in CH_3CN . —, $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$; ·····, $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$; ---, $[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$; - · -, $[\text{Os}(\text{bpy})_2(\text{dpb})](\text{PF}_6)_2$.

$[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$) and the spectra shown in the Figure are those we obtained in CH_3CN ; this was done to make comparisons with our systems more valid. The compounds themselves are intensely colored and possess complex spectra with absorptions tailing well into the near infrared ($> 750 \text{ nm}$) region of the spectrum. The absorption spectra consist of ligand localized $\pi-\pi^*$ transitions in the UV and a series of metal to ligand charge transfer (MLCT) transitions in the visible. The lowest lying MLCT transitions are assigned as $\text{Os}(d\pi) \rightarrow \text{BL}(\pi^*)$ [2, 13, 14].

Each complex has structural bands in the UV similar to those in the corresponding free ligands and are assigned to ligand localized $\pi-\pi^*$ transitions. For the mixed ligand complexes $\pi-\pi^*$ transitions are evident which are due to both bpy and BL localized transitions. Some of the low wavelength, ligand based, absorptions show a slight solvent dependence similar to those observed by Murphy and co-workers [6] for $\text{Re}(\text{I})$ monometallic complexes possibly due to $n-\pi^*$ transitions [15].

The lower energy absorption bands between 400–600 nm are solvent dependent, shifting to lower energies in solvents with lower dielectric constants. This phenomenon has been noted by many other authors and is consistent with an MLCT assignment [6, 16–27]. The positions of the lowest energy maxima are sensitive to the nature of the BL, shifting to lower energies (higher wavelengths), as the electronegativity of the bridging ligand increases. For these reasons the peaks at 486, 536 and 566 nm for $[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$, $[\text{Os}(\text{bpy})_2(\text{dpq})]^{2+}$ and $[\text{Os}(\text{bpy})_2(\text{dpb})]^{2+}$, respectively, are assigned as singlet $\text{Os}(d\pi) \rightarrow \text{BL}(\pi^*)$ MLCT transitions [6, 8, 28].

Due to significant spin-orbit coupling in osmium, the MLCT excited states mix such that all metal associated absorption transitions exhibit significant amounts of both singlet and triplet character. The components of principally triplet parentage exhibit diminished intensities and generally appear on the low energy side of the spectra [29]. Kalyanasundaram and Nazeeruddin have assigned these low energy peaks as triplet ligand to metal charge transfer transitions ($^3\text{LMCT}$) [8]. This is in contrast to the assignments of previous workers [3, 4, 14, 29] and seems less likely since the $^3\text{MLCT}$ levels lie lower in energy than the corresponding $^3\text{LMCT}$ levels. Evidence supporting assignment of these $^3\text{MLCT}$ transitions is provided by the long tails in the electronic spectra which extend to the red of the lowest energy $^1\text{MLCT}$ transitions.

Electrochemistry

The electrochemical data for these complexes is summarized in Table 2 and the cyclic voltammograms are shown in Fig. 3. The complexes display ΔE_p ($\Delta E_p = E_p^a - E_p^c$) values slightly greater than the expected value of 59 mV. Our system under the same conditions exhibits a similar ΔE_p value of 75 mV. The mononuclear osmium complexes each display one reversible oxidation and three reversible reductions in the potential region from +1.40 to −1.95 V versus SCE. The general scheme for the electrochemical processes is as follows:

TABLE 2. Cyclic voltammetric data for osmium polypyridyl complexes^a

Complex	$E_{1/2}$ (V)	ΔE_p (mV)
$[\text{Os}(\text{bpy})_3]^{2+}$	+0.82	86
	−1.26	85
	−1.44	73
	−1.74	77
$[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$	+0.94	82
	−1.02	74
	−1.38	78
	−1.58	80
$[\text{Os}(\text{bpy})_2(\text{dpq})]^{2+}$	+0.99	65
	−0.76	71
	−1.26	70
	−1.57	56
$[\text{Os}(\text{bpy})_2(\text{dpb})]^{2+}$	+1.00	78
	−0.61	71
	−1.16	63
	−1.55	63

^aPotentials were recorded vs. a Ag/AgCl reference electrode (0.268 vs. SHE) in 0.1 M Bu_4NPF_6 in CH_3CN at a scan rate of 200 mV/s. ΔE_p is the difference between anodic (E_p^a) and cathodic (E_p^c) peak potentials.

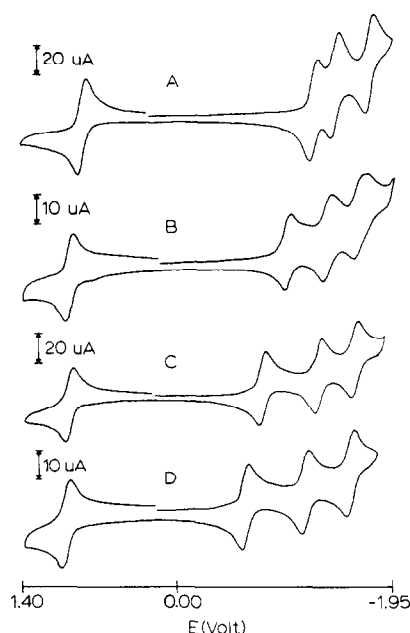
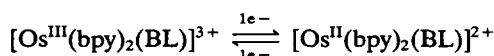
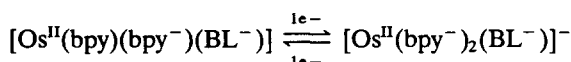
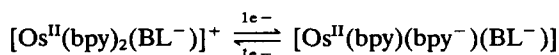
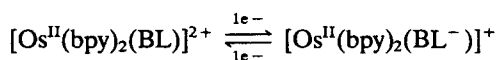


Fig. 3. Cyclic voltammograms ($\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$) of: A, $[\text{Os}(\text{bpy})_3]^{2+}$; B, $[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$; C, $[\text{Os}(\text{bpy})_2(\text{dpq})]^{2+}$; D, $[\text{Os}(\text{bpy})_2(\text{dpb})]^{2+}$.

Oxidation process:



Reduction processes:



All of the reductions are ligand based with the first reduction in these complexes being assigned as a bridging ligand reduction [6, 8, 12]. The second and third reductions are assigned to sequential reductions of the two bpy ligands by analogy to $[\text{Os}(\text{bpy})_3]^{2+}$ [3]. It is interesting to note that the position of the first bridging ligand based reduction varies dramatically as a function of the bridging ligand present while the positions of the subsequent bipyridine reductions remain essentially unchanged.

Meyer and co-workers have noticed that within a series in which the polypyridyl ligands remain unchanged, the ligand based reduction potential remains essentially constant. On the other hand they also noticed that the metal-based $\text{Os}(\text{III}/\text{II})$ potential varies considerably with changes in the non-polypyridyl ligands [3]. In these complexes, as we ex-

pected, the reduction of the bpy ligands remain relatively constant, while the reduction potential of the bridging ligand varies considerably. In addition, the change in the ligand field about the metal ion caused by the variation in the bridging ligand produces only a small shift in the metal oxidation potential.

The substitution of more electronegative bridging ligands into the metal framework results in more easily reduced complexes with the half wave potentials for the reduction of the dpp, dpq and dpb complexes occurring at -1.02 , -0.76 and -0.61 V , respectively. The oxidative process involves oxidation of $\text{Os}(\text{II})$ to $\text{Os}(\text{III})$ and occurs at $+0.94$, $+0.99$ and $+1.00 \text{ V}$ for the complexes containing dpp, dpq and dpb, respectively. Thus, while the first reduction potential varies dramatically as a function of the bridging ligand present, the oxidation potential remains essentially constant.

Spectroelectrochemistry

Spectroelectrochemical measurements were used in correlation of electronic transitions with electrochemical redox processes. These measurements were also used to investigate the stabilities of the oxidized and reduced forms of each complex. The apparatus used has been previously described in detail [30]. All electrochemical experiments were carried out in dried acetonitrile. All three complexes could be reversibly oxidized in these solutions however bulk reduction reactions were not reversible.

Oxidation of approximately 1 mM solutions of $[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$, $[\text{Os}(\text{bpy})_2(\text{dpq})]^{2+}$ and $[\text{Os}(\text{bpy})_2(\text{dpb})]^{2+}$ at a platinum electrode ($E = +1.4 \text{ V}$ versus SCE) resulted in an essentially colorless solution after passage of approximately 1 equiv. of charge (Fig. 4(a), (b) and (c), respectively). In all cases oxidation can be reversed by changing the electrolysis potential to 0.0 V . After passing 1 reduction equiv., the original spectra of the species are obtained with greater than 95% regeneration of the original species. Our cell design required approximately 15 min to affect a complete oxidation or reduction.

Upon oxidation of the $[\text{Os}(\text{bpy})_2(\text{BL})]^{2+}$ compounds significant loss of absorbance between 450 and 800 nm is observed. This supports the assignment of the transitions in this region as $\text{Os}(\text{d}\pi) \rightarrow \text{BL}(\pi^*)$ charge transfer transitions. Other transitions expected to be lost upon oxidation of the metal center include higher energy bpy based MLCT transitions as well as some $n(\text{metal})-\pi^*$ (ligand) transitions. As expected with a metal-based oxidation, transitions which involve promotion of a ligand based electron should not be effected. This expectation is supported by retention of BL and bpy based $\pi-\pi^*$ transitions

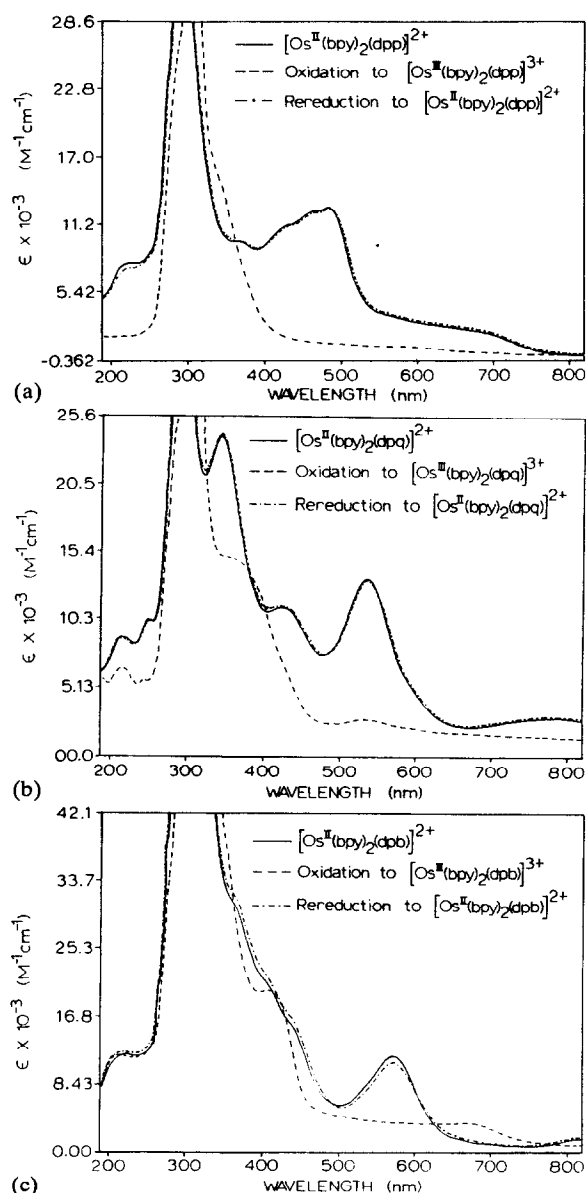


Fig. 4. Spectroelectrochemical results of Os(II) polypyridyl complexes in CH_3CN (0.1 M Bu_4NPF_6): (a) $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$, (b) $[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$, (c) $[\text{Os}(\text{bpy})_2(\text{dpb})](\text{PF}_6)_2$. (—) Original spectra; (---) spectra after oxidation with approximately 1.0 equivalent at +1.4 V (Ag/Ag^+) at a Pt mesh electrode; (- · -) spectra after rereduction with 1.0 equiv. at 0.0 V.

in the spectrum of electrogenerated $[\text{Os}(\text{bpy})_2(\text{BL})]^{3+}$.

In summary, our spectroelectrochemical experiments are consistent with the following assignments. Metal to ligand charge transfer bands in the visible for $[\text{Os}(\text{bpy})_2(\text{dpp})]^{2+}$ which shift to lower energies in $[\text{Os}(\text{bpy})_2(\text{dpq})]^{2+}$ and $[\text{Os}(\text{bpy})_2(\text{dpb})]^{2+}$. Peaks at slightly higher energies in the three complexes which disappear upon metal oxidation and could be

due to $n-\pi^*$ or metal to bpy transitions. The UV region of the spectrum exhibits both bpy and bridging ligand based $\pi-\pi^*$ transitions in all of our systems.

Correlation of spectroscopic and electrochemical results

As has been noted by several authors [2, 3, 31–38], a plot of the absorption energies for the lowest energy transitions (E_{abs} (eV)) versus the difference in redox potentials for the Os(II/III) and ligand-based (BL/BL^-) ($\Delta E_{1/2} = E_{1/2}(\text{Os}^{\text{II/III}}) - E_{1/2}(\text{BL}/\text{BL}^-)$) should be linear if the same $d\pi-\pi^*$ MLCT orbitals are involved in both the electrochemical and optical processes. A plot of E_{abs} (eV) versus $\Delta E_{1/2}$ for the three complexes reported herein as well as $\text{Os}(\text{bpy})_3^{2+}$ (Fig. 5) produced a linear correlation in which a linear least-squares fit yielded

$$E_{\text{abs}} = 0.5477 + 1.0053\Delta E_{1/2} \quad r = 1.00$$

where r is the correlation coefficient. As can be seen from the equation, the slope of the least-squares line for the absorption process is nearly unity, as was to be expected [33, 35, 36]. This supports our assertion that the lowest energy absorptions are indeed MLCT in character. Extrapolation of this technique for the least negative ligand-based (bpy/bpy^-) reduction ($\Delta E_{1/2} = E_{1/2}(\text{Os}^{\text{II/III}}) - E_{1/2}(\text{bpy}/\text{bpy}^-)$) yielded values for the metal to bpy charge transfers of 437 nm for $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$, 432 nm for $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$, 443 nm for $[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$ and 410 nm for $[\text{Os}(\text{bpy})_2(\text{dpb})](\text{PF}_6)_2$. These calculated values correspond very well to observed transitions at 440 nm for $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$, 432 nm for $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$, 428 nm for $[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$ and

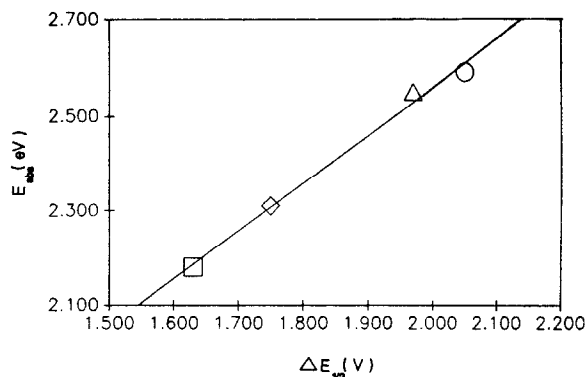


Fig. 5. Plot of energies of the lowest energy absorption band (eV) vs. $\Delta E_{1/2}$ (V) of $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ (○), $[\text{Os}(\text{bpy})_2(\text{dpp})](\text{PF}_6)_2$ (Δ), $[\text{Os}(\text{bpy})_2(\text{dpq})](\text{PF}_6)_2$ (◇), $[\text{Os}(\text{bpy})_2(\text{dpb})](\text{PF}_6)_2$ (□) in acetonitrile.

408 nm for $[\text{Os}(\text{bpy})_2(\text{dcb})](\text{PF}_6)_2$ giving further support to the assignment of these transitions as $\text{Os}^{\text{II}}\text{-bpy}$ MLCT bands.

Conclusions

Comparison of the electronic absorption spectra and the electrochemical behavior of the monometallic complexes demonstrates that incorporation of electronegative polypyridyl bridging ligands into the metal framework results in the shift of the MLCT absorption maxima to lower energies. The systematic variation in the ease of reduction of the BL allows us to specifically choose the ligand based π^* (acceptor) levels while keeping the metal-based $d\pi$ levels relatively constant and has led to the development of complexes that absorb lower energy visible light. Continuing study of these complexes and their polymetallic derivatives will be the subject of a forthcoming report.

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References

- 1 E. M. Kober, J. V. Caspar, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, **27** (1988) 4587.
- 2 (a) R. S. Lumpkin, E. M. Kober, L. A. Worl, Z. Murtaza and T. J. Meyer, *J. Phys. Chem.*, **94** (1990) 239; (b) E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, **24** (1985) 2755, and refs. therein; (c) D. Pinnick and B. Durham, *Inorg. Chem.*, **23** (1984) 1440.
- 3 S. R. Johnson, D. T. Westmorland, J. V. Caspar, K. R. Barqawi and T. J. Meyer, *Inorg. Chem.*, **27** (1988) 3195.
- 4 C. Creutz, M. Chou, T. L. Netzel, M. Okumura and N. Sutin, *J. Am. Chem. Soc.*, **102** (1980) 1309.
- 5 H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **81** (1959) 6415.
- 6 A. J. Baiano, D. L. Carlson, G. M. Wolosh, D. E. DeJesus, C. F. Knowles, E. G. Szabo and W. R. Murphy, Jr., *Inorg. Chem.*, **29** (1990) 2327.
- 7 D. A. Buckingham, F. P. Dwyer, H. A. Goodwin and A. M. Sargeson, *Aust. J. Chem.*, **17** (1964) 325.
- 8 K. Kalyanasundaram and Md. K. Nazeeruddin, *Chem. Phys. Lett.*, **158** (1989) 45.
- 9 F. J. Burstall, F. P. Dwyer and E. C. Gyrfus, *J. Chem. Soc.*, (1950) 953.
- 10 G. E. Stout and L. H. Jensen, *X-Ray Structure Determination, A Practical Guide*, Macmillan, London, 1968, p. 65.
- 11 M. M. Richter, B. Scott, K. J. Brewer and R. P. Willett, *Acta Crystallogr., Sect. C*, in press.
- 12 S. C. Rasmussen, M. M. Richter, E. Yi, H. Place and K. J. Brewer, *Inorg. Chem.*, **29** (1990) 3926.
- 13 (a) J. Ferguson, F. Herren, E. R. Krausz and J. Vrbancich, *Coord. Chem. Rev.*, **64** (1985) 21; (b) G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, **24** (1971) 275.
- 14 (a) B. J. Pankuch, D. E. Lacky and G. A. Crosby, *J. Phys. Chem.*, **84** (1980) 2061; (b) D. E. Lacky, B. J. Pankuch and G. A. Crosby, *J. Phys. Chem.*, **84** (1980) 2068.
- 15 M. Kasha, *Discuss. Faraday Soc.*, **9** (1950) 14.
- 16 M. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, **96** (1974) 998.
- 17 P. J. Giordano and M. S. Wrighton, *J. Am. Chem. Soc.*, **101** (1979) 2888.
- 18 T. Ishikawa, S. Nitta and S. Kondo, *J. Chem. Soc., Faraday Trans. 1*, **82** (1986) 2401.
- 19 J. C. Luong, R. A. Faltynek and M. S. Wrighton, *J. Am. Chem. Soc.*, **101** (1979), 1597.
- 20 J. C. Luong, R. A. Faltynek and M. S. Wrighton, *J. Am. Chem. Soc.*, **102** (1980), 7892.
- 21 J. V. Caspar, B. P. Sullivan, E. M. Kober and T. J. Meyer, *Chem. Phys. Lett.*, **91** (2) (1986) 91.
- 22 O. T. Sostero and G. A. Mazzocchin, *Inorg. Chim. Acta*, **11** (1974) 237.
- 23 E. M. Kober, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, **23** (1984) 2098.
- 24 A. Sugimori, M. Matsui, T. Akiyama and M. Kajitani, *Bull. Chem. Soc. Jpn.*, **53** (1980) 3263.
- 25 R. A. Marcus, *J. Chem. Phys.*, **43**, 4 (1965) 1261.
- 26 S. F. Clark, R. J. Watts, D. L. Dubois, J. S. Connolly and C. C. Smart, *Coord. Chem. Rev.*, **64** (1985) 273.
- 27 J. Ferguson and R. Krausz, *Chem. Phys. Lett.*, **93** (1) (1982) 21.
- 28 (a) D. P. Rillema and K. B. Mack, *Inorg. Chem.*, **21** (1982) 3849; (b) D. P. Rillema, R. W. Callahan and K. B. Mack, *Inorg. Chem.*, **21** (1982) 2589.
- 29 E. M. Kober and T. J. Meyer, *Inorg. Chem.*, **21** (1982) 3967.
- 30 K. J. Brewer, R. S. Lumpkin, J. W. Otvos, L. O. Spreer and M. Calvin, *Inorg. Chem.*, **28** (1989) 4446.
- 31 (a) E. M. Kober, B. P. Sullivan, W. J. Dressick, J. V. Caspar and T. J. Meyer, *J. Am. Chem. Soc.*, **102** (1980) 7385; (b) J. V. Caspar, E. M. Kober, B. P. Sullivan and T. J. Meyer, *J. Am. Chem. Soc.*, **104** (1982) 630.
- 32 A. Juris, P. Belser, F. Barigelletti, A. von Zewelsky and V. Balzani, *Inorg. Chem.*, **25** (1986) 256.
- 33 E. S. Dodworth and A. Lever, *Chem. Phys. Lett.*, **119** (1985) 61.
- 34 T. Saji and J. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.*, **60** (1975) 1.
- 35 A. Juris, S. Campagna, I. Bidd, J. M. Lehn and R. Ziessel, *Inorg. Chem.*, **27** (1988) 4007.
- 36 J. V. Caspar, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, **23** (1984) 2104.
- 37 E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, **24** (1985) 2755.
- 38 F. Barigelletti, A. Juris, V. Balzani, P. Belser and A. von Zewelsky, *Inorg. Chem.*, **26** (1987) 4115.