Application of Resonance Raman Spectroscopy to Electronic Structure in Metal Complex Excited States. Excited-State Ordering and Electron Delocalization in Dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz): Complexes of Re(I) and Ru(II)

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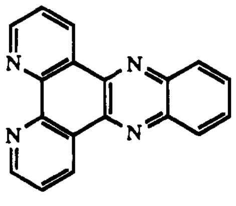
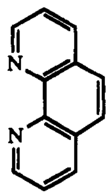
Polypyridyl complexes of Ru(II) containing the ligand dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) have played an important role in the study of DNA intercalation.[1] An initial report suggested that in the excited states reached following $Ru^{II}(d\pi) \rightarrow dppz(\pi^*)$ metal-to-ligand charge transfer (MLCT) excitation of $[Ru(dppz)_3]^{2+}$ and $[Ru(bpy)_2(dppz)]^{2+}$ (bpy is 2,2′-bipyridine) the excited electron is localized on the phenazine portion of dppz.[2] In this interpretation, MLCT excitation leads to a redox-separated state with Ru^{III} and phenazine anion weakly coupled through a bpy bridge. Another possibility is that a dppz-based MLCT excited state is reached, perhaps with considerable charge on the phenazine portion, but strongly coupled to Ru^{III}. A second issue, in Re(I) dppz complexes, is the relative ordering of dppz-based $^3\pi\pi^*$ states and MLCT states. *fac*-$[Re(dppz)(CO)_3Cl]$ is a $\pi\pi^*$ emitter at 77 K, but a MLCT emitter at $T > 145$ K.[3] *fac*-$[Re(dppz)(CO)_3(L)]^+$ with L = 4-ethylpyridine (4-Etpy) or triphenylphosphine (PPh_3) are $^3\pi\pi^*$ emitters at 77 and 298 K. In this preliminary account we report the application of ground- and excited-state resonance Raman spectroscopy to both of these issues.



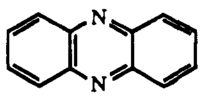
dppz

In the UV−visible spectrum of $[Ru(dmb)_2(dppz)]^{2+}$ in CH_3CN, a band at 450 nm has been assigned to $Ru^{II}(d\pi) \rightarrow dppz(\pi^*)$, and bands at 360 and 368 nm have been assigned to $\pi \rightarrow \pi^*(dppz)$. CW resonance Raman spectra were acquired between 1000 and 1700 cm^{-1} with excitation at 363.8, 432.2, and 496.5 nm. The 363.8 nm spectrum is dominated by dppz bands which appear at 1237, 1305, 1342, 1380, 1404, 1445, 1466, 1487, 1570, and 1594 cm^{-1}, consistent with resonance enhancement from a dppz-localized $\pi \rightarrow \pi^*$ transition. In the 432.2 nm spectrum the pattern of bands, 1022, 1199, 1259, 1270, 1318, 1482, 1550, and 1617 cm^{-1}, is that observed for $[Ru(dmb)_3]^{2+}$ upon $d\pi(Ru^{II}) \rightarrow \pi^*(dmb)$ excitation. In the 496.5 nm spectrum, dppz bands reappear at 1181, 1304, 1404, 1446, 1469, 1488, 1569, and 1595 cm^{-1}. Their appearance provides evidence for a masked $d\pi(Ru^{II}) \rightarrow \pi^*(dppz)$ band in this region. From the UV−visible difference spectrum between $[Ru(bpy)_2(dppz)]^{2+}$ and $[Ru(bpy)_2(dmb)]^{2+}$ this band occurs at λmax ~490 nm with $\epsilon \sim 3000\ M^{-1}\ cm^{-1}$,[3] consistent with the results of semiempirical CNDO/S calculations by Kaim and co-workers.[4]

Excited state resonance Raman spectra of $[Ru(bpy)_2(dppz)]^{2+}$ and $[Ru(dmb)_2(dppz)]^{2+}$ are compared with the spectra of $[Ru(bpy)_3]^{2+}$ and $[Ru(dmb)_3]^{2+}$ in Figure 1. The excited state spectra of the dppz complexes reveal that dppz is the acceptor ligand. Bands for $bpy^{\bullet-}$ or $dmb^{\bullet-}$ are not observed. The bands that do appear have a pattern similar to that for $dppz^{\bullet-}$ prepared electrochemically.[3] The pattern can be modeled as a superposition of $phen^{\bullet-}$ bands (phen is 1,10-phenanthroline) that appear at 1120, 1321, 1447, 1527, 1550, and 1568 cm^{-1} in the excited state spectrum of $[Ru(phen)_3]^{2+}$ and phenazine bands at 1037, 1276, 1400, and 1466 cm^{-1}.[5,6] This is reasonable given the structures of phen and dppz, but only if the excited electron is delocalized somewhat over the entire dppz ligand framework.



1,10-phenanthroline (phen)



phenazine

Resonance enhancements and frequency shifts for the phenazine bands in the excited-state spectra are small relative to phenazine and its radical anion.[6,7] For example, the dominant ring vibration near 1400 cm^{-1} shifts by $-4\ cm^{-1}$ in the excited state spectra of $[Ru(bpy)_2(dppz)]^{2+}$ and $[Ru(dmb)_2(dppz)]^{2+}$ and $-56\ cm^{-1}$ in $phenazine^{\bullet-}$. The phen-based dppz bands at 1597 and 1576 cm^{-1} shift −29 and $-19\ cm^{-1}$ in the excited state spectrum of $[Ru(dmb)_2(dppz)]^{2+}$. The corresponding shifts in $[Ru(phen)_3]^{2+}$ are −45 and $-29\ cm^{-1}$. Decreases in band enhancements and band shifts are consistent with delocalization of the excited electron over the entire ligand skelton. Similar observations have been made for the bbpe-based, MLCT excited state of $[(dmb)_2Ru(\mu\text{-bbpe})Ru(dmb)_2]^{4+}$ (bbpe is trans-1,2-bis-

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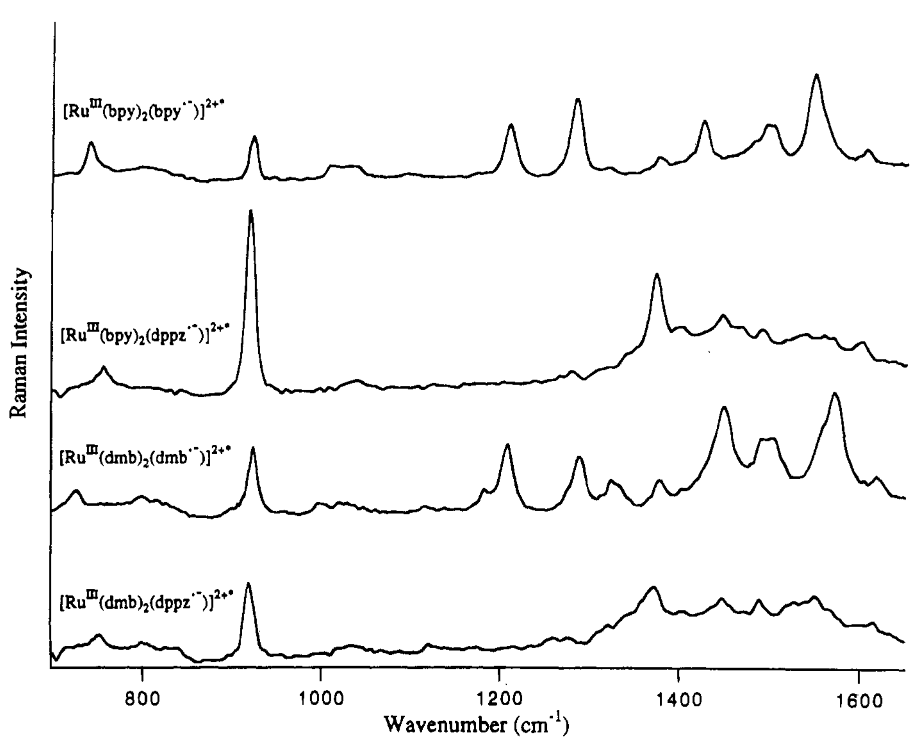
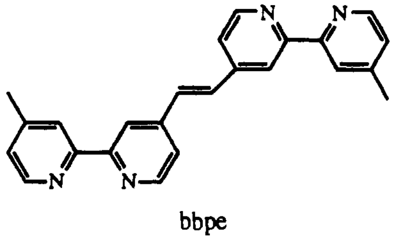


Figure 1. Transient resonance Raman spectra (700–1700 cm^{-1}) of $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$, $[\mathrm{Ru^{II}(bpy)_2(dppz)}]^{2+}$, $[\mathrm{Ru^{II}(dmb)_3}]^{2+}$, and $[\mathrm{Ru^{II}(dmb)_2(dppz)}]^{2+}$ in $\mathrm{CH_3CN}$ at room temperature. The spectra are labeled with the electronic distribution of the excited states. The spectra were measured with 354.7 nm laser excitation as a source for both excitation and Raman scattering. Details of the experimental apparatus and parameters can be found in ref 11.



bbpe

(4-(4′-methyl)-2,2′-bipyridyl)ethane) and an Os analog where the excited electron is partially delocalized over the entire ligand framework.[8] These results are also consistent with partial electronic delocalization in dppz as the acceptor ligand.

The photophysical properties of *fac*-[Re(dppz)(CO)$_3$Cl] are equivocal. It is a $\pi\pi^*$ emitter at 77K in 4:1 (v:v) EtOH–MeOH) based on lifetime measurements and the appearance of the characteristic $\pi\pi^*$ vibronic structure.[3] It is a MLCT emitter at room temperature based on its broad structureless emission and short lifetime. A close interplay between ligand-localized and MLCT excited states is known to be a complicating feature in the photophysics of other Re(I) polypyridyl complexes. Examples are *fac*-[Re(phen)(CO)$_3$(CN)] and *fac*-[Re(3-benzoylpyridine)$_2$(CO)$_3$Cl], where $^3\pi\pi^*$ or $^3n\pi^*$ states lie in close proximity to MLCT states and complicate excited-state ordering and photophysical properties.[9,10]

The ambiguity for *fac*-[Re(dppz)(CO)$_3$Cl] is resolved by excited state resonance Raman measurements on *fac*-[Re(dppz)(CO)$_3$(PPh$_3$)]$^+$ and *fac*-[Re(dppz)(CO)$_3$Cl] in CH$_2$Cl$_2$ at room temperature. Excited state spectra of both complexes acquired with 420 nm pulse and probe were identical with bands appearing at 1029, 1131, 1260, 1290, 1312, 1346, 1382, 1400, 1473, 1526, 1540, 1555, and 1577 cm^{-1}. This pattern is related to but different in detail from the pattern for the Ru^{III}(dppz$^{\bullet-}$) MLCT excited states reported above. For the PPh$_3$ complex both emission and excited state IR are consistent with a lowest energy, dppz-centered $^3\pi\pi^*$ state.[3] The Raman comparison shows that the lowest state in *fac*-[Re(dppz)(CO)$_3$Cl] at room temperature is also $^3\pi\pi^*$ even though it is a MLCT emitter. The room temperature photophysical properties can be interpreted by a two-state model with $^3\pi\pi^*$ lowest and a thermally populated, MLCT state at slightly higher energy. Because of its shorter radiative and nonradiative lifetimes the MLCT state dominates emission and excited state decay at room temperature.[3]

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