

Reply to the Comment on "Resonance Raman Investigation of Ru(phen)₂dppz²⁺ and Related Complexes in Water and in the Presence of DNA"

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Our recent paper describes the rR spectra of Ru(phen)₂dppz²⁺, Ru(phen)₂(F₂-dppz)²⁺, and Os(phen)₂(dppz)²⁺ (phen = 1,10-phenanthroline, dppz = dipyrido[3,2-a:2',3'-d]phenazine, F₂-dppz = 7,8-difluoro-dppz) obtained utilizing 354.7 nm excitation (fwhm ~ 10 ns).¹ The spectra collected for Ru(phen)₂(F₂-dppz)²⁺ and Os(phen)₂(dppz)²⁺ were assigned to the ground state of the complexes at both high and low pulse energies. In the case of Ru(phen)₂dppz²⁺, the power dependence of the peaks at 1365 and 1453 cm⁻¹ were consistent with an excited state. Our interpretation described below and on the recent paper was not based on the assumption that the ³ππ* state of the dppz ligand lies below the MLCT in Ru(phen)₂dppz²⁺, but rather that pumping directly into the dppz ¹ππ* manifold could lead to trapping of the excitation at short time scales on the lowest LC dppz state (³ππ*) if crossing to the MLCT required activation. Lowering of the MLCT relative to the ³ππ* in Ru(phen)₂(F₂-dppz)²⁺ and Os(phen)₂(dppz)²⁺ would result in lowering the activation barrier and much faster crossing to the MLCT.

At the time of our interpretation our knowledge consisted of (1) Coate's spectrum of Ru(phen)₂dppz²⁺ with 354.7 nm pulsed excitation—1261, 1318, 1366, 1434, 1457, 1544, and 1575 cm⁻¹ (from Figure 2)²— and (2) Schoonover's spectra of Ru(L)₂dppz²⁺ with CW 363.8 nm excitation—1237, 1305, 1342,

1380, 1404, 1445, 1466, 1487, 1570, and 1594 cm⁻¹.³ The peak positions for the spectra collected with pulsed 354.7 nm excitation were not listed. Although it was interpreted that the spectrum with 354.7 nm pulsed excitation was due to dppz^{•-}, the peak positions of dppz^{•-} were not reported. None of the reported bands in the excited-state spectrum of Ru(phen)₃²⁺ (1120, 1321, 1447, 1527, 1550, and 1568 cm⁻¹) or those of phenazine (1037, 1276, 1400, and 1466 cm⁻¹) were in good agreement with our largest excited-state peaks at 1365 and 1453 cm⁻¹.³ Neither were those of the Li⁺phen⁻ spectrum collected with 363.8 nm CW excitation, with largest peaks at 1273 and 1576 cm⁻¹.⁴ (3) The reported phenazine ³ππ* spectrum possessed its largest peak at 1371 cm⁻¹ and another large peak at 1447 cm⁻¹, shifted down from 1403 and 1479 cm⁻¹ in the ground state, respectively.⁵ These were correlated to the ground-state peaks of Ru(phen)₂dppz²⁺ at 1403 and 1493 cm⁻¹, shifted down in the excited state to 1365 and 1453 cm⁻¹, respectively.

Given the dppz^{•-} frequencies reported in the preceding Letter by McGarvey and co-workers and the Re(dppz^{•-}) spectrum in press (from ref 9) with peaks at 1365 and 1455 cm⁻¹, it can be concluded that the two excited-state peaks that we observed in our spectrum of Ru(phen)₂dppz²⁺ under pulsed 354.7 nm excitation are from the reduced dppz ligand. The lack of excited-state peaks in Ru(phen)₂(F₂-dppz)²⁺ or Os(phen)₂dppz²⁺ can be explained by their shorter excited-state lifetime and/or lower extinction coefficient of the excited state at 354.7 nm.

References and Notes

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