

# COMMENTS

## Comment on “Resonance Raman Investigation of [Ru(phen)<sub>2</sub>(dppz)<sup>2+</sup>] and Related Complexes in Water and in the Presence of DNA”

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Received: February 4, 1998

In a recent paper,<sup>1</sup> Chen and co-workers described an investigation by transient resonance Raman (TR<sup>2</sup>) spectroscopy of the interaction between [Ru(phen)<sub>2</sub>dppz]<sup>2+</sup> (**1**) and DNA (dppz is dipyrido[3,2-a:2',3'-c]phenazine). Spectra recorded of **1** in aqueous buffer in the absence of DNA using the TR<sup>2</sup> technique at an excitation wavelength of 354.7 nm were interpreted as showing that the species populated and probed by the 354.7 nm laser pulse is the <sup>3</sup>ππ\* state of the dppz ligand and not the dppz ligand-localized MLCT (metal-to-ligand charge transfer) excited state containing the dppz<sup>•−</sup> radical anion. Viewing the spectra in terms<sup>2</sup> of contributions from phen and phenazine fragments of the dppz ligand, they argue that bands at 1365 and 1456 cm<sup>−1</sup> correspond to Raman bands observed<sup>3</sup> in the TR<sup>2</sup> spectrum of the <sup>3</sup>ππ\* state of phenazine.

This assignment of the TR<sup>2</sup> spectrum as due to a dppz ligand-centered <sup>3</sup>ππ\* state differs from that in two previous studies<sup>2,4</sup> of mixed-ligand polypyridyl–dppz complexes with Ru(II), both of which propose a dppz-localized MLCT (i.e., dppz<sup>•−</sup>) excited state. Schoonover et al.<sup>2</sup> studied [Ru(bpy)<sub>2</sub>dppz]<sup>2+</sup> (**2**) and [Ru(dmb)<sub>2</sub>dppz]<sup>2+</sup> (bpy is 2,2'-bipyridine; dmb is 4,4-dimethyl-2,2'-bipyridine) in CH<sub>3</sub>CN while Coates et al.<sup>4</sup> investigated both **1** and **2** in aqueous buffer and in CH<sub>3</sub>CN.<sup>5</sup> Chen et al.<sup>1</sup> describe their results as in good agreement with Schoonover et al. (though no reference is made to the difference in interpretation) but that those reported by Coates et al.<sup>4</sup> “appear different”.<sup>1</sup>

The primary features listed by Chen et al.<sup>1</sup> for **1** (with principal bands at 1262, 1310, 1342, 1365, 1403, 1453, and 1572 cm<sup>−1</sup>) also appear in spectra measured by Coates et al.<sup>4</sup> of the same complex (bands at 1261, 1309 (sh), 1347 (sh), 1366, 1404,<sup>6</sup> 1457, and 1575 cm<sup>−1</sup>). Additionally, TR<sup>2</sup> spectra for (**2**)<sup>4</sup> exhibit the same pattern of bands as reported by Schoonover et al.<sup>2</sup> (1260, 1344, 1370, 1400, 1450, and 1570 cm<sup>−1</sup>). Schoonover et al. assigned this series of bands as originating from dppz<sup>•−</sup> in the MLCT excited state best described as [Ru<sup>III</sup>(bpy)<sub>2</sub>(dppz<sup>•−</sup>)]<sup>2+\*</sup>. This assignment was made by the comparison of the transient data to the resonance Raman

spectrum (363.8 nm) of dppz<sup>•−</sup> prepared electrochemically (bands at 1257, 1286, 1320, 1374, 1400, and 1466 cm<sup>−1</sup>).<sup>7</sup>

Much of the confusion over the lowest excited state of ruthenium(II) dppz complexes may stem from data for ruthenium(I) dppz complexes. There is known to be a close interplay between ligand-centered ππ\* and MLCT excited states for the Re complexes.<sup>8</sup> The transient Raman data for [Re(dppz)(CO)<sub>3</sub>-(PPh<sub>3</sub>)]<sup>+</sup> and [Re(dppz)(CO)<sub>3</sub>Cl] (420 nm pulse and probe; PPh<sub>3</sub> is triphenylphosphine) demonstrate similar bands (1260, 1290, 1312, 1346, 1382, 1400, 1473, 1526, 1540, 1555, and 1570 cm<sup>−1</sup>) as reported for the Rudppz complexes. This pattern is related to but different in detail from the pattern reported for Ru<sup>III</sup>(dppz<sup>•−</sup>) excited states. Importantly, for [Re(dppz)(CO)<sub>3</sub>-Cl], the TR<sup>2</sup> spectrum is different from the RR spectrum of the reduced complex [Re(dppz<sup>•−</sup>)(CO)<sub>3</sub>Cl], which exhibits<sup>9</sup> bands at 1363 and 1456 cm<sup>−1</sup>, close to those observed<sup>1,4,5</sup> in the TR<sup>2</sup> spectrum of ruthenium(II) dppz complexes and consistent with assignment of the latter spectrum to dppz<sup>•−</sup>. From transient infrared studies and emission spectroscopy the lowest excited state of [Re(dppz)(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>+</sup> is clearly ππ\* in character.<sup>10</sup> Considerable caution must be exercised in using transient Raman data exclusively to assign the lowest-lying excited state.

In support of their comments, Chen et al. suggested that the differences between their results and the other studies<sup>2,4</sup> are due to differences in laser pulse energies. This comment is not valid since in the transient Raman experiment the more important consideration is how tightly the laser is focused on the sample. Furthermore, in a preliminary communication,<sup>4</sup> the pulse energies used for our TR<sup>2</sup> studies were not quoted. Chen et al.'s assertion appears to be based on a misreading of a figure caption. In fact, the laser energies routinely used in our TR<sup>2</sup> studies<sup>2,5</sup> are consistently in the region of 3 mJ/pulse, somewhat lower than the lowest pulse energies reported by Chen et al. Coates et al. also carried out investigations<sup>5</sup> at both lower and higher pulse energies (0.5–6 mJ), the latter figure being equal to the highest energy used by Chen et al.<sup>1</sup>

The major question to be addressed is the identity of the species responsible for the TR<sup>2</sup> spectra of **1** and **2**. Chen et al.'s suggestion that it is a <sup>3</sup>ππ\* state of the dppz ligand runs counter to previous conclusions,<sup>2,4,11</sup> and we believe their assignment is unlikely. Wavelength-dependent RR studies of [Ru(dmb)<sub>2</sub>(dppz)]<sup>2+</sup> demonstrate the presence of a masked low-energy Ru → dppz MLCT absorption (λ<sub>max</sub> = 490 nm), suggesting an MLCT state as the most plausible assignment for the lowest-lying excited state in ruthenium(II) dppz complexes.<sup>2</sup> To test their hypothesis, Chen et al.<sup>1</sup> also studied [Os(phen)<sub>2</sub>(dppz)]<sup>2+</sup> (**3**) and attributed the absence of excited-state RR features in the TR<sup>2</sup> spectrum to fast deactivation from the proposed <sup>3</sup>ππ\* state to the lower-lying MLCT state, stated by them to have a lower extinction coefficient relative to the ground state at 354.7 nm. However, an alternative explanation for the absence of excited-state features here is the very short lifetime<sup>11</sup> (ca. 10 ps) of the lowest excited state of **3**. Although it is possible in a single color pump and probe transient RR experiment to populate an excited state of subnanosecond lifetime with a laser pulse of some 10 ns duration (as in the studies<sup>1,4,5</sup> on **1** and **2** in aqueous buffer), provided the laser

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photon flux is sufficiently high,<sup>12</sup> the efficiency of population rapidly decreases with decreasing lifetime.<sup>12,13</sup> For a lifetime as short as 10 ps, the pseudo-steady-state population during a 10 ns laser pulse will not be detectable.

## References and Notes

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