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Localized ^{3}MLCT Excitations of $[Ru(bpy)_{3-x}(bpy\text{-}6,6'\text{-}d_2)_x]^{2+}$ ($x = 0-3$) in $[Zn(bpy)_3](ClO_4)_2$ (bpy = 2,2′-Bipyridine)

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It is accepted that the lowest excited ^{3}MLCT (metal-to-ligand charge transfer) states of $[Ru(bpy)_3]^{2+}$ in solutions and frozen glasses are localized.[1,2] The system in these excited states can be described, crudely, as $[Ru^{3+}(bpy^-)(bpy)_2]^{2+}$. We have shown by a wide range of experiments that this is also the case in high-symmetry crystalline environments.[3] (See ref 3h for a review.) Nevertheless, in a recent issue of this journal, another research group stated[4] that "the charge density is largely delocalized...". The evidence cited was that ^{3}LC (ligand centered) luminescence shows vibrational sidelines in the high-frequency region only of the ligand directly involved in the emission process, whereas ^{3}MLCT spectra of $[Ru(bpy)_{3-x}(bpy\text{-}d_8)_x]^{2+}$ (x = 1, 2) exhibit vibrational sidelines due to bpy and bpy-d_8. This comparison is inappropriate.[3e,h,i] In contrast to ^{3}LC luminescence, the ^{3}MLCT emission is a two center process where the central metal ion changes oxidation state. The neutral "spectator" ligands are coupled to this process. The lowest excited ^{3}MLCT states of $[Ru(bpy)_2(bpz)]^{2+}$ (bpz = 2,2′-bipyrazine) and $[Ru(bpy)_2(bprid)]^{2+}$ (bprid = 3,3′-bipyridazine) are localized on bpz and bprid, respectively, as their π^* orbitals are $\approx$3000 cm^{-1} lower in energy than that of bpy. Nevertheless, bpy modes appear in luminescence over the entire frequency range.[3e,i]

Specific deuteration experiments were especially fruitful in determining the localized nature of the ^{3}MLCT states. Independent ^{3}MLCT transitions to bpy and bpy-d_8 were observed in the spectroscopy of the complexes $[Ru(bpy)_{3-x}(bpy\text{-}d_8)_x]^{2+}$ (x = 1, 2).[3a] Our assignments were tested directly by further deuteration/protonation[3b] of $[Ru(bpy)(bpy\text{-}d_8)_2]^{2+}$. Transitions assigned to ^{3}MLCT origins of bpy/bpy-d_8 in the parent complex shift to higher/lower energy upon further deuteration/protonation as predicted. A minimal variation of the bpy ligand can be achieved by specific deuteration of the *6,6′* positions.[5] Racemic $[Zn(bpy)_3](ClO_4)_2$ provides a well-defined host lattice for $[Ru(bpy)_3]^{2+}$ with little inhomogeneous broadening.[3a] $[M(bpy)_3](ClO_4)_2$ (M = Ru, Zn) crystallizes in the monoclinic space group *C*2/*c* with two ligands being crystallographically related by the crystal *b* axis (*C*2) and a crystallographically distinct ligand lying on *b*.[6] The ^{3}MLCT transitions to the distinct ligand position are several hundred wavenumbers higher in energy than the corresponding transitions to the crystallographically equivalent ligands.[3a,e,i,7] Specifically deuterated complexes $[Ru(bpy)_{3-x}(bpy\text{-}6,6'\text{-}d_2)_x]^{2+}$ with x = 1, 2 can enter the single crystallographic site of the lattice in the two ways sketched in Figure 1. The lowest excited ^{3}MLCT states would shift gradually to higher energy as a function of the deuteration degree if they were delocalized.[3a,b,h] In the case of localized states, one expects independent ^{3}MLCT excitations to bpy and bpy-*6,6′*-d_2. Furthermore, the intensity ratio in excitation of ^{3}MLCT transitions to bpy-*6,6′*-d_2 or bpy is predicted to be 1:2 and 2:1 for the x = 1 and x = 2 systems, reflecting the number of bpy-*6,6′*-d_2 and

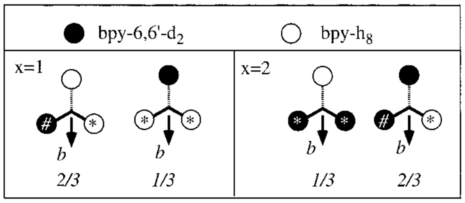

Figure 1. The two ways by which the $[Ru(bpy)_{3-x}(bpy\text{-}6,6'\text{-}d_2)_x]^{2+}$ (x = 1, 2) complexes can enter the single crystallographic site in the $[Zn(bpy)_3](ClO_4)_2$ *C*2/*c* lattice. $*$ denotes ligands from which ^{3}MLCT emission can occur at 1.8 K; # denotes ligands from which thermally activated ^{3}MLCT emission can occur at $\approx$15 K. Probabilities for the two ways of substitution are indicated.

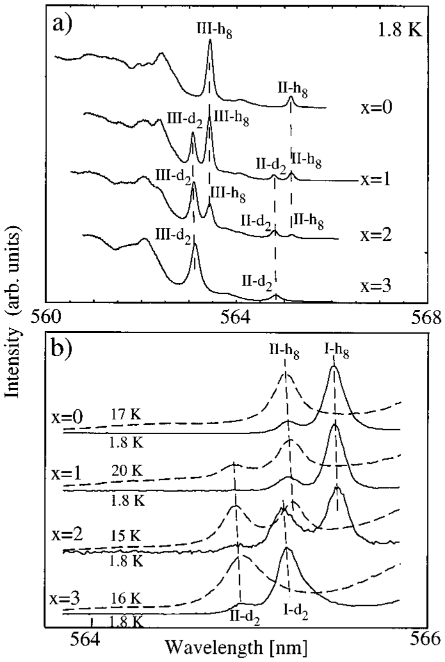

Figure 2. Nonselective (a) excitation and (b) luminescence spectra of $[Ru(bpy)_{3-x}(bpy\text{-}6,6'\text{-}d_2)_x]^{2+}$ (x = 0−3) in $[Zn(bpy)_3](ClO_4)_2$ at 1.8 K in the region of the lowest-energy ^{3}MLCT origins (I, II, III). Concentrations of dopants is <0.1%.

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bpy ligands. In luminescence at 1.8 K, the $x = 1$ system is expected to show ^{3}MLCT emission from bpy whereas the $x = 2$ system should show bpy-*6,6′*-d_2 and bpy ^{3}MLCT emission with a ratio of 1:2 because one-third of the complexes can enter the lattice with the bpy-*6,6′*-d_2 ligands in the equivalent positions (i.e., at lower energy than the bpy ligand in the distinct position). The bpy-*6,6′*-d_2 ^{3}MLCT emission is predicted to rise as a function of temperature due to back-transfer of excitation energy in both systems (high-temperature limits for bpy-*6,6′*-d_2/bpy emission are 2:1 for $x = 2$ and 1:2 for $x = 1$). The bpy/bpy-*6,6′*-d_2 systems are ideally engineered chromophores in which localized origins, with their distinctive spectroscopy, and thermally induced back-transfer can be unambiguously displayed. In the bpy/bpy-d_8 system such back-transfer occurs at 4 times higher temperatures because of the 4 times larger energy gap between corresponding ^{3}MLCT transitions of the bpy and the bpy-d_8 ligands. Observations are obscured in the latter systems by broadening, which becomes severe above 30 K. In Figure 2a, nonselective excitation spectra of the title series are shown in the region of the lowest energy ^{3}MLCT origins. In the $x = 0$ and $x = 3$ systems, three origins denoted as I-h_8, II-h_8, III-h_8 and I-d_2, II-d_2 and III-d_2, respectively, are observed (see also Figure 2b). Origin I is hardly visible in the excitation spectra due to its low oscillator strength ($\approx 10^{-8}$). The origins in the $x = 3$ system display the same energy spacings and relative intensities as the $x = 0$ system but are shifted by ≈ 9 cm^{-1} to higher energy. This is one-fourth of the shift observed for perdeuteration, as expected. In full agreement with the prediction, two sets of origins are observed for the $x = 1$ and $x = 2$ systems. The two sets coincide with the transitions in the $x = 0$ and $x = 3$ systems and thus can readily be assigned to ^{3}MLCT transitions to the bpy or bpy-*6,6′*-d_2 ligands. This assignment is corroborated by the III-d_2:III-h_8 and II-d_2:II-h_8 intensity ratios of 1:2 and 2:1 in excitation for the $x = 1$ and $x = 2$ systems, in full agreement with the prediction. Figure 2b presents the luminescence spectra ($x = 0-3$) at two temperatures. The spectra are dominated by luminescence from origin I at 1.8 K and origin II around 15 K. At 1.8 K, the $x = 1$ system shows ^{3}MLCT luminescence predominantly from bpy. In contrast, the $x = 2$ system shows also ^{3}MLCT luminescence from bpy-*6,6′*-d_2, and the observed ratio of bpy-*6,6′*-d_2 to bpy luminescence is 1:2 as predicted. At higher temperature, the ^{3}MLCT energy can be transferred back to the bpy-*6,6′*-d_2 ligand in both the $x = 1$ and the $x = 2$ systems. The intensity ratios as a function of temperature are in full agreement with a calculation based on a Boltzmann distribution.[5b] The independence of the two sets of transitions is demonstrated in selective spectroscopy.[5b] Independent ^{3}MLCT transitions to bpy and bpy-*6,6′*-d_2 are also observed for the neat [Ru(bpy)$_{3-x}$(bpy-*6,6′*-d_2)$_x$]-(PF$_6$)$_2$ ($x = 1$, 2) crystals.[5b] Our systematic studies of deuteration effects in [Ru(bpy)$_3$]$^{2+}$ establish beyond dispute that the transferred charge in the lowest excited ^{3}MLCT states of [Ru(bpy)$_3$]$^{2+}$ is localized even in high-symmetry crystalline hosts.

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