100205-95-6; $[TbL(OH)(ClO_4)]ClO_4$, 100205-97-8; $[HoL(OH)(ClO_4)]ClO_4$, 100205-99-0; $[ErL(OH)(ClO_4)]ClO_4$, 100206-01-7; $[YbL(OH)(ClO_4)]ClO_4$, 100206-03-9; $[LaL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100228-62-4; $[CeL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-06-2; $[PrL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-09-5; $[NdL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-12-0; $[SmL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-15-3; $[EuL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-18-6; $[GdL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}6H_2O$, 100206-21-1; $[TbL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-24-4; $[DyL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-27-7; $[HoL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-30-2; $[ErL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-33-5; $[TmL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-36-8; $[YbL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-39-1; $[LnL(CH_3COO)(H_2O)](CH_3COO)Cl{\cdot}nH_2O$, 100206-42-6; 2,6-diacetylpyridine, 1129-30-2; 1,2-diaminoethane, 107-15-3.

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Emission from $[Ru(bpy)_3]^{3+}$ in Solids and the Question of Delocalization

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The much studied[1] emitting states of $[Ru(bpy)_3]^{2+}$ (I) are now generally assigned, in solution at least, to a ^{3}(MLCT) manifold, with the promoted electron localized on one ligand only,[2] as in the formulation $[Ru^{III}(bpy^-)(bpy^0)_2]^{2+}$ proposed[3] by us from analogy with the partly reduced species, and closely similar treatments have been applied to the $[Ru^{II}(bpy)]$ chromophore in a range of $[Ru^{II}(bpy)]$ and $[Ru^{II}(bpy)_2]$ complexes.[4] However, the situation in condensed phases and at low temperatures may be more complicated.[5]

Recently, Yersin et al. reported the results of elegant experiments on the polarized emission spectra of crystals containing I.[6] We must, however, question any inference that their data provide evidence regarding the degree of delocalization of I in the solid. On the contrary, as we shall show, their experiment is systematically silent on this point, although in principle variants of it could perhaps give more definite information.

Yersin's experiment distinguished between emission polarized along the molecular z axis and that lying in the molecular (xy) plane. The results were interpreted in terms of a D_3' structure for I and in these terms gave a valid distinction between E′ and A_2' levels, with the former giving emission perpendicular, and the latter emission parallel, to the molecular z axis. However, an interpretation in terms of a localized excited state would be equally valid. What is required is a test for *differences* between x- and y-polarized emission intensities when excitation is along, e.g., the molecular x axis, and both these intensities are *combined* in Yersin's experiment. An excited-state distortion, lowering the symmetry to C_2', would split the E′ emission into A′ and B′ components; but unfortunately Yersin's experiment does not give the separate intensities of these components. Thus the central question—whether the x- and y-polarized emissions are concentrated *within* the xy plane along the direction of the electric vector of the exciting light—remains unanswered.

In principle, it may be possible to test for localization in the crystalline phase by irradiating along the z axis with light polarized along the molecular x axis. If the excited state produced is truly of D_3 symmetry, then x and y emissions will be of equal intensity and the 180° scattering will be unpolarized. But if, as our model maintains, I is to be regarded at low exciting energy as three separate, noncommunicating linear parallel absorber–emitters at 120° to each other, then simple geometric considerations show[7] that the ideal intensity ratio $I(\|):I(\perp)$ is 3:1; curiously, this is independent of where the incident light polarization is chosen within the xy plane.[7] It would, of course, be necessary for the exciting light to be of sufficiently long wavelength to provoke the well-known[8] polarization anomaly of I in disordered phases, to which the predicted effect is in our model[2h] directly related. It would also be necessary to avoid loss of polarization through *intermolecular* energy transfer, a goal that might be obtainable with sufficiently dilute crystals. Elementary summation shows, fortunately, that for some structures at least the consequences of inter- and intramolecular energy transfer need not be identical.[9]

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(7) Let the oscillating electric vector of the light lie at angle ϕ to chromophore 1. Then the probability of absorption by chromophore 1 followed by emission is of the form $K\Phi \cos^2 \phi$, and the probability of absorption by chromophore 1 followed by parallel emission is of the form $K\Phi \cos^4 \phi$. Summing over all three chromophores, we have total emission probability of the form $K\Phi[\cos^2 \phi + \cos^2 (\phi + \pi/3) + \cos^2 (\phi + 2\pi/3)]$ and parallel emission probability of the form $K\Phi[\cos^4 \phi + \cos^4 (\phi + \pi/3) + \cos^4 (\phi + 2\pi/3)]$. These expressions reduce to $3K\Phi/2$ and $9K\Phi/8$, respectively, independent of ϕ.

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