Dalton Communication

Application of Deuteriation to Determine the Location of the Emitting State in Mixed-ligand Ru^{II} Polypyridyl Complexes

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The location of the emitting triplet state in heteroleptic Ru^{II} polypyridyl complexes has been determined by a new method using deuteriated ligands and emission-lifetime measurements, and a new single-step, high yield synthesis of perdeuteriated 2,2′-bipyridyl has been developed.

With the increasing interest in supramolecular chemistry, and in particular in the design of photonic devices,[1] simple methods to determine the location of excited states in mixed-ligand metal complexes are needed. A number of methods are available which achieve this objective, amongst them time-resolved resonance Raman spectroscopy.[2] Here we report a new simple method to determine the emitting ligand in heteroleptic Ru^{II} complexes, based on the effect of deuteriation of one of the ligands on the emission lifetime of the Ru^{II} complex.

Although it has long been noted that upon deuteriation of the ligands in homoleptic Ru^{II} polypyridyl complexes the excited-state lifetimes of the metal complexes increase,[3,4] a systematic investigation of this phenomenon in mixed-ligand Ru^{II} complexes has not been carried out. There are a small number of reports in the literature, where deuteriation of polypyridyl ligands has been employed either to simplify ^{1}H NMR spectra,[5] or to obtain information about the excited-state behaviour of the complexes, using either time-resolved resonance Raman spectroscopy[2] or by investigating the detailed fine structure of emission spectra at low temperatures.[4]

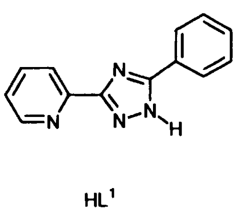
Ligand deuteriation as a tool for the study of excited states is a relatively under-exploited method, mainly due to the synthetic difficulties in obtaining deuteriated compounds. At present the most convenient preparation of perdeuteriated 2,2′-bipyridyl reported in the literature involves several steps. As proposed by Cook *et al.*,[6] 2,2′-bipyridyl 1,1′-dioxide can be deuteriated with D_2O–NaOD and then reduced with PCl_3. However, this synthesis is arduous, particularly because of the low overall yield. Furthermore, the bis(*N*-oxide) must be prepared from 2,2′-bipyridyl.

The improved synthesis reported here employs mild conditions and allows for a single-step, direct deuteriation of 2,2′-bipyridyl. Although the reaction times are long, the synthesis is simple and the yields are high. In a typical run, 2,2′-bipyridyl (bipy) (3 g, 0.19 mol) was added to 30 cm^3 of D_2O (deuteriation 99.9%) and the reaction mixture allowed to react in the presence of the H–D exchange catalyst Pd/C (Aldrich, 10% Pd) (0.5 g) in a Teflon-coated steel high pressure reactor at 200 °C for 8 d. The contents of the reactor were then collected and filtered hot to remove the Pd catalyst and D_2O was removed under vacuum to obtain the product. The Pd/C catalyst was washed with acetone to remove any product present on its surface and the material obtained in this manner was recrystallised from hot water. The ^{1}H NMR spectrum of the product obtained revealed four singlets, indicating > 80% deuteriation. To achieve complete deuteriation, the same procedure was repeated with fresh D_2O for another week and the reaction mixture worked up as described above. The overall yield of the fully deuteriated product [$^2H_8$]bipy was > 80%, and the material obtained was ^{1}H-NMR silent. Infrared spectroscopy showed bands at 2250–2295 cm^{-1}, attributed to ν_{C-D} vibrations.

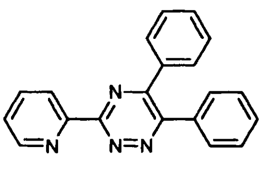
Our method to determine the emitting and spectator ligands in mixed-ligand complexes is best illustrated by considering two different Ru^{II} complexes $[Ru(bipy)L^1]^+$ **1** and $[Ru(bipy)L^2]^{2+}$ **2** [HL^1 = 3-phenyl-5-(pyridin-2-yl)-1,2,4-triazole, L^2 = 5,6-diphenyl-3-(pyridin-2-yl)-1,2,4-triazine]. (Similar results were obtained for a range of other Ru^{II} polypyridyl compounds.[7]) These complexes were isolated as their PF_6 salts using literature methods,[8,9] yielding the undeuteriated $[Ru(bipy)_2L][PF_6]_n$ compounds **1h** ($L = L^1$, $n = 1$) and **2h** ($L = L^2$, $n = 2$) and the deuteriated $[Ru([^2H_8]bipy)_2L][PF_6]_n$ compounds **1d** and **2d**.

For the undeuteriated complexes **1h** and **2h**, emission lifetimes (room temperature, acetonitrile, deaerated) of 225 and 740 ns were obtained respectively. Their deuteriated counterparts, **1d** and **2d**, yielded values of 410 and 780 ns under the same conditions (all values ± 15 ns). No significant differences were observed in the absorption and emission energies for the bipy and [$^2H_8$]bipy species. The absorption and emission maxima are found at respectively 482 nm and 690 nm for **1h** and **1d** and at 480 nm and 714 nm for **2h** and **2d** (all values ± 5 nm).

According to Siebrand's theory of the non-radiative transition,[10] high energy, anharmonic C–H stretching vibrations



HL^1



L^2

are important promotional modes in non-radiative decay. This implies that excited-state lifetimes should increase upon deuteriation. For compound **1**, the expected increase of the emission lifetime upon deuteriation of bipy is indeed observed. However, for compound **2** no significant change in the emission lifetime is observed upon deuteriation of bipy. We propose that this behaviour is associated with the location of the excited state, *i.e.* whether the excited state is bipy or L based. In compound **1**, which contains an electron-rich triazolate donor, the emitting state is firmly bipy based.[8] In the triazine-containing complex **2**, however, the emitting state is based on the electron-poor triazine ligand[9] and as a result the vibrational modes affected by the deuteriation are *not available* for a deactivation of the excited state.

Our results therefore suggest strongly that in heteroleptic compounds the emission lifetimes will only increase upon deuteriation of a particular ligand when the excited state is located on this ligand. This result is on reflection not unexpected. However, there is to the best of our knowledge no prior mention of this phenomenon in the literature, which may be of considerable importance in the field of supramolecular chemistry. By a sytematic deuteriation of the different components in a supramolecular system information about the relative excited-state energies of these components in the supramolecular system can be obtained in a very direct manner. Importantly, we expect that our method can be adapted to other polypyridyl-type ligands. Experiments have already shown that perdeuteriated 1,10-phenanthroline can be prepared by the same method. In particular, we see application of our method in the study of mixed-ligand ruthenium dyes used in solar-energy conversion systems[11] and in the investigation of large multinuclear ruthenium and osmium clusters such as those reported by Balzani and co-workers.[12]

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