

A fast time-resolved infrared spectroscopic investigation into the nature of the lowest excited state and excimer formation in Pt^{II} diimine cyanides

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Time-resolved infrared spectroscopy (TRIR) has been used to probe the nature of the lowest excited state of [Pt^{II}(dpphen)(CN)₂] (dpphen = 4,7-diphenyl-1,10-phenanthroline) both in fluid solution at room temperature and in a glass at 77 K. The positions of the ν(CN) bands in [Pt^{II}(dpphen)(CN)₂] are only slightly (less than 5 cm⁻¹) shifted upon formation of the excited state, thus supporting their assignment as the π–π* intraligand state. At 77 K [Pt^{II}(dpphen)(CN)₂] has a highly structured luminescence with a lifetime of 170 μs, which is also characteristic of a π–π* excited state. In contrast, the lowest excited state of [Ru(bpy)₂(CN)₂] has MLCT character in both fluid solution at ambient temperature and at 77 K as shown by a large positive shift of ν(CN) relative to the ground state. Also we have monitored the monomer–excimer equilibrium of [Pt^{II}(dpphen)(CN)₂] in fluid solution using the ns-TRIR technique.

Introduction

The photochemistry of square planar platinum(II) polyimine complexes is of great interest particularly because of their potential use as probes for DNA,¹ in solar energy conversion and storage and in photocatalysis.² These complexes exhibit rich photochemistry/photophysics because of the existence of a manifold of low-lying excited states of different orbital parentage. However, luminescence from Pt^{II} polyimines in fluid solutions is a rare phenomenon. For those complexes which do emit in fluid solutions, the LUMO is predominantly centered on the polyimine ligand, but the localization of the HOMO can vary depending on the particular complex.³ In the series of complexes [Pt(diimine)X₂] (diimine = 2,2'-bipyridine, X = Cl;⁴ diimine = 4,4'-Y₂-2,2'-bipyridine, Y = NH₂, OEt, Me, H, Ph, Cl or CO₂Me, X = Cl;⁵ diimine = 2,2'-bipyridine or 1,10-phenanthroline, X = Cl, Br, I, SCN and N₃;⁶) the lowest excited state is known to be metal-to-ligand charge transfer (MLCT) in nature. However, the nature of the lowest excited state of [Pt(diimine)(CN)₂] is less clear.

In solution, the lowest excited state of [Pt(bpy)(CN)₂] (bpy = 2,2'-bipyridine) was assigned to MLCT by analogy with the early absorption data for [Pt(bpy)Cl₂].⁷ However the emissive state of [Pt(biquin)(CN)₂] (biquin = 3,3'-biisoquinoline) was reported to have mixed d–π*/π–π* character.⁸ A large percentage of metal-to-ligand charge transfer character was also demonstrated for the lowest excited state of [Pt(5-Ph-phen)(CN)₂] (5-Ph-phen = 5-phenyl-1,10-phenanthroline) in fluid solution.⁹ Electrochemical studies can provide valuable and complementary information for elucidating the localization of the HOMO and LUMO of transition metal complexes. [Pt(5,5'-dmbpy)(CN)₂] (dmbpy = 5,5'-dimethyl-2,2'-bipyridine) has an irreversible oxidation that was attributed to a metal-based Pt^{II} → Pt^{III} process.¹⁰ Two reversible ligand-centered reductions were also observed. In principle, the electrochemical data suggest that the lowest excited state in [Pt(5,5'-dmbpy)(CN)₂] should have MLCT character. In practice, the structured emission of [Pt(5,5'-dmbpy)(CN)₂] in room temperature solutions was assigned to a π–π* state perturbed by the Pt^{II}

ion¹⁰ and the concentration dependence of the excited state lifetime was interpreted in terms of self-quenching.¹⁰

Most square planar Pt^{II} polyimine complexes have excited state lifetimes that are concentration dependent, which is consistent with self-quenching of the excited state, which is sometimes accompanied by excimer formation.³ It has previously been stated that the emission spectrum of [Pt(dpphen)(CN)₂] (dpphen = 4,7-diphenyl-1,10-phenanthroline) is due to a combination of π–π* intraligand (IL) emission and emission from an excimer.^{11,12} At low concentration the luminescence spectrum of [Pt(dpphen)(CN)₂] in CH₂Cl₂ is dominated by a structured (not clearly resolved) band centered at 525 nm, which was assigned to a dpphen localized π–π* IL excited state. Increasing the concentration of [Pt(dpphen)(CN)₂] resulted in a decrease in luminescence intensity and lifetime of this high-energy band and the appearance of a broad unstructured low energy band (665 nm) attributed to an excimer emission.

Fast time-resolved IR spectroscopy (TRIR), a combination of UV flash photolysis and fast infrared detection, is a powerful tool for probing the nature of the excited states of coordination compounds.^{13–15} This is particularly true for complexes containing groups such as CO and CN since these act as a direct probe of the electron density on the metal. Peripheral IR reporter groups such as carboxylic acids, esters and amides on substituted diimine ligands have also been used to indirectly probe charge transfer processes using TRIR.¹⁶

In this paper we compare the photophysics of [Pt(dpphen)(CN)₂] and [Ru(bpy)₂(CN)₂], both in room temperature solution and in 77 K glass using TRIR and luminescence measurements in order to probe the nature of the lowest excited state and excimer formation in [Pt(dpphen)(CN)₂].

Results and discussion

Luminescence measurements of [Pt(dpphen)(CN)₂]

The electronic absorption spectrum of [Pt(dpphen)(CN)₂] in fluid CH₂Cl₂ solution at 298 K shows absorption bands in the

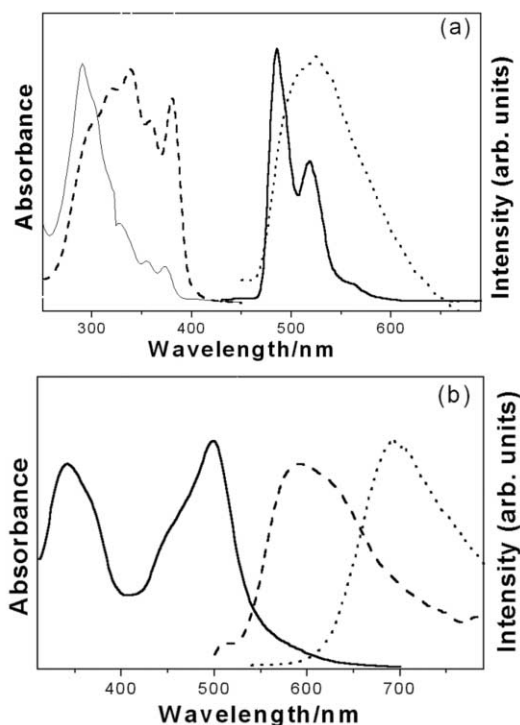


Fig. 1 (a) [Pt(dpphen)(CN)₂] in CH₂Cl₂ solution at 298 K: absorption spectrum (—), emission spectrum under 355 nm excitation (···). [Pt(dpphen)(CN)₂] in BuCN/PrCN glass at 77 K: emission spectrum under 355 nm excitation (—) and excitation spectrum registered at 490 nm (---). (b) [Ru(bpy)₂(CN)₂] in CH₂Cl₂ solution at 298 K: absorption spectrum (—), emission spectrum under 500 nm excitation (···). [Ru(bpy)₂(CN)₂] in BuCN/PrCN glass at 77 K: emission spectrum under 450 nm excitation (---).

200–370 nm region (Fig. 1a). Excitation into the 370 nm band leads to an emission spectrum, which consists of one relatively structured band centered at 530 nm (18900 cm⁻¹) and a structureless band at 610 nm (16400 cm⁻¹). The shape of the emission spectrum is concentration dependent, with the 16400 cm⁻¹ band becoming more prominent upon increasing concentration of [Pt(dpphen)(CN)₂] in solution. These results are consistent with the luminescence data previously reported for [Pt(dpphen)(CN)₂].¹¹ Therefore, the emission bands at 18900 cm⁻¹ and 16400 cm⁻¹ were assigned to monomer and excimer emission respectively. Excitation into the 370 nm band in the rigid glass (BuCN/PrCN) at 77 K leads to a highly structured emission (Fig. 1a) with maxima at 490, 530 and 560 nm (20420, 18870 and 17850 cm⁻¹). Vibronic spacings in the emission spectrum (1020 cm⁻¹ and 1550 cm⁻¹) are in good agreement with the vibrations of the dpphen ligand (KBr pellet).

The luminescence decay traces at 77 K remain mono-exponential along the emission profile, giving a lifetime of (170 ± 10) μs. The excitation spectra recorded at 20420, 18870 and 17850 cm⁻¹ all correspond to the absorption spectrum (Fig. 1a), revealing that the three emission features originate from the same electronic state. A small (less than 600 cm⁻¹) increase in emission energy observed (Fig. 1a) in the rigid glass at 77 K *versus* fluid solution reveals only small changes in the electronic structure taking place upon promotion to the excited state. This should be contrasted with the larger (more than 2600 cm⁻¹) shift of the emission maximum on going from fluid solution to the rigid low temperature glass observed for [Ru(bpy)₂(CN)₂] (Fig. 1b), whose lowest excited state is MLCT.¹⁷

For MLCT it is known that the emission shifts to higher energy on going from fluid solution to a rigid glass, so called luminescence rigidochromism. The difference between the luminescence rigidochromism observed for [Ru(bpy)₂(CN)₂] and [Pt(dpphen)(CN)₂] is noteworthy, since the formation of an

MLCT excited state is accompanied by a much larger electronic redistribution compared to formation of a π-π* IL excited state.

On the basis of the luminescence data in the rigid media at 77 K the emission spectrum of [Pt(dpphen)(CN)₂] is likely to correspond to the π-π* excited state of the dpphen ligand. However, the luminescence spectrum of the complex in fluid solution at room temperature is obscured by the excimer formation and the nature of the lowest excited state remains less clear.

Time-resolved infrared measurements

[Pt(dpphen)(CN)₂] in CH₂Cl₂ solution at room temperature.

The ground state FTIR spectrum of [Pt(dpphen)(CN)₂] in CH₂Cl₂ is characterized by two overlapping bands at 2148 and 2138 cm⁻¹ (Fig. 2a), which correspond to the symmetric and

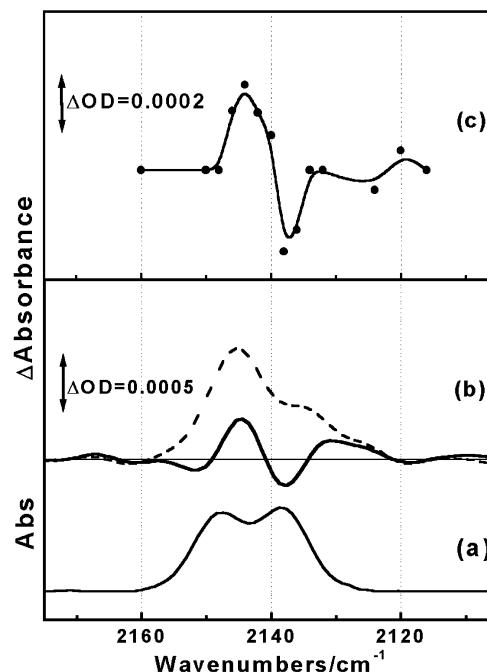


Fig. 2 (a) Ground-state FTIR of [Pt(dpphen)(CN)₂] in CH₂Cl₂ at 298 K, (b) time-resolved FTIR (—) obtained by averaging over the first 5 μs after 355 nm excitation of this solution and excited state IR spectrum (---) revealed after scaled addition of ground state spectrum, (c) point-by-point TRIR spectrum of [Pt(dpphen)(CN)₂] in BuCN/PrCN at 77 K (●) after 355 nm excitation. The solid line corresponds to the cubic spline through the data points.

antisymmetric ν(CN) vibrations, respectively. The step-scan time-resolved FTIR (s²-FTIR) spectrum of this solution (2 × 10⁻⁴ M), following laser excitation (355 nm), is shown in Fig. 2b (—).

It is clear that neither bleaching of the parent absorption, nor distinct formation of the new bands is observed. However, a clearer picture can be obtained by the scaled addition of the ground state FTIR to the s²-FTIR spectra, since this produces the IR spectrum of the excited state. The excited state spectrum (Fig. 2b, ---), generated by this approach, has two overlapping ν(CN) bands at approximately 2143 and 2135 cm⁻¹. Therefore, it appears that the ν(CN) vibrations of the excited state decrease slightly in frequency compared to the ground state. There are no new absorption bands with increased wavenumbers relative to the parent bands, which would be characteristic of an MLCT excited state.^{13,15} The very slight shift of the ν(CN) bands upon going from the ground state to the excited state was also observed when the experiment was performed at 77 K (Fig. 2c).

The MLCT excited states of coordination compounds have been widely studied by TRIR. The characteristic shift observed for ν(CO) in metal carbonyls upon formation of the MLCT

excited state is $+(50-60) \text{ cm}^{-1}$.^{13,15} For metal cyanides the $\nu(\text{CN})$ shift upon formation of the MLCT state is somewhat smaller (approximately 30 cm^{-1}),¹⁵ reflecting the better σ -donor and weaker π -acceptor properties of the CN-ligand compared to CO.

We have studied $[\text{Ru}(\text{bpy})_2(\text{CN})_2]$ using TRIR since this complex is known¹⁷ to possess an MLCT lowest excited state. This allows a direct comparison with $[\text{Pt}(\text{dpphen})(\text{CN})_2]$. The ground state FTIR spectrum of $[\text{Ru}(\text{bpy})_2(\text{CN})_2]$ in room temperature CH_2Cl_2 has two overlapping bands at 2082 and 2068 cm^{-1} (Fig. 3a). The point-by-point TRIR spectrum of this

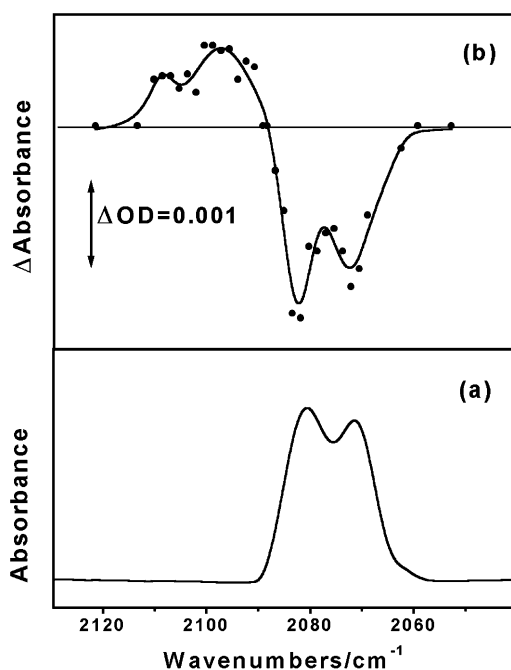


Fig. 3 (a) Ground-state FTIR of $[\text{Ru}(\text{bpy})_2(\text{CN})_2]$ in CH_2Cl_2 at 298 K, (b) point-by-point TRIR spectrum obtained 0.4 μs after the 355 nm excitation (●) and a multi-gaussian fit to the TRIR data (—).

solution presented in Fig. 3b shows that the $\nu(\text{CN})$ bands are increased in frequency by *ca.* 35 cm^{-1} upon promotion to the excited state.

To the best of our knowledge, there have been no reports so far on small (less than 20 cm^{-1}) $\nu(\text{CN})$ shifts in the IR spectra of the excited states of metal complexes.

The few reports available on small $\nu(\text{CO})$ shifts in the TRIR spectra of metal complexes are concerned with either $\pi-\pi^*$ ^{15,18} or $\sigma-\pi^*$ charge transfer¹⁹ excited states, the formation of which is not accompanied by significant changes of electronic density on the metal center.

The small shift in $\nu(\text{CN})$ bands that we have observed with $[\text{Pt}(\text{dpphen})(\text{CN})_2]$ is consistent with the formation of a $\pi-\pi^*$ excited state. However, the emission studies¹¹ revealed the existence of a monomer–excimer equilibrium in fluid solution at room temperature (see above). Since formation of an excimer generally is not accompanied by large changes in the electronic density,²⁰ the TRIR spectrum obtained in fluid solution for $[\text{Pt}(\text{dpphen})(\text{CN})_2]$ could also be due to an excimer absorbance. Thus, the small change of $\nu(\text{CN})$ in the TRIR spectrum of $[\text{Pt}(\text{dpphen})(\text{CN})_2]$ could correspond to either a $\pi-\pi^*$ excited state of the monomer or excimer, or to a superposition of the spectra of both species. To investigate this further, TRIR kinetic measurements were performed using the IR diode based spectrometer (point-by-point approach) in fluid solution at room temperature at different concentrations of $[\text{Pt}(\text{dpphen})(\text{CN})_2]$.

Typical kinetic traces obtained are shown in Fig. 4 and 5. The transient decay kinetics at 2145 cm^{-1} (Fig. 4c, d) and the parent

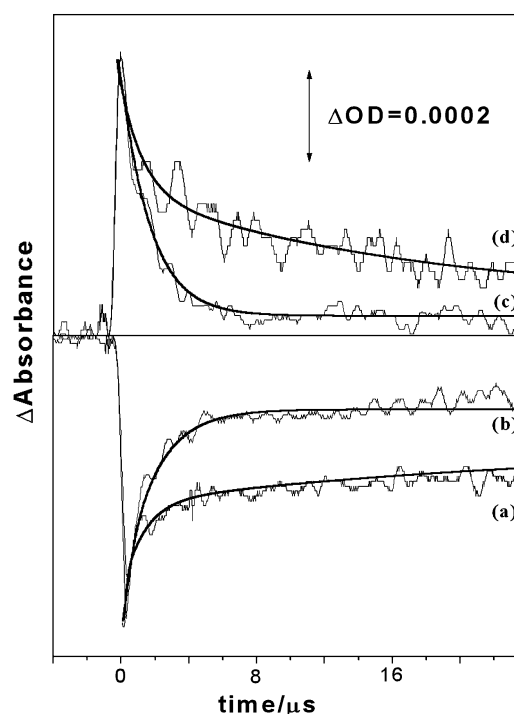


Fig. 4 Kinetic traces obtained at 2139 cm^{-1} (a, b) and 2145 cm^{-1} (c, d) after 355 nm excitation of a $1 \times 10^{-5} \text{ M}$ (a, d) and a $1 \times 10^{-4} \text{ M}$ (b, c) solution of $[\text{Pt}(\text{dpphen})(\text{CN})_2]$ in CH_2Cl_2 at 298 K. — are double-exponential fits for these data.

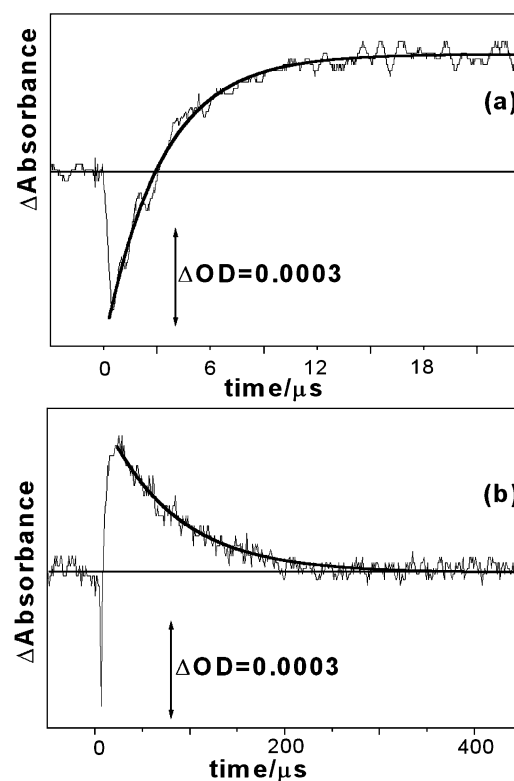


Fig. 5 Kinetic traces obtained at 2134 cm^{-1} after 355 nm excitation of a $1 \times 10^{-5} \text{ M}$ solution of $[\text{Pt}(\text{dpphen})(\text{CN})_2]$ in CH_2Cl_2 at 298 K: (a) shows the initial part of the trace from 0 \rightarrow 20 μs and (b) shows the complete trace from 0 \rightarrow 0.4 ms. — correspond to mono- (a) and double-exponential (b) fits for the kinetic traces.

recovery kinetics at 2139 cm^{-1} (Fig. 4a, b) are dominated by the fast decay, but show a residual absorbance within the timescale of 20 μs . The TRIR trace at 2134 cm^{-1} is more complex with a bleach followed by a fast growth of a positive absorbance, which then decays slowly (Fig. 5a, b).

The TRIR kinetic traces remain biexponential along the whole spectral range, revealing the presence of at least two species in the excited state with overlapping bands.

The relative contributions of the two components (fast and slow) are concentration dependent. An increase in the relative amplitude of the longer-lived transient is observed upon dilution from 1×10^{-4} to 1×10^{-5} M. This is clearly seen in both transient decay and parent recovery (Fig. 4). The lifetimes obtained from the TRIR experiments for the long-lived ($\tau \approx 100$ μ s) and short-lived ($\tau \approx 3$ μ s) components are in good agreement with the luminescence decay rates reported for the monomer and the excimer of [Pt(dpphen)(CN)₂] respectively.¹¹ The increase in the relative amount of the long-lived component upon dilution is also consistent with the existence of the monomer–excimer equilibrium. Therefore, we are able to assign the short and long lived components observed in the TRIR kinetic traces to the excimer and the [Pt(dpphen)(CN)₂] monomer in the excited state respectively.

The difference in the TRIR spectra at high and low concentration of [Pt(dpphen)(CN)₂] is shown in Fig. 6. At high

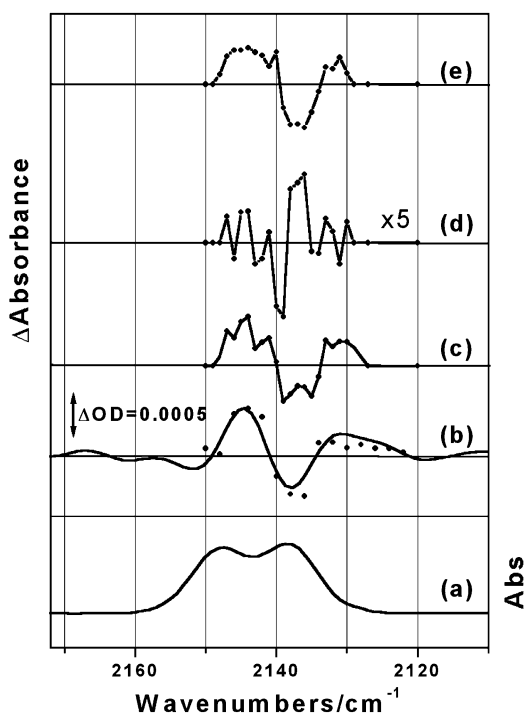


Fig. 6 (a) Ground-state FTIR spectrum of [Pt(dpphen)(CN)₂] in CH₂Cl₂ at 298 K; (b) TRIR spectra of 2×10^{-4} M solution obtained with step-scan FTIR (—) by averaging over the first 5 μ s after 355 nm after 355 nm laser excitation and by the point-by-point technique (●) at 400 ns after laser excitation; (c) point-by-point TRIR spectrum of a 1×10^{-5} M solution obtained 400 ns after laser excitation (●); (d) point-by-point TRIR spectrum of a 1×10^{-5} M solution at 20 μ s after laser excitation (the difference IR spectrum of the monomer in the excited state); (e) difference IR spectrum of the excimer obtained by subtraction of spectrum (d) from spectrum (c). Lines (c, d, e) are straight connections between the experimental points.

concentration (2×10^{-4} M) the step-scan FTIR (Fig. 6b, —) and IR diode laser based technique (Fig. 6b, ●●●) show similar changes in absorbance, which should represent the overlap of the excimer bands and parent bleach. The TRIR point-by-point measurements of this solution show the monoexponential decay of both parent and transient absorptions. This confirms that only one type of excited state species is present in the saturated solution of [Pt(dpphen)(CN)₂] after excitation.

The low concentration measurements (1×10^{-5} M) were obtained with a diode laser-based spectrometer. The spectrum recorded 400 ns after the laser pulse (Fig. 6c) is the superposition of the monomer and excimer spectra. The TRIR

spectrum, recorded 20 μ s after the laser pulse (Fig. 6d) would correspond to the π – π^* excited state of the monomer of [Pt(dpphen)(CN)₂], since all the excimer has decayed away at this longer time. The difference between the spectrum at 400 ns (monomer and excimer) and a pure monomer spectrum at 20 μ s represents the TRIR spectrum of the excimer of [Pt(dpphen)(CN)₂]. Both monomer in the π – π^* excited state (Fig. 6d) and excimer (Fig. 6e) spectra are characterized by the very small shift of ν (CN) absorptions *versus* the ground state.

[Pt(dpphen)(CN)₂] in BuCN/PrCN glass at 77 K. Results from both step-scan time-resolved FTIR and IR diode laser point-by-point TRIR measurements for [Pt(dpphen)(CN)₂] in BuCN/PrCN glass at 77 K show only a small shift of ν (CN) upon promotion to the excited state (Fig. 2c). From these data we could assign the lowest excited state of [Pt(dpphen)(CN)₂] in a glass at 77 K to a π – π^* intraligand excited state of the dpphen ligand. This result is consistent with the low temperature luminescence measurements.

Conclusions

Nanosecond TRIR and low temperature luminescence measurements have allowed us to elucidate the π – π^* nature of the lowest excited state of [Pt^{II}(dpphen)(CN)₂] both in fluid solution at room temperature and in a glass at 77 K. The positions of the ν (CN) bands in [Pt^{II}(dpphen)(CN)₂] are only slightly (less than 5 cm^{-1}) shifted upon formation of the excited state. In contrast, the lowest excited state of [Ru(bpy)₂(CN)₂] is characterized by a large positive shift of ν (CN) if compared to the ground state, thus supporting its MLCT assignment.

The monomer–excimer equilibrium for the [Pt^{II}(dpphen)(CN)₂] fluid solution has been monitored by the TRIR technique, which allowed us to obtain the time-resolved infrared spectra of both the excimer and the π – π^* intraligand excited state of a metal cyanide complex.

Experimental

Time-resolved infrared (TRIR) apparatus

The Nottingham TRIR apparatus had been described in detail elsewhere.²¹ In these experiments two different types of TRIR instrumentation were used, both using a pulsed Nd:YAG laser (Spectra Physics Quanta-Ray GCR-12). We used either a step-scan FTIR interferometer (Nicolet Magna 860) or a continuous wave (cw) IR diode laser (Mütek MDS 1100) to monitor the transient IR absorptions. The Nottingham step-scan FTIR apparatus has been described in detail elsewhere.²² Briefly, the apparatus comprises of a commercially available step-scan FTIR spectrometer (Nicolet Magna 860) equipped with a 100 MHz 12-bit digitizer and a 50 MHz MCT detector interfaced with a Nd:YAG laser (Spectra Physics GCR-12). Synchronization of the Nd:YAG laser with data collection was achieved using a pulse generator (Stanford DG535). A commercially available IR cell (Harrick, 1 to 3 mm pathlength) was used with a home-built flow system. In the experiments using cw IR lasers the change in IR transmission at one particular IR frequency was measured following UV excitation and IR spectra were built up on a “point-by-point” basis by repeating the measurements at different infrared frequencies. In principle, both TRIR approaches should give the same information. In practice, for a high resolution TRIR measurements over a narrow spectral region, the IR diode based technique can obtain data more easily. This is especially true when detecting small absorbance changes. Low-temperature experiments were performed in a home-built IR cell.

Emission measurements

Emission measurements were performed on deaerated solutions, using an Edinburgh Instruments FS-900 apparatus, in

either 1 cm (RT) or 3 mm quartz cells (77 K). Emission spectra were registered with a Xe lamp as the excitation source. Lifetime measurements were performed in single photon counting mode, with a nanosecond flash lamp as the excitation source.

Synthesis and materials

All operations were performed under an inert gas atmosphere. The complexes $[K_2Pt(CN)_4]$ (Aldrich), $[Ru(bpy)_2Cl_2]$ and $K_2[RuCl_5(H_2O)]$ (Lancaster) were used as supplied; $[Pt(dpphen)(CN)_2]^{23}$ and $[Ru(bpy)_2(CN)_2]^{24}$ were synthesized by adaptation of the existing literature procedures. Dichloromethane, butyronitrile, propionitrile and acetonitrile (Aldrich HPLC grade) were distilled over CaH_2 prior to use.

$[Pt(dpphen)(CN)_2]^{23}$ $[K_2Pt(CN)_4]$ (0.07 g, 0.18 mmol.) and dpphen (0.07 g, 0.21 mmol.) were refluxed in ethylene glycol (30 ml) for 2 hours at 150 °C. After dropwise addition of 2 M H_2SO_4 (5 ml) the solution was refluxed for an additional 3 hours to give a light yellow precipitate, which was filtered off and washed with hot water and ethanol. Yield 87% (0.09 g, 0.15 mmol.). 1H NMR (DMSO- d_6) (ppm): 9.47 (d, 2H), 8.24 (d, 2H), 8.17 (s, 2H), 7.7 (s, 10H). FTIR (CH_2Cl_2): 2148, 2138 cm^{-1} .

$[Ru(bpy)_2(CN)_2]^{24}$ $[Ru(bpy)_2(CN)_2]$ was synthesized in two steps.

$[Ru(C_2O_4)(bpy)_2]$. The procedure according to Liu *et al.*²⁵ was adapted. A solution of 2,2'-bipyridine (0.10 g, 0.64 mmol.) and $K_2C_2O_4$ (0.10 g, 0.90 mmol.) in water/methanol 1 : 1 v/v (20 ml) was added to a solution of $K_2[RuCl_5(H_2O)]$ (0.14 g, 0.37 mmol.) in hot water (20 ml). The mixture was refluxed for 24 hours and then filtered to remove a dark solid. The solvent was removed and the resulting dark-purple product was recrystallized from methanol. Yield 52% (0.09 g, 0.20 mmol.).

We have also used the following alternative procedure: $[Ru(bpy)_2Cl_2]$ (0.11 g, 0.23 mmol.) and $K_2C_2O_4$ (0.10 g, 0.90 mmol) in water/methanol 1 : 1 v/v (50 ml) were refluxed for 5 hours to yield a dark-red solution. After removal of the solvent by rotary evaporation, the dark purple product was recrystallized from methanol. Yield 83% (0.09 g, 0.19 mmol.). 1H NMR (DMSO- d_6) (ppm): 8.88 (d, $J = 6$ Hz, 2H), 8.76 (d, $J = 6$ Hz, 2H), 8.61 (d, $J = 7.5$ Hz, 2H), 8.15 (t, $J = 7.5$ Hz, 2H), 7.81 (mult, 4H), 7.58 (d, $J = 7.5$ Hz, 2H), 7.19 (t, $J = 6$ Hz, 2H).

$[Ru(bpy)_2(CN)_2]^{24}$ A mixture of $[Ru(C_2O_4)(bpy)_2]$ (0.20 g, 0.41 mmol.) in methanol (25 ml) and NaCN (0.20 g, 4.08 mmol.) in hot water (5 ml) was refluxed for 60 hours. The reaction mixture was cooled down, and evaporated to dryness. The product $[Ru(bpy)_2(CN)_2]$ was purified on a silica column with methanol. Yield 63% (0.12 g, 0.26 mmol.). 1H NMR (DMSO- d_6) (ppm): 8.60 (mult, 4H), 8.09 (t, $J = 9$ Hz, 2H), 7.93 (t, $J = 9$ Hz, 2H), 7.72 (t, $J = 6$ Hz, 2H), 7.49 (d, $J = 6$ Hz, 2H), 7.33 (t, $J = 6$ Hz, 2H), 6.28 (d, $J = 6$ Hz, 2H). FTIR (CH_2Cl_2): 2082, 2070 cm^{-1} .

Acknowledgements

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