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LUMINESCENT DONOR-ACCEPTOR PLATINUM(II) COMPLEXES

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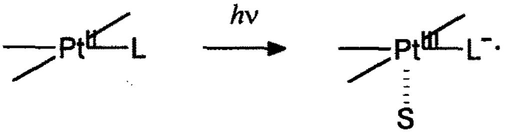
ABSTRACT

The emission properties of the complexes $[Pt(dppm)(5,6\text{-}Me_2phen)](ClO_4)_2$, $[Pt(phen)(C\equiv CPh)_2]$, $[Pt(5\text{-}Ph\text{-}phen)(CN)_2]$ and $[Pt(C\text{^}N\text{^}N\text{-}dpp)(NCCH_3)](ClO_4)$ have been studied. The large percentage of metal-ligand charge transfer character in the lowest excited states of these platinum(II) complexes has been demonstrated. Excited state oxidation and reduction potentials of $[Pt(phen)(C\equiv CPh)_2]$ have been determined. The ^{3}MLCT excited state of Pt(II) is highly electrophilic as suggested by the large kinetic isotope effect ($k_H/k_D = 6.7$) observed in the quenching of the photoexcited $[Pt(dppm)(5,6\text{-}Me_2phen)](ClO_4)_2$ complex by cyclohexene and d_{10}-cyclohexene. Facile replacement of the coordinated acetonitrile in $[Pt(C\text{^}N\text{^}N\text{-}dpp)(NCCH_3)](ClO_4)$ by pyridine ligands provides an entry to a new class of emissive donor-acceptor cyclometallated platinum(II) complexes.

INTRODUCTION

The design of new platinum(II) complexes having long-lived and emissive MLCT excited states is an area of growing interest in inorganic photochemistry [1-3]. Because Pt(II) complexes usually adopt square planar configuration, MLCT excitation of these complexes will produce coordinative unsaturated excited states (equation 1),



(1)

S = solvent or substrate

the physical and emission properties of which are expected to be sensitive to environmental changes. The Pt(III) produced in this way would be highly electrophilic and could be regarded as a highly reactive 17*e* metal centred radical, which is of great interest in the context of developing new photocatalyst for C-H and C-X bonds activation [2]. However, despite the extensive investigations on the MLCT photochemistry of the octahedral $[M(2,2'\text{-bipyridine})_3]^{n+}$ complexes, related studies on the Pt(II) systems are sparse. Zelewsky and coworkers first reported that cyclometallated Pt(II) complexes display emissive MLCT excited states in fluid solutions [3]. Recent works by Eisenberg [1e] and Che [1b-1d] and others also claimed a number of platinum(II) complexes of chelating α-diimine ligands to exhibit MLCT emission at room temperature. Nevertheless, the MLCT photochemistry of monomeric Pt(II) complexes still in its infancy. In this contribution, the design of new platinum complexes having long-lived MLCT excited states and the fabrication of donor-acceptor complexes

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consisting of cyclometallated Pt(II) luminophore and organic quenchers are described. Donor-acceptor platinum(II) complexes are of special interest in molecular recognition reactions because of the coordinative unsaturation of the Pt(II) center.

EXPERIMENTAL

Material 2,9-Diphenyl-1,10-phenanthroline (dpp) was prepared by literature method [4]. Acetonitrile and dichloromethane were purified by the standard procedure [5]. Methanol (GR, E. Merck) was used as received.

Physical Measurements Infrared spectra were measured on a Nicolet 20 SXC FT-IR spectrometer. UV-visible spectra were obtained on a Milton Roy Spectronic 3000 diode-array Spectrophotometer. Proton NMR spectra were obtained on Jeol GSX 270 FT-NMR Spectrometer with TMS as internal reference. Elemental analysis was performed by Butterworth Laboratories Ltd. Steady state emission spectra were recorded on SPEX 1681 FLUOROLOG-2 series F111AI spectrometer equipped with 450 W xenon lamp, a rhodamine-B reference quantum counter, and a Hamamatsu R928 photomultiplier tube. The luminescence spectra were corrected for monochromator and photomultiplier efficiency, and for xenon lamp stability. Quantum yield of emission was measured in a 1 cm cell and calculated with the equation by Crosby [6] and referenced to $[Ru(bpy)_3](PF_6)_2$ in degassed acetonitrile [7]. Sample solutions were degassed through not less than three freeze-pump-thaw cycles.

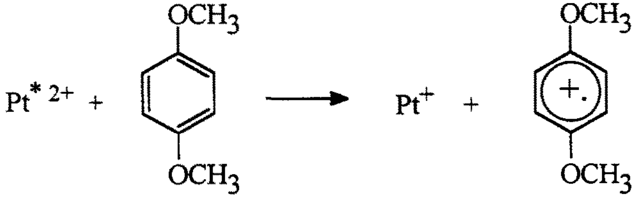
Emission lifetime was measured with a conventional laser system. The excitation source was the third harmonic (355 nm) of a Quanta-Ray Q-switched DCR-3 pulsed Nd-YAG laser (10Hz, G-resonator). The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model 2430 digital oscilloscope. The digitized signal was interfaced to an IBM AT personal computer and analyzed with a commercial software.

Synthesis The complexes $[Pt(dppm)(5,6\text{-}Me_2phen)](ClO_4)_2$, $[Pt(phen)(C{\equiv}CPh)_2]$ and $[Pt(C\hat{}N\hat{}N\text{-}dpp)(NCCH_3)](ClO_4)$ were prepared according to literature procedures [8]. $[Pt(5\text{-}Ph\text{-}phen)(CN)_2]$ was prepared by refluxing $Pt(CN)_2{\cdot}xH_2O$ [9] (1 mmol) and a slightly excess amount of 5-Ph-phen in dimethylformamide for 24 hrs [1d]. The yellow precipitated solid after cooling was recrystallized by diffusion of diethyl ether to a dichloromethane solution. Yield 27%. Anal. (%) for $PtC_{20}H_{12}N_4$: Calc. C 47.72, H 2.40, N 11.13; Found C 46.27, H 2.18, N 10.70. IR ($\nu_{C\equiv N}$): 2150, 2139 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.77 (d, 1H), δ 8.03 (dd, 1H), δ 9.68 (d, 1H), δ 8.06 (s, 1H), δ 9.64 (d, 1H), δ 9.76 (dd, 1H), δ 8.75 (d, 1H), δ ~7.6 (m, 5H).

RESULTS AND DISCUSSION

$[Pt(dppm)(5,6\text{-}Me_2phen)](ClO_4)_2$ $[1]\cdot(ClO_4)_2$

We have previously communicated that [1c] in acetonitrile the $[Pt(5,6\text{-}Me_2phen)(dppm)]^{2+}$ ($5,6\text{-}Me_2phen$ = 5,6-dimethyl-1,10-phenanthroline; dppm = *bis*(diphenylphosphino)methane) complex (1) shows broad absorption bands with ε_{max} $\sim 10^3$ $mol^{-1}.dm^3.cm^{-1}$ at 382 and 367 nm. Upon photoexcitation a poorly resolved vibronic structured emission centred at 490 nm with a lifetime of 25 μs at room temperature has been recorded. The nature of the emissive excited state of this complex is still a matter of controversy. A tentative assignment would be ^{3}MLCT $^3[(d\pi^*)(\pi^*_{phen})]$ although mixing with the $^3(\pi\pi^*)$ of $5,6\text{-}Me_2phen$ is anticipated. The excited state, which is a powerful oxidant with a $E°$ value $[Pt^{2+*} + e \rightarrow Pt^+]$ of ~2.1 V vs. NHE, is highly electrophilic. Flash-photolysis and Stern-Volmer quenching experiments established that the excited state readily oxidizes 1,4-dimethoxybenzene with a rate constant of $\sim 1 \times 10^{10}$ $mol^{-1}dm^3s^{-1}$ at 25°C in acetonitrile (equation 2)



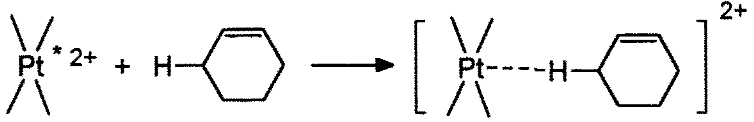
(2)

Quenching of the emission by cyclo-alkenes has been observed, with rate constants falling between 10^6–10^7 $mole^{-1}dm^3s^{-1}$ (Table 1).

TABLE 1 Stern-Volmer quenching rate constants for the quenching of $^3[1]^*$ by cyclo-alkenes in acetonitrile at 20 ± 2°C.

Substrates	k_q ($mol^{-1}dm^3s^{-1}$)
Cyclohexene	4.68×10^6
Cyclooctene	2.21×10^7
Cycloheptene	4.20×10^6
Cyclopentene	1.28×10^6
d_{10}-Cyclohexene	6.99×10^5; $k_H/k_D = 6.70$

Interaction between the allylic C–H bond with the Pt(II) (equation 3) should play some role in the quenching reactions as a primary kinetic isotope effect (k_H/k_D) of 6.70 has been observed in the quenching studies with cyclohexene and d_{10}-cyclohexene.

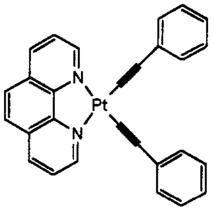


(3)

However, steady-state photolysis of $[1]\cdot(ClO_4)_2$ with cyclohexene in acetonitrile gave no detectable radical coupling product identified by gas chromatography and the platinum complex was found to decompose after photolysis.

$[Pt(phen)(C{\equiv}CPh)_2]$

Because $PhC{\equiv}C^-$ is a good σ-donor, the $Pt \rightarrow \pi^*_{diimine}$ transition of the Pt(II)-diimine complexes will be significantly red-shifted by replacing the phosphine and CN^- ligands with it. The $[Pt(phen)(C{\equiv}CPh)_2]$ complex was prepared as an air stable yellow solid. X-ray crystal analysis [8b] revealed that the intermolecular Pt-Pt separation is 5.223 Å, suggesting no molecular stacking in the solid state.



2

As expected, **2** shows a broad and lower energy absorption at 400 nm, which is assigned to the MLCT $[Pt \rightarrow \pi^*_{phen}]$ transition. The assignment is supported by the result of Extended Hückel molecular orbital calculations [8b] in which the LUMO and HOMO are primarily the π* of phen and Pt d_{xy} respectively. As shown in table 2, changing the solvent has no observable effect on the absorption spectrum.

TABLE 2 Spectroscopic and photophysical data of $[Pt(phen)(C{\equiv}CPh)_2]$ at room temperature.

Solvent	CH_2Cl_2	Me_2CO	CH_3CN	C_5H_5N	EtOH
E_{em} (nm)	578	581	581	585	583
E_{ab} (nm)	399	398	394	401	~400
τ_o (μs)	2.1	0.9	1.0	0.4	0.3

The complex is emissive in fluid solution at room temperature. The broad emission centred at 578 nm, shown in figure 1, is partly resolved in an ethanol matrix at 77 K . The vibronic structure (1290 cm^{-1} progression) as well as the small "Huang-Rhys" factor (~1.0) are supportive of a $[^3(d\pi^*)(\pi^*_{phen})]$ excited state.

Quite contrary to the expectation described in the introduction section (equation 1), the emission properties of **2** are only slightly affected by the solvents (Table 2).

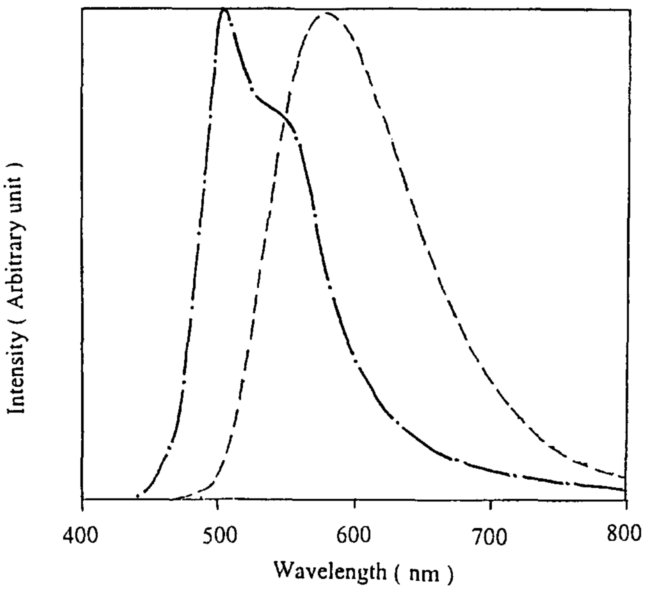
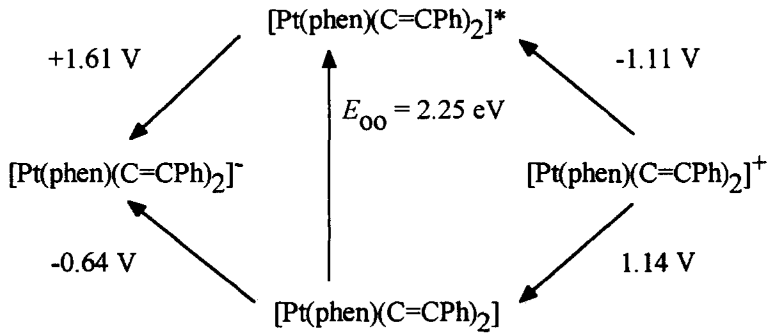


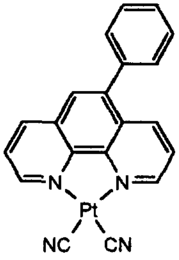
Figure 1 Emission spectra of [Pt(phen)(C≡CPh)$_2$] in ethanol at 298 K (- - - -)and 77 K (— · —).

For example, changing the solvent from dichloromethane to ethanol only leads to a slight red-shift of the emission energy and a small reduction of the excited state lifetime. The excited state potentials of **2** have been estimated. The E_{red}* and E_{ox}* were obtained through quenching studies with a series of organic donors (aromatic amines) and organic acceptors (pyridinium salts). The Latimer diagram below illustrates that the ^{3}MLCT state of **2** is a much better oxidant and reductant than its ground state.



Latimer Diagram of [Pt(phen)(C≡CPh)$_2$] (all potentials are versus SSCE)

[Pt(5-Ph-phen)(CN)$_2$] (5-Ph-phen = 5-phenyl-1,10-phenanthroline)



3

Previous studies revealed that some [Pt(diimine)(CN)$_2$] complexes display interesting photoluminescent properties, but in most cases, the emissions are mostly intraligand in nature [1b,1d,1g]. In this context, the [Pt(5-Ph-phen)(CN)$_2$] complex (**3**) was synthesized. It has higher solubilities in non-polar solvents and furthermore, the low energy π^* orbital of 5-Ph-phen makes the $d\pi \rightarrow \pi^*$(5-Ph-phen) transition to occur at lower energy.

In fluid solution and at a complex concentration $\leq 10^{-4}$ mol.dm^{-3}, no oligomerisation and excimeric emission of **3** are observed. Its UV-vis spectrum shows broad absorption bands with $\varepsilon_{max} \sim 10^3$ at 350-400 nm (figure 2), which are not very much affected by the solvents.

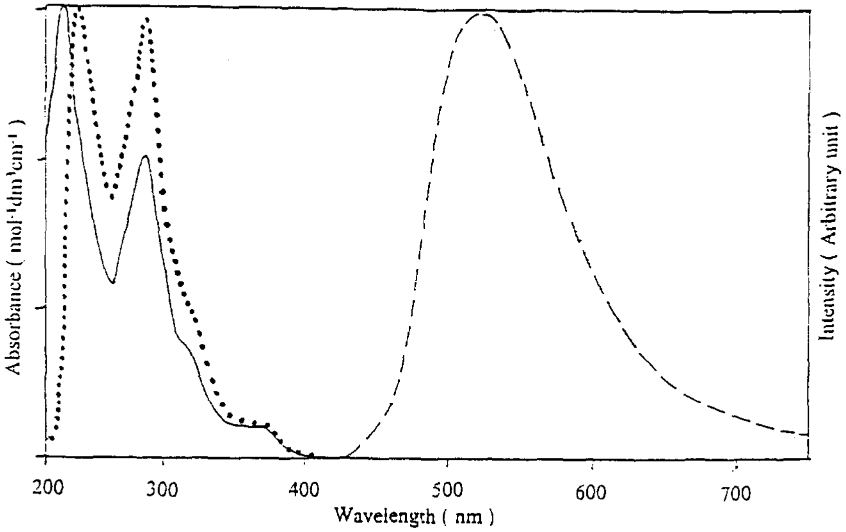


Figure 2 UV-vis absorption spectra (——), excitation spectra (•••••) and emission spectra (- - - -) of [Pt(5-Ph-phen)(CN)$_2$] in dichloromethane at room temperature.

Upon photoexcitation, **3** displays an intense emission at 500-550 nm (figure 2), which is tentatively assigned to come from the $^3[\mathrm{Pt}(d\pi)(\pi^*{}_{5\text{-Ph-phen}})]$ excited state. Unlike the ^{3}MLCT emission of **2**, its emission energy red shifts with decreasing solvent polarity. Changing the solvent from dichloromethane to acetone increases the emission lifetime from 2.6 μs to 223 μs and emission quantum yield from 6.1×10^{-4} to 9.7×10^{-2}. A summary of the photophysical data is tabulated in Table 3.

TABLE 3 The photophysical data of $[\mathrm{Pt(5\text{-}Ph\text{-}phen)(CN)_2}]$ in various solvents at room temperature.

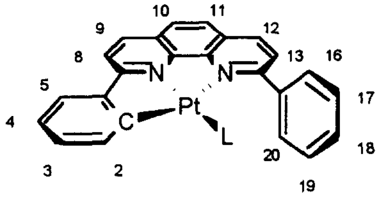
Solvent	CH_2Cl_2	CH_3CN	C_2H_5OH	$(CH_3)_2CO$
μ (D)	1.60	3.92	1.69	2.88
k_r ($\times 10^2$ s^{-1})	4.52	2.46	1.34	2.11
k_{nr} ($\times 10^3$ s^{-1})	4.03	26.2	193.9	347.6
ln k_{nr}	8.30	10.17	12.18	12.76
τ_o (μs)	223	38	5.2	2.6
ϕ_o ($\times 10^{-4}$)	970	92	7.3	6.1
λ_{em} (nm)	525	529	539	542

λ_{em}: emission peak maxima.

From the table, it is obvious that the effect of the solvent is to affect both the k_{nr} (non-radiative decay rate constant) and emission energy. The k_{nr} increases with decreasing solvent polarity. As illustrated in equation 1, solvent coordination to the MLCT excited state of Pt(II) is expected. In this case, MLCT excitation of **3** would produce $[\mathrm{Pt^{III}(5\text{-}Ph\text{-}phen^{-\bullet})(CN)_2}]$ with a large dipole along the Pt-CN bonds. As a consequence, the excited state should be stabilized to a greater extent than the ground state by polar solvents. This is in agreement with the experimental results which show a general trend of decreasing E_{em} with the polarity of the solvents. The decrease in k_{nr} with decrease in the λ_{max} is in qualitative agreement with the energy gap law. This would suggest that solvent induced relaxation is solely responsible for the non-radiative decay of the excited state species.

Donor-Acceptor Cyclometallated Platinum Complexes

Attempts to prepare $[\mathrm{Pt(dpp)_2}]^{2+}$ by reacting $[\mathrm{Pt(CH_3CN)_4}]^{2+}$ with dpp in acetonitrile were unsuccessful. Instead, the cyclometallated Pt(II) complex **4** was obtained and its structure, determined by x-ray crystal analysis, is similar to that of the one reported by Constable and co-workers previously [10].



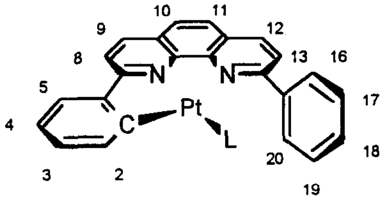
L = CH$_3$CN

4

In the crystal lattice the complex exists as a dimeric unit $\{4\}_2$, with a Pt-Pt separation of 3.37 Å. This structural feature has been proved to be useful in correlating the solid state emission (λ_{max} at 670 nm) with the excimeric emission at ~650 nm from a concentrated dichloromethane solution of **4** at room temperature.

In dilute acetonitrile solution (concentration < 10^{-4} mol.dm^{-3}), **4** shows an intense absorption band at 335 nm (ε ~10^4) with a shoulder at around 380 nm, the latter is assigned to the MLCT transition. There are also some weak absorption bands tailing from 380 to 450 nm. Upon excitation at 380–450 nm, a long-lived vibronic structural emission at 530–570 nm (τ_0 ~8.7 μs) is observed. We tentatively assign it to be the ^{3}MLCT emission.

A new class of emissive cyclometallated platinum(II) complexes having similar spectroscopic properties as that of **4** has been prepared by replacement of the coordinated acetonitrile with substituted pyridine ligands.



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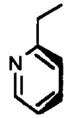
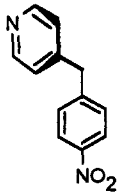
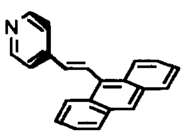
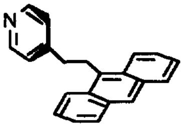
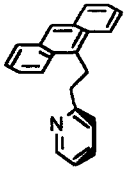




5 **6** **7**







8 **9** **10**

A representative crystal structure illustrated in figure 3 has been obtained.

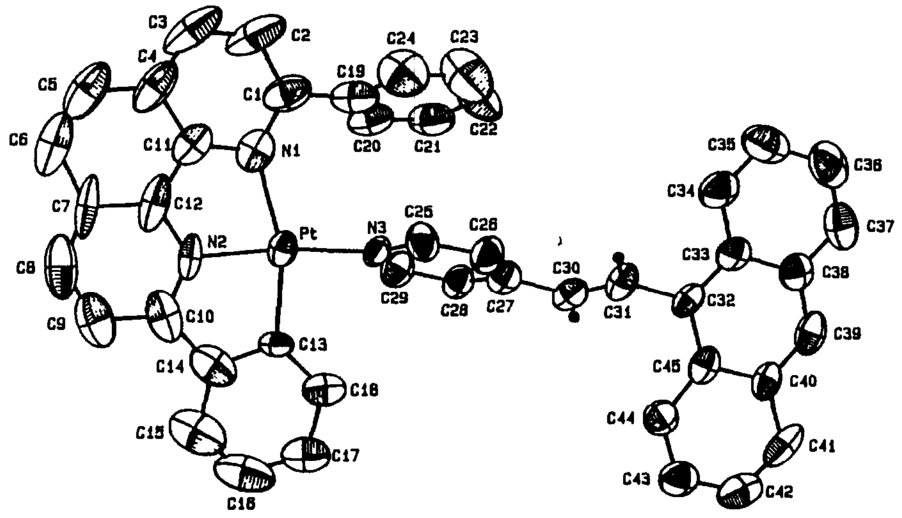


Figure 3 A perspective view of complex **8**.

The photophysical properties of **5**, **6**, **9** and **10** are summarized in Table 4. While the emission properties of **5** and **7** are not very much different from each other, there is enhancement of both the emission lifetime and quantum yield in the case of **6**. This may be due to the *ortho*-substituent on the pyridine ligand, which prohibits the approach of the solvent molecule to the Pt(II) centre, leading to a decrease in the non-radiative decay rate of the excited state.

TABLE 4 Lifetime (τ_o) and emission quantum yield of the ^{3}MLCT state for compounds **5**, **6**, **9** and **10** in acetone, excitation at 355 nm.

Compound	**5**	**6**	**9**	**10**
τ_o (μs)	1.55	46	1.73	10.4
ϕ_o	0.035	0.30	0.01	0.40
				0.048 (excitation at 450 nm)

Preliminary photophysical studies on the covalently linked anthracene complexes **9** and **10** have been undertaken. While the emission spectrum of **9** (Figure 4) comprises of both the MLCT emission and anthracene fluorescence, the latter one is completely quenched in the case of **10**. We attribute this to the closer separation between the anthracene moiety and the Pt(II) centre, leading to a faster intramolecular energy transfer process.

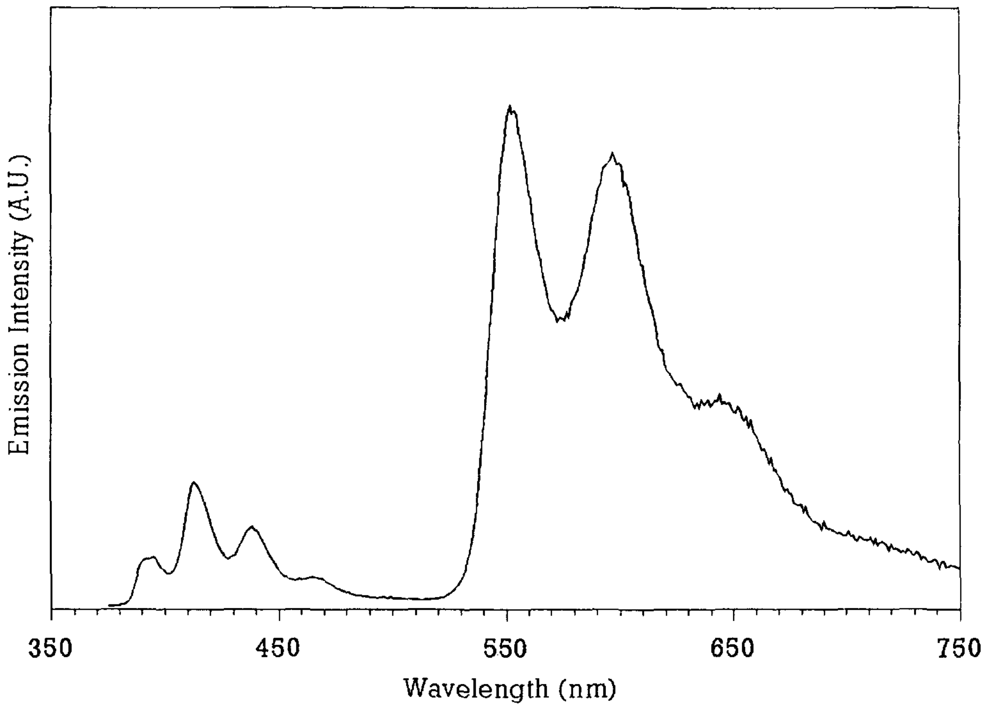


Figure 4 Room temperature emission spectrum of complex **9** in degassed acetone, λ excite = 355 nm.

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