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## Characterization of intraligand charge transfer transitions in $\text{Pd}(\text{qol})_2$ , $\text{Pt}(\text{qol})_2$ and $\text{Pt}(\text{qtl})_2$ investigated by Shpol'skii spectroscopy

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### Abstract

$\text{Pd}(\text{qol})_2$ ,  $\text{Pt}(\text{qol})_2$  and  $\text{Pt}(\text{qtl})_2$  are investigated in *n*-octane Shpol'skii matrices at  $T = 1.2$  K. For the first time, it is possible to obtain highly resolved phosphorescence and triplet as well as singlet excitation spectra. The corresponding excited states are assigned to intraligand charge transfer (ILCT) transitions. Their characteristic electronic and vibrational properties are studied in detail.

**Keywords:** Shpol'skii spectroscopy; Intraligand charge transfer; Platinum metal compounds; Spin polarization

Coordination compounds of the ligands 8-quinolinolato-N,O ( $\text{qol}^-$ ) and 8-quinolinethiolato-N,S ( $\text{qtl}^-$ ) exhibit a series of interesting properties which are determined by the still largely unexplored type of intraligand charge transfer (ILCT) transitions. For example, recently,  $\text{Al}(\text{qol})_3$  has attracted much interest, since it plays an important role in the development of 'organic' white light emitting LEDs for future flat panel displays (e.g. see Ref. [1]). Some transition metal-qol-compounds, like  $\text{Pt}(\text{qol})_2$ , show an intense phosphorescence in solution at  $T = 298$  K [2], and their use as photosensitizers for solar energy conversion was proposed [3]. For a deeper understanding of such devices a detailed characterization of the lowest electronic states is required. Applying Shpol'skii matrices, about 400 times better resolved optical

spectra of the title compounds are obtained than hitherto known (cf. Fig. 1(a) with 1(b)). The phosphorescence spectra recorded represent a superposition of different emitting sites. For the dominant sites, the energy positions of the triplet origins are listed in Table 1. With selective detection at these origins, site-selected highly resolved singlet excitation spectra are obtained. Due to the energy positions, oscillator strengths, and room temperature absorption spectra published in Ref. [2], these singlets are assigned to <sup>1</sup>ILCT states for all compounds investigated (for details see Ref. [5]). These transitions are characterized by a charge transfer from the lone pair p-orbital at the oxygen (or sulfur) to the lowest  $\pi^*$ -orbital possessing more electron density on the pyridyl moiety. The singlet origins of the title compounds (Table 1) exhibit Lorentzian line shapes which is typical for homogeneous line widths. From their FWHM one can estimate the upper limit of the respective intersystem

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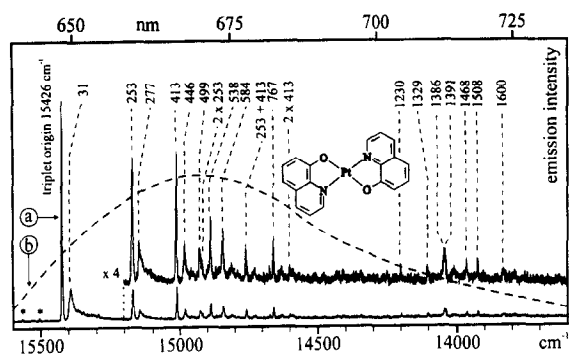


Fig. 1. (a)  $^3\text{ILCT}$  phosphorescence spectrum of  $\text{Pt}(\text{qol})_2$  in an *n*-octane Shpol'skii matrix at  $T = 1.2$  K, site-selectively excited at  $18767\text{ cm}^{-1}$  ( $532.85\text{ nm}$ ,  $^1\text{ILCT}$  origin). Spectral resolution:  $0.6\text{ cm}^{-1}$ . Vibrational satellites are specified relative to the electronic origin at  $15426\text{ cm}^{-1}$ . The asterisks indicate residual intensities of origins of different sites. For experimental details see Ref. [4]. (b) Phosphorescence spectrum of spectral resolution hitherto known [2]. For comparison it is shifted by  $400\text{ cm}^{-1}$  to the red.

crossing rate. For example, for  $\text{Pt}(\text{qol})_2$  one obtains  $\approx 2 \times 10^{12}\text{ s}^{-1}$ . Moreover, the highly resolved vibrational patterns found for the singlets exhibit distinct Franck–Condon (FC) progressions (for energies see Table 1) indicating shifts of the excited state potential hypersurfaces with respect to those of the ground state along the specific normal coordinates. The occurrence of these FC modes observed is connected with the charge redistributions upon excitation. A recent normal coordinate analysis for  $\text{Pt}(\text{qol})_2$  [6] showed that these in-plane vibrational modes exhibit distinct metal-nitrogen ( $253/242\text{ cm}^{-1}$ ) and metal-oxygen/sulfur ( $413/371\text{ cm}^{-1}$ ) character, respectively.

After excitation into the singlet origins, site-selective triplet emission spectra resulting from the  $^3\text{ILCT}$  are obtained (see the example given in Fig. 1). The zero-field splitting (zfs) of the triplet is smaller than  $1\text{ cm}^{-1}$  for all three compounds indicating only a small metal d-orbital admixture to this  $^3\text{ILCT}$  (see also Ref. [7]). At  $T = 1.2\text{ K}$ , the sub-levels emit independently (spin polarization). Thus, the phosphorescence decay can be fitted triexponentially (Table 1 and Ref. [5]). The decay becomes monoexponential only at relatively high temperatures due to the thermalization of the sub-levels. In contrast to the  $^1\text{ILCT}$  spectrum, the  $^3\text{ILCT}$  shows only weak progressions, signifying

Table 1  
Triplet Physical Data of the Lowest Excited Singlet ( $^1\text{ILCT}$ ) and Triplet ( $^3\text{ILCT}$ ) States of  $\text{Pd}(\text{qol})_2$ ,  $\text{Pt}(\text{qol})_2$  and  $\text{Pt}(\text{qtl})_2^a$

	$\text{Pd}(\text{qol})_2$	$\text{Pt}(\text{qol})_2$	$\text{Pt}(\text{qtl})_2$
<i>Singlet excitation</i>			
$0-0^b$ ( $\text{cm}^{-1}$ )	20617	18767	15193
FWHM <sup>b</sup> ( $\text{cm}^{-1}$ )	80	12	5.5
Strong FC vibr. ( $\text{cm}^{-1}$ )	— <sup>d</sup>	253/413	242/371
Huang-Rhys factor $S^c$	— <sup>d</sup>	$\approx 1$	$\approx 2$
<i>Triplet emission</i>			
$0-0^b$ ( $\text{cm}^{-1}$ )	16090	15426	13158
FWHM <sup>b</sup> ( $\text{cm}^{-1}$ )	$\approx 3$	$\approx 3$	$\approx 3$
zfs <sup>e</sup> ( $\text{cm}^{-1}$ )	$< 1$	$< 1$	$< 1$
$\tau_{\text{III}}/\tau_{\text{II}}/\tau_{\text{I}}^f$ ( $\mu\text{s}$ )	80/180/ $\approx 90 \cdot 10^3$	4.5/13/60	0.55/2.8/7.0
$T_{\text{av}}^g$ (K)	$\approx 5$	20	$\approx 60$
$\tau_{\text{av}}^h$ ( $\mu\text{s}$ )	160	10	1.4
Strong FC vibr. ( $\text{cm}^{-1}$ )	236/407	253/413	241/361
Huang-Rhys factor $S^c$	0.1	0.2	0.5
$^1\text{ILCT}-^3\text{ILCT}^i$ ( $\text{cm}^{-1}$ )	4527	3341	2035
<i>Triplet excitation</i>			
Strong FC vibr. ( $\text{cm}^{-1}$ )	—	247/407	239/372

<sup>a</sup>*n*-octane Shpol'skii matrix at  $T = 1.2\text{ K}$ ; concentration of compounds  $10^{-5}\text{ M}$ .

<sup>b</sup>Electronic origin.

<sup>c</sup>Largest Huang-Rhys factor.

<sup>d</sup>Not yet determined.

<sup>e</sup>Total zero-field splitting of the triplet sublevels.

<sup>f</sup>Fit components of decay curves at  $T = 1.2\text{ K}$ ; I, II, III: emitting triplet sublevels.

<sup>g</sup>Temperature of thermalization of triplet sublevels.

<sup>h</sup>Monoexponential decay at  $T_{\text{av}}$ .

<sup>i</sup>Energy separation between electronic origins.

only small shifts of the triplet equilibrium positions with respect to those of the ground state.

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