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Characterization of intraligand charge transfer transitions in Pd(qol)$_2$, Pt(qol)$_2$, and Pt(qtl)$_2$ investigated [illegible]

Abstract

Pd(qol)$_2$, Pt(qol)$_2$ and Pt(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 (qol$^-$) and 8-quinolinethiolato N,S (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, Al(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 [illegible] 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 [illegible]

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 [illegible] 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 π^*-orbital possessing more [illegible] geneous line widths. From their FWHM one can estimate the upper limit of the respective intersystem

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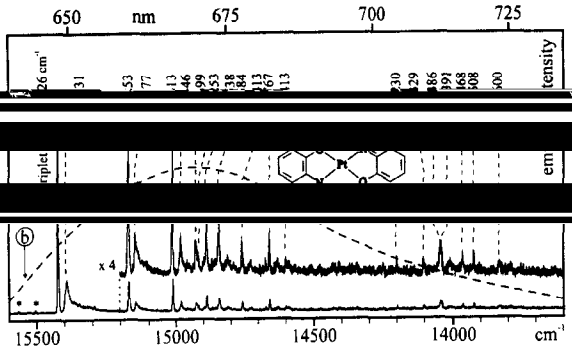

18 767 cm⁻¹ (532.85 nm, ¹ILCT origin). Spectral resolution: 0.6 cm⁻¹. Vibrational satellites are specified relative to the electronic origin at 15 426 cm⁻¹. The asterisks indicate residual intensities of origins of different sites. For experimental details see Ref.

Table 1
Photophysical Data of the Lowest Excited Singlet (¹ILCT) and Triplet (³ILCT) States of $Pd(qol_2)$, $Pt(qol)_2$ and $Pt(qtl)_2$[a]

Singlet excitation			
Strong FC vibr. (cm^{-1})	—[d]	253/413	242/371
Huang-Rhys factor S[c]	—[d]	≈1	≈2
Triplet emission			
0–0[b] (cm^{-1})	16 090	15 426	13 158
FWHM[b] (cm^{-1})	≈3	≈3	≈3
T^{g}_{av}(K)	≈5	20	≈60
τ^{h}_{av} (μs)	160	10	1.4
Strong FC vibr. (cm^{-1})	236/407	253/413	241/361
Triplet excitation			
Strong FC vibr. (cm^{-1})	—	247/407	239/372

[a] n-octane Shpol'skii matrix at $T = 1.2$ K; concentration of compounds 10^{-5} M.
[b] Electronic origin.
[c] Largest Huang-Rhys factor.
[d] Total zero-field splitting of the triplet sublevels.
[f] Fit components of decay curves at $T = 1.2$ K; I, II, III: emitting triplet sublevels.
[g] Temperature of thermalization of triplet sublevels.
[h] Monoexponential decay at T_{av}.
[i] Energy separation between electronic origins.

crossing rate. For example, for $Pt(qol)_2$ one obtains $\approx 2 \times 10^{12}\ s^{-1}$. 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 $Pt(qol)_2$ [6] showed that these in-plane vibrational modes exhibit distinct metal-nitrogen (253/242 cm^{-1}) and metal-oxygen/sulfur (413/371 cm^{-1})

After excitation into the singlet origins, site-selective triplet emission spectra resulting from the ³ILCT are obtained (see the example given in Fig. 1). The zero-field splitting (zfs) of the triplet is smaller than 1 cm^{-1} for all three compounds indicating only a small metal d-orbital admixture to this ³ILCT (see also Ref. [7]). At $T = 1.2$ K, the sublevels 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

levels. In contrast to the ¹ILCT spectrum, the ³ILCT shows only weak progressions, signifying only small shifts of the triplet equilibrium positions with respect to those of the ground state.

References

[1] J. Kido, M. Kimura and K. Nagai, Science 267 (1995) 1332.
[2] R. Ballardini, G. Varani, M.T. Indelli and F. Scandola, Inorg. Chem. 25 (1986) 3858.
[3] E. Borgarello, E. Pelizzetti, R. Ballardini and F. Scandola, Nov. J. Chim. 8 (1984) 567.
[4] H. Wiedenhofer, S. Schützenmeier, A. von Zelewsky and H. Yersin, J. Phys. Chem. 99 (1995) 13 385.
[5] D. Donges, J.K. Nagle and H. Yersin, Inorg. Chem. (1997), in press.
[6] J. Degen, Universität Düsseldorf, private communication (1996).
[7] H. Yersin and J. Strasser, J. Lumin., these Proceeding (ICL'96), J. Lumin. 72–74 (1997).