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Magnetic field effects on the phosphorescence of Pt(4,6-dFppy)(acac) – Tunability of the vibrational satellite structure

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ABSTRACT

Effects of high magnetic fields on the properties of the lowest triplet state of the OLED emitter Pt(4,6-dFppy)(acac) are studied by site-selective high-resolution optical spectroscopy. Application of high fields strongly alters the pattern and magnitude of splitting of the triplet term, the oscillator strengths of the purely electronic 0–0 transitions between the T_1 substates and the singlet ground state, and the vibrational satellite structures. In particular, the mechanism of radiative vibrational deactivation of the lowest triplet substate I changes with increasing field from a vibronically induced (Herzberg–Teller) to a Franck–Condon induced mechanism.

1. Introduction

Within the last decade, phosphorescent organo-transition metal compounds have stepped into the focus of scientific and industrial interest due to their applicability as efficient emitters in organic light emitting diodes (OLEDs) [1–7]. As a consequence of spin–orbit coupling (SOC) induced by the heavy metal center, devices incorporating such triplet emitting materials allow both singlet and triplet excitons to be utilized for the emission in an electroluminescence process, leading to a principally four times higher internal electroluminescence quantum yield than achievable with fluorescent emitters (triplet harvesting effect) [7,8].

Due to relatively short emission decay times and high emission quantum yields, many Pt(II) and Ir(III) compounds have been established as promising phosphorescent OLED emitters. It has been shown that detailed characterizations of such materials allow to obtain valuable information on the emitting triplet states with respect to electronic and vibronic properties [9,10], decay dynamics and relaxation processes [9,11–14], ancillary ligand and matrix effects [10,15,16], and spin–orbit coupling routes to higher lying states [17–20].

The compound Pt(4,6-dFppy)(acac) (see inset of Fig. 1) represents a well known material and was – in low concentrations – successfully applied as phosphorescent dopant in blue–green emitting OLEDs [21,22]. The lowest triplet state T_1 of Pt(4,6-dFppy)(acac) has already been characterized in detail and it could be shown that this state is mainly of ligand centered (LC) character with only moderate metal-to-ligand charge transfer (MLCT) admixtures [11,17]. Further, like many other Pt(II) complexes [23–26], this material has a strong tendency to form aggregates of electronically strongly interacting monomers in solid films and concentrated solutions [27,28]. These aggregates exhibit a broad and red-shifted emission band compared to the monomer phosphorescence. A balanced combination of the blue–green monomer emission and the red aggregate emission covers a large spectral range of visible light, which could be utilized for efficient white light emitting OLEDs [21,29–31]. The aggregate formation has been investigated in detail experimentally [27,28] and theoretically [32].

In this contribution, we study the effects of high magnetic fields on the properties of the lowest triplet state of the Pt(4,6-dFppy)(acac) monomer at cryogenic temperatures by use of site-selective matrix isolation spectroscopy with the main focus on the magnetic-field induced tunability of the vibrational satellite structures. Zeeman studies of transition metal compounds are well established in the literature and it is known that application of high *B*-fields leads to distinct changes of oscillator strengths, splittings, and energy shifts of the triplet substates (e.g., see Refs. [33–37]). However, the influence of magnetic fields on highly resolved vibrational satellite structures and in particular, on the radiative vibronic deactivation mechanisms has only been studied in a few cases [37–39] and to our knowledge not yet for a Pt(II)-based emitter.

2. Experimental

Pt(4,6-dFppy)(acac) was synthesized according to the procedure described in Ref. [40].

Spectroscopic measurements were carried out with Pt(4,6-dFppy)(acac) dissolved in *n*-octane with a concentration of about

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Abbreviations: MLCT, metal-to-ligand charge transfer; LC, ligand-centered; ZFS, zero-field splitting; SOC, spin–orbit coupling.

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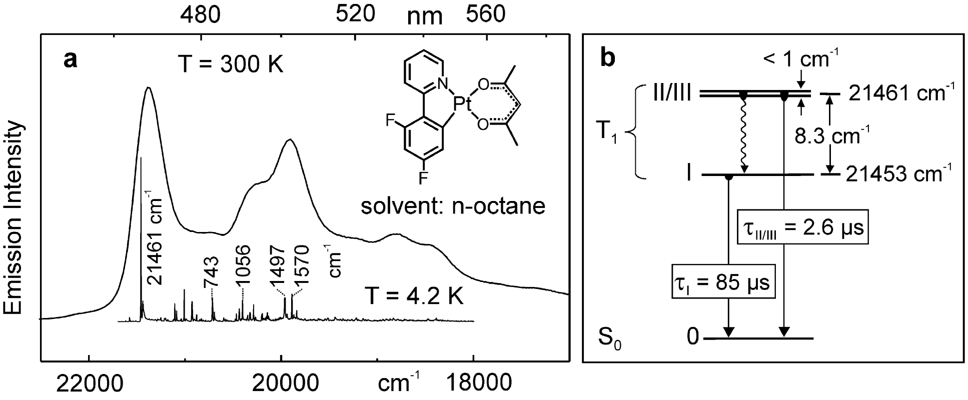

Fig. 1. (a) Comparison of the emission spectra of Pt(4,6-dFppy)(acac) in *n*-octane at $T = 300$ K ($\lambda_{exc} = 370$ nm) and at $T = 4.2$ K. The 4.2 K spectrum represents the emission of a dominant site, which was selectively excited at 22 161 cm^{-1} ($0 \rightarrow$ II/III + 700 cm^{-1} vibration). The energies of some prominent vibrational satellites are also given. (b) Energy level diagram of the emitting triplet state T_1. (Compare also Ref. [11].)

10^{-5} mol/L. Emission spectra at 300 K were measured with a steady-state fluorescence spectrometer (Jobin Yvon Fluorolog 3). The experiments at low temperatures were carried out in a He cryostat (Cryovac Konti Cryostat IT) in which the He gas flow, He pressure, and heating were controlled. For magnetic field experiments, an Oxford Instruments MD10 cryostat equipped with a 12 T magnet was used. The sample was cooled down to liquid helium temperatures without the presence of magnetic fields. A pulsed Nd:YAG laser (IB Laser Inc., DiNY pQ 02) with a pulse width of about 7 ns was applied as excitation source for decay time measurements, using the third harmonic at 355 nm (28 170 cm^{-1}). For recording site-selective emission and excitation spectra, a pulsed dye laser (Lambdaphysik Scanmate 2C) was operated, using Coumarin 102 and Coumarin 120, respectively. The spectra were measured with an intensified CCD camera (Princeton PIMAX) or a cooled photomultiplier (RCA C7164R) attached to a triple spectrograph (S&I Trivista TR 555). Decay times were registered using a FAST Comtec multichannel scaler PCI card with a time resolution of 250 ps.

3. Results and discussion

3.1. Photophysical background

A discussion of spectroscopic properties of Pt(4,6-dFppy)(acac) at ambient temperature is presented in Refs. [17,18,40]. Highly resolved emission spectra could be obtained by dissolving the compound in *n*-octane at low concentration, cooling the sample to cryogenic temperatures and applying techniques of site-selective laser spectroscopy [11,17,18]. To introduce to the compound's T_1 state properties, results of these experiments are summarized in Fig. 1. A comparison of the selectively excited 4.2 K emission spectrum in *n*-octane with the 300 K spectrum in the same solvent (Fig. 1a) illustrates the tremendous gain in resolution. Fig. 1b displays the energy level diagram as determined for the emitting triplet state T_1. The higher lying substates II and III were found to lie within an energy of about 1 cm^{-1} or less. Temperature dependent studies of the thermalized emission decay time revealed a combined emission decay time for these two substates to the ground state of 2.6 μs, while substate I, lying 8.3 cm^{-1} lower in energy, decays with a distinctly longer time constant of 85 μs.

3.2. Electronic 0–0 transitions and tuning of allowedness

In Fig. 2, excitation spectra of the dominant site of Pt(4,6-dFppy)(acac) in *n*-octane are shown for the region of the electronic 0–0 transitions at different magnetic field strengths. At zero field, two lines are observed. The line at 21 453 cm^{-1} represents the transition from the electronic ground state to the lowest T_1 substate I, while the stronger line at 21 461 cm^{-1} corresponds to the electronic 0–0 transitions from the ground state to the substates II and III. These latter transitions could not be resolved at zero magnetic field. From the intensity ratio of the lines, it can be concluded that $0 \rightarrow$ II/III is by a factor of 190 ± 10 more allowed than $0 \rightarrow$ I. (Note the scaling factor in the spectrum at $B = 0$ T in Fig. 2.)

Application of high magnetic fields leads to distinct changes in the excitation spectra. These are consequences of the *B*-field induced mixings of the wavefunctions of the three T_1 sublevels (Zeeman effect, compare [33,34–36,44]). With increasing *B*-field, the excitation line at 21 461 cm^{-1} splits into two lines, revealing that it corresponds to the electronic origins of two triplet substates. Further, the state mixing causes an increase of the total splitting from $\Delta E_{II/III-I} = (8.3 \pm 0.3)\ \text{cm}^{-1}$ at $B = 0$ T to $\Delta E_{III-I}(B) = (23.6 \pm 0.3)\ \text{cm}^{-1}$ at $B = 12$ T. Moreover, a distinct variation of the allowedness of the 0–0 transition $0 \rightarrow I(B)$ occurs with increasing field. The intensity of the excitation line $0 \rightarrow$ I increases from 1/190 at zero field to 1/3.5 at $B = 12$ T as compared to the combined intensities of the lines $0 \rightarrow II(B)$ and $0 \rightarrow III(B)$.

However, the given values for the *B*-field induced energy splittings and intensity redistributions cannot be taken too strictly, since the orientations of the dopants in the polycrystalline host are not known. The appearance of relatively sharp lines even at high magnetic fields indicates a certain non-isotropic distribution of the Pt(4,6-dFppy)(acac) molecules. This might be induced by the surface of the quartz glass tubes [41]. A corresponding behavior has been proposed for another Pt(II) compound in Ref. [42]. On the other hand, the asymmetric lineshapes at high fields (compare the excitation spectrum of substate II(*B*) at $B = 12$ T in Fig. 2) are indicative of a distinct distribution of orientations (compare the discussion in Ref. [43]). Further, it has been observed that the degree of lineshape asymmetry depends on the speed of cooling of the sample as well as on tempering [42]. Thus, a detailed quantitative description of the magnetic anisotropy of the T_1 state cannot be easily worked out for the present situation.

The discussed increase of dipole allowedness of the 0-0 transition of substate I to the ground state has a drastic effect on the emission decay time of this lowest triplet substate. Fig. 3 shows that at $T = 1.5$ K the decay time decreases from $\tau_I(B = 0\ \text{T}) = 85$ μs to $\tau_I(B = 12\ \text{T}) = 11$ μs.

In several cases, it has been shown that the *B*-field dependence of the emission decay time can, by use of first order perturbation theory, successfully be described by a B^2 relation [36–38,44]. However, in the present case, this simple approach cannot be applied,