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Simultaneous Two-Photon Excited Fluorescence and One-Photon Excited Phosphorescence from Single Molecules of an Organometallic Complex $Ir(ppy)_3$

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Transition metal complexes are an important class of materials in many areas of science and technology. Recently, various iridium or platinum complexes have attracted attention as emitters in organic light emitting diodes (OLED).[1] A common feature of many of these complexes is strong phosphorescence observable even at room temperature. For the most widely studied iridium complex, *fac*-tris(2-phenylpyridine)iridium ($Ir(ppy)_3$), it has been shown that triplet metal-to-ligand charge transfer state (^{3}MLCT) is the lowest-lying emissive state.[2] Quantum efficiency and lifetime of the corresponding MLCT phosphorescence vary depending on the solvent used; in a polystyrene matrix, phosphorescence quantum efficiency of 0.92 and a lifetime of 1.2 μs have been reported.[3] The emission spectrum is dominated by a phosphorescence band centered around 510 nm. A weaker band at 450 nm has also been reported[4,5] and ascribed to ligand-centered $^3\pi-\pi^*$ phosphorescence[4] or to ^{1}MLCT fluorescence.[5]

The high emission quantum yield and short luminescence lifetime enabled the study of several organometallic complexes on a single-molecule level.[6−9] In this work, we used a time-resolved technique to measure excited-state lifetime of $Ir(ppy)_3$ molecules on ensemble and a single-molecule level. The results reveal that at low concentrations strong two-photon absorption gives rise to fast nanosecond transitions coexisting with the slow microsecond phosphorescence. We interpret the fast decay as fluorescence corresponding to the 450 nm emission band.

$Ir(ppy)_3$ was dispersed in thin films of poly(methyl methacrylate) and measured in nitrogen atmosphere on a scanning confocal microscope with picosecond laser diode excitation (438 nm) and avalanche photodiode detection. Emission lifetimes are obtained using time-correlated single-photon counting detection scheme. Figure 1 insets show logarithmic plots of emission decay profiles at various concentrations. The bulk concentration sample (5×10^{-4} M) decays, as expected, exponentially with the lifetime of 1.1 μs. In lower concentration samples, the microsecond decay is accompanied by a fast component of a 3 ns lifetime. On a single-molecule level, the slow component is barely discernible (but still present) and the fast component dominates the decay profile. We have verified that the fast component is not due to residual scattering of the excitation light or due to impurities. The phenomenon is quantified in Figure 1 by plotting the F_0/P_0 ratio as a function of concentration, where the initial intensities F_0 and P_0 of the fast and slow components were determined from the pre-exponential coefficients obtained by two-component fitting of the decays. F_0 and P_0 are related to the total emission counts F_T and P_T via the respective lifetimes τ_F, τ_P as $F_T = F_0\tau_F$ and $P_T = P_0\tau_P$. The F_0/P_0 ratio, which is proportional to F_T/P_T, decreases rapidly to 0 for concentrations above 10^{-6} M.

The concentration dependence points to the presence of qualitatively different absorption processes with different cross sections. The stronger absorption process corresponds to direct excitation of the ^{3}MLCT state followed by phosphorescence. In high concentration samples, the strong absorption in the first few layers of molecules prevents the other absorption process from occurring in the rest of the sample. With decreasing concentration, the number of photons available per molecule increases and the weaker absorption process sets in. This effect leads to F_0/P_0 decreasing as the inverse of concentration, as seen from the fit in Figure 1. The relatively long ^{3}MLCT state lifetime raises the possibility of excited-state absorption followed by intersystem crossing to ^{1}MLCT and fluorescence as the origin of the fast component. Excited-state absorption in $Ir(ppy)_3$ complexes has been reported elsewhere,[10] with an extinction coefficient of approximately 2000 M^{-1} cm^{-1} at 440 nm. Another possible origin of the fast component related to the excited ^{3}MLCT state is stimulated emission. In any of these

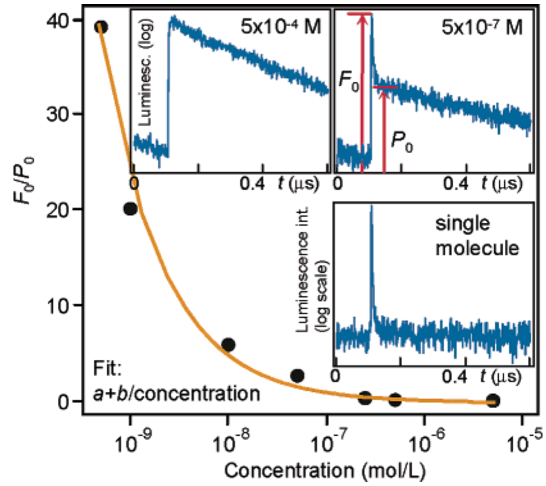

Figure 1. Concentration dependence of the F_0/P_0 ratio of the fast and slow components of emission decay of $Ir(ppy)_3$ molecules dispersed in a thin film of PMMA. The concentration values refer to solution concentrations before spin coating. Insets: Log plots of the decay profiles at different concentrations.

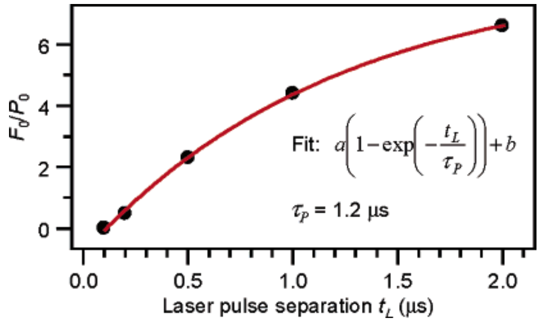

Figure 2. Dependence of the F_0/P_0 ratio of the fast and slow emission components on the excitation laser pulse separation for a sample of the concentration of 5×10^{-8} M.

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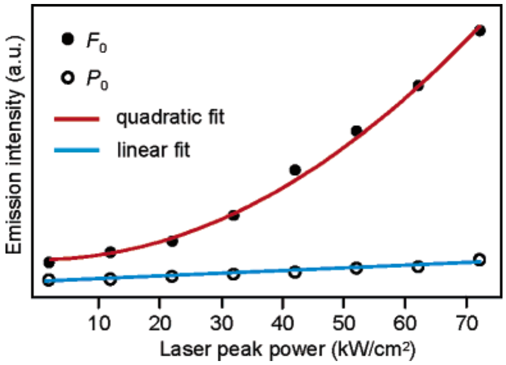

Figure 3. Dependence of the fast F_0 and slow P_0 emission components on the excitation laser peak power for a sample of the concentration of 5×10^{-8} M.

cases, the relative intensity of the fast component would be proportional to the number of molecules originally in their excited states at the time of the arrival of the excitation laser pulse. When the laser pulse separation, t_L, is increased by decreasing the repetition frequency, one would expect a decrease of the fast component or of the F_0/P_0 ratio. Results of the measurement of F_0/P_0 as a function of pulse separation are presented in Figure 2.

To avoid the problem of photobleaching, the experiment was carried out on a low-concentration sample (5×10^{-8} M). Contrary to the expectation, the F_0/P_0 ratio increases with increasing t_L, pointing to the ground state as the origin of the weaker absorption process. Assuming $M_g(t)$ and $M_e(t)$ to be the numbers of molecules in their ground and excited states, respectively, at time t after excitation, $M_g(t)$ can be expressed as

$$M_g(t) = M_e(0)\left(1 - \exp\left(-\frac{t}{\tau_P}\right)\right) + \text{const.} \qquad (1)$$

F_0 is proportional to the number of molecules in their ground states at time t_L of the excitation pulse arrival. P_0 is proportional to the number of molecules in their ^{3}MLCT excited states immediately after excitation. The F_0/P_0 ratio can be written as

$$\frac{F_0}{P_0} = a\frac{M_g(t_L)}{M_e(0)} = a\left(1 - \exp\left(-\frac{t_L}{\tau_P}\right)\right) + b \qquad (2)$$

where a and b are constants. Figure 2 shows also a fit to the experimental data using eq 2. The fit gives the lifetime value of 1.2 μs, in excellent agreement with the value obtained from the slow component decay.

The 438 nm laser excites directly the lowest-lying ^{3}MLCT state which decays by long-lived phosphorescence. To account for the fast decay component, it is necessary to consider processes, such as two-photon absorption (TPA), that lead to population of higher energy states. Excitation intensity dependence presented in Figure 3 shows that the fast component F_0 grows quadratically with increasing laser peak power, suggesting the TPA origin of the fast decay process. The slow component P_0 depends linearly on the excitation intensity, as expected for a one-photon process. The excitation intensity dependence is difficult to perform on single molecules because of the photobleaching problem. We have, however, verified the phenomenon on a single-molecule level at several different excitation power values.

To provide further support for the existence of the TPA mechanism, we carried out one- and two-photon excited fluorescence imaging of single Ir(ppy)$_3$ molecules using a *cw* laser. The right part of Figure 4 shows an image excited at 488 nm and detected between 370 and 450 nm. Apart from the different noise level, the image is similar to the one-photon excited image (left), giving a direct proof of the TPA origin of the emission.

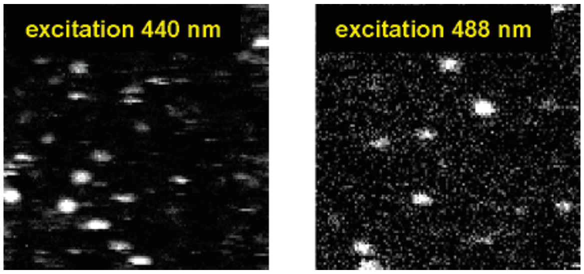

Figure 4. One-photon (left) and two-photon (right) fluorescence imaging of single Ir(ppy)$_3$ molecules. Left: Excitation 442 nm (*cw*, 4.9 kW/cm^2); detection window 475−575 nm. Right: Excitation 488 nm (*cw*, 130 kW/cm^2); detection window 370−450 nm.

The TPA in question is probably a ligand-centered $\pi-\pi^*$ transition corresponding in wavelength to the 242 nm absorption band reported for Ir(ppy)$_3$ elsewhere.[11] We propose that the following fast decay is fluorescence from the ^{1}MLCT state which is populated by internal conversion from higher π^* states. This assignment is supported by the spectral location of the fast component between 450 and 475 nm, which might correspond to the 450 nm emission band observed by others[4,5] and to the 456 nm band reported here (Figure S1). On the other hand, the relative intensity of the fast component with respect to total emission intensity is approximately 6% at the single-molecule level. This is in contradiction to the intersystem crossing probability of 3% reported in polymer films[5] and to the fast subpicosecond intersystem crossing measured in solution elsewhere[12] and indicates that either intersystem crossing is more efficient upon TPA or that other transitions might be involved.

TPA at the single-molecule level has been reported before.[13−15] The system studied here is unique in the sense that the strength of the TPA allows it to occur alongside the one-photon absorption of the same wavelength and that each absorption process gives rise to a different emission process.

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Supporting Information Available: Luminescence spectra and energy level scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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