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Photophysical and Photochemical Studies of [Pt(binap)$_2$]: Excited State Quenching by Oxygen

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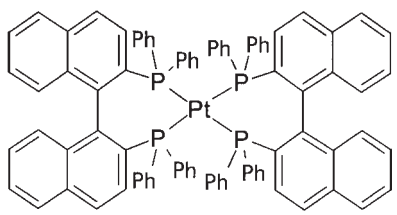
The quenching of the photoluminescence of [Pt(binap)$_2$] by oxygen has been studied. Generation of singlet oxygen was confirmed by NIR spectroscopy. The usefulness of the Pt complex as a photosensitizer was established using a singlet oxygen scavenger, 1,3-diphenylisobenzofuran (DBF). The mechanism for the generation of singlet oxygen is discussed.

Luminescent transition metal complexes have attracted considerable interest because of their possible use in new display devices and in photocatalysis.[1] Recently, many reports have presented d^{10} metal complexes having long-lived MLCT excited states in fluid solution.[2] However, the photophysics and photochemistry of platinum(0) and palladium(0) are much less explored. We reported that the platinum(0) complex [Pt(binap)$_2$] **1** (Chart 1) shows relatively intense luminescence in fluid solution at room temperature,[3] here binap, (*S*)- or (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, is one of the most widely used chiral phosphine ligands. The long-lived excited state (1.5 μs in benzene at 20 °C) of the complex has an triplet MLCT character and undergoes photoredox reactions with alkyl halides.[4]

Platinum(0)–phosphine complexes are generally not stable under aerobic conditions, but the Pt complex **1** can be handled in air even in solution. The crystal structure of **1**[3] shows that the Pt–P$_4$ core is almost completely hidden by the phenyl and naphthyl aromatic moieties. The combined aromatic moiety may effectively shield the core from the outer sphere and prevent substitution and/or redox reactions. This would account for the stability of the complex. In this report, photochemical generation of singlet oxygen and the mechanism of the reaction are to be described.



[Pt(binap)$_2$]

Chart 1. Structure of **1**.

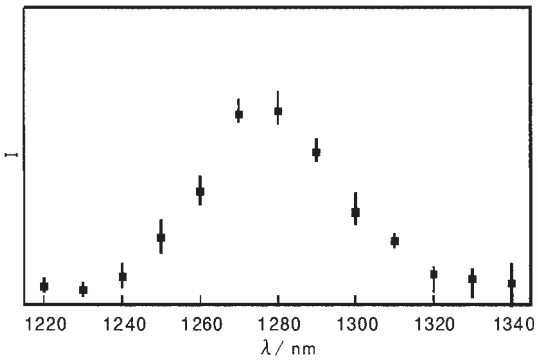


Fig. 1. The emission of $^1O_2$ generated in a solution containing [Pt(binap)$_2$] (4×10^{-4} M in C_6D_6) upon irradiation of light (410–490 nm).

The luminescence of **1** was found to be effectively quenched by oxygen, but the intensity of the luminescence was recovered when the solution was again deoxygenated by freeze-pump-thaw cycles. The lifetime of the luminescence obeys a Stern–Volmer plot, and the bimolecular quenching rate constant was calculated to have a diffusion controlled value of 6.6×10^9 M^{-1} s^{-1} in benzene at 20 °C. To identify the active oxygen species generated by the platinum complex in the excited state, NIR emission spectra were recorded. It is well known that singlet oxygen emits NIR luminescence at 1270 nm, and the detection of the luminescence is the most reliable evidence for the formation of singlet oxygen.[5] We have assembled a NIR detection system equipped with a germanium photodiode. Although the sensitivity of the detector is not high, the 1270-nm emission was clearly detected from the C_6D_6 solution of **1** under irradiation of visible light (see Fig. 1).

In order to investigate the activity of **1** as a sensitizer for photochemical generation of singlet oxygen, we measured the change in the absorption spectra of a solution containing both **1** and DBF. DBF has an absorption band at 410 nm and is known as a good scavenger of singlet oxygen.[6] The platinum complex **1** shows an MLCT band at 530 nm, but the spectrum of **1** has a valley at the 410 nm region. Figure 2 shows the change in the absorption spectra under aerobic condition. A 250-W high-pressure mercury lamp equipped with a glass filter ($\lambda > 470$ nm) was used as a light source. The absorption intensity of 410 nm decreases rapidly upon irradiation of visible light within a minute, which shows that a reaction of DBF with singlet oxygen occurs. The intensity of the MLCT band of **1** does not change during the reaction. After freeze-pump-thaw cycles, very slow decrease of the intensity of the 410 nm band was observed (30% decrease after 5 min irradiation of the light). We also confirmed that 1) the reaction of DBF does not occur in the absence of the platinum complex and 2) the spectrum was not changed in the dark.

When a benzene solution containing complex **1** (0.1 mM) and DBF (1.5 mM) was irradiated with visible light, the 410-nm band completely disappeared after 5 min. The results show that the photocatalytic degradation of DBF occurs mediated by [Pt(binap)$_2$].

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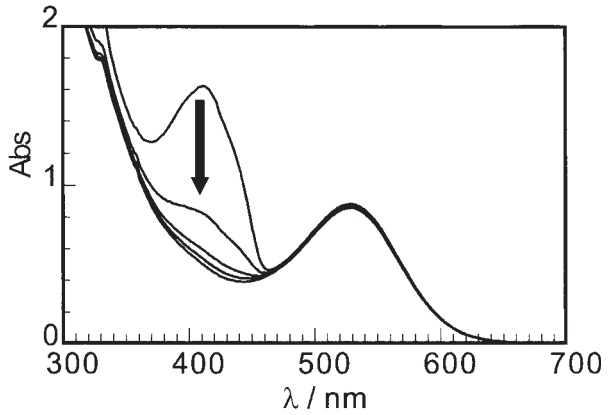

Fig. 2. The change in the absorption spectra of a solution containing DBF (1×10^{-4} M) and **1** (1×10^{-4} M) upon irradiation of light ($\lambda > 470$ nm) with irradiation time 0, 10, 20, 30, 40 s.

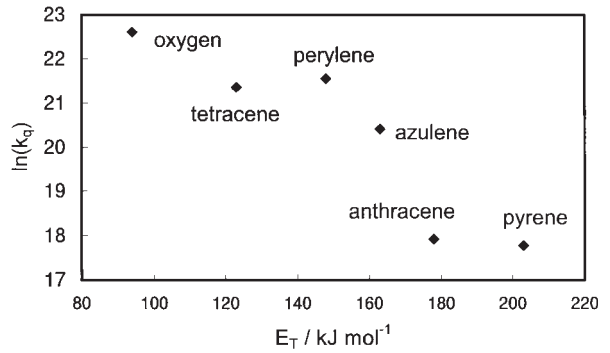

Fig. 3. The correlation between the quenching constants determined from the S–V plots of the luminescence decay of [Pt(binap)$_2$] and the triplet energy of the quencher. The energy of the lowest excited singlet state of oxygen is also shown.

Energy transfer from the MLCT state of the complex to oxygen is a common mechanism for generation of singlet oxygen.[7] Some aromatic compounds which have low triplet-state energies were used as quenchers of the luminescence to confirm the mechanism for the quenching. The result of the experiment is shown in Fig. 3. Clearly, the quenching rates correlate with the triplet-state energies of the quenchers. The energy between the lowest excited singlet state and ground triplet state of oxygen is also shown. The result strongly supports the assertion that energy transfer from the triplet excited-state of the platinum complex to oxygen is a dominant mechanism for the sensitization of oxygen, but a redox-mechanism including electron transfer to oxygen[8] cannot be completely ruled out, because the platinum complex was shown to be a photo-reductant in the photochemical reaction with alkylhalides.[4]

The present results demonstrate the usefulness of the Pt–binap complex as a good material for photochemical study. It may be possible to construct a new asymmetric photochemical reaction using the platinum complex.

Experimental

The complex **1** was prepared according to the previously reported method.[3] The spectroscopic properties were measured using a quartz cell connected to a glass tube and a Teflon stop-cock. Absorption and luminescence spectra were measured with a Shimadzu UV-2100 spectrophotometer, and a Shimadzu RF-5000 fluorometer, respectively. Luminescence decay-curves were measured on a laboratory-made apparatus; the sample was excited using a nitrogen laser (USHIO AN-200) and the emission light was focused into a Jovin-Ybon H-20 monochromator equipped with a photomultiplier, Hamamatsu R-955. The output of the photomultiplier was digitized by a HP 54510 digital oscilloscope and then downloaded to a PC. The concentration of oxygen in the C_6D_6 solution of **1** was calculated by Henry's law using a literature value of the concentration (1.9×10^{-3} M in the solution equilibrated with 1 atom air[9]). The NIR detection system was made in our laboratory as follows. The excitation-light (250-W high-pressure mercury lamp) was passed through a 20 Hz light-chopper, and an aqueous $CuSO_4$ and $NaNO_2$ solution filter.[9] The visible light of 410–490 nm wavelength was focused into the sample. The emission was analyzed by a monochromator (Optometrics Mini-Chrom, 750 nm-blaze model) equipped with a germanium photodiode (Optometrics GDM-1). The output of the photodiode was fed into a lock-in amplifier.

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