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The Long-wavelength $n\pi^*$ Phosphorescence Spectra of *p*-Quinones in Polycrystalline Solutions at 77 K

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Besides the usual $n\pi^*$ phosphorescence spectra, broad, long-wavelength $n\pi^*$ phosphorescence spectra are observed in normal paraffine solutions, such as a heptane solution, of 1,4-naphthoquinone, and in a benzene solution of 5,14 : 7,12-pentacenediquinone at 77 K. The energy difference between the two spectra are *ca.* 750 and 980 cm^{-1} respectively. The intensity of the long-wavelength spectra relative to the short-wavelength spectra becomes weaker with decreases in the concentrations of the quinones, and the lifetimes of the long-wavelength spectra are shorter than those of the short-wavelength spectra. These long-wavelength spectra are assigned to those of the quinone aggregates. The excitation spectra of these phosphorescences have also been obtained. An explanation of the above red-shift of the $n\pi^*$ phosphorescence spectra of the aggregates is presented; in it, the phosphorescence state of the aggregates corresponds to the $n\pi^*$ triplet excimer state.

Heretofore, we have studied the phosphorescence spectra of quinones in solutions at 77 K.[1] normal paraffin polycrystalline solutions, such as a heptane solution, of 1,4-naphthoquinone(NQ)[1e] at 77 K show a regular broad phosphorescence spectrum besides a sharp $n\pi^*$ phosphorescence spectrum; the broad spectrum is at considerably longer wavelengths than the sharp spectrum. A similar, broad, long-wavelength phosphorescence spectrum is also found in a benzene crystalline solution of 5,14 : 7,12-pentacenediquinone (PDQ)[2] at 77 K. In this work, these broad, long-wavelength phosphorescene spectra of the *p*-quinones have been studied.

Experimental

Measurements. The phosphorescence spectra in solutions at 77 K were measured using an Aminco-Bowman spectrofluorometer (Instrument I, PM tube R105UH) and an SPF-500 spectrofluorometer (Instrument II, PM tube R777) in the manner described in previous papers.[1a,1c,1e] The phosphorescence excitation spectra were obtained using Instrument II, equipped with a photon counter (PM tube 1P28). The energy distribution of the exciting light (a 250-W Xenon arc lamp) and the spectral transmittance of the monochromator have not been taken into account. The temperature dependence of the phosphorescence spectra was measured by means of the Instrument II equipped with a cryostat (Model CF 204, Oxford Electric Instrument, Ltd.). Two kinds of cooling speeds, fast and slow, were used.[1b] normal paraffin and benzene solutions, and methylcyclohexane and toluene solutions, formed polycrystalline and glassy states respectively at 77 K.

Materials. Commercially-available NQ was purified in the same manner as has been described in a previous work.[1e] PDQ of the Tojin Gosei Kogyo Co. was purified by means of vacuum sublimation, and its purity was checked by the TLC method. The solvents used were all of spectro-grade except for dodecane. Dodecane of GR grade of the Tokyo Kasei Kogyo Co. was used.

Results. The phosphorescence spectra and their excitation spectra obtained are shown in Figs. 1, 2, 4, and 5, and Figs. 3 and 6, respectively. The peak wavelengths of the phosphorescence spectra obtained are shown in Table 1. The broad, long-wavelength phosphorescence spectra observed in the heptane and octane solutions of NQ (Figs. 1 and 2) and the benzene solution of PDQ (Figs. 4 and 5) can not be observed using the phosphoroscope (10600 min^{-1}) because of their short lifetimes. They are weaker in slow-cooling than in rapid-cooling, as in the

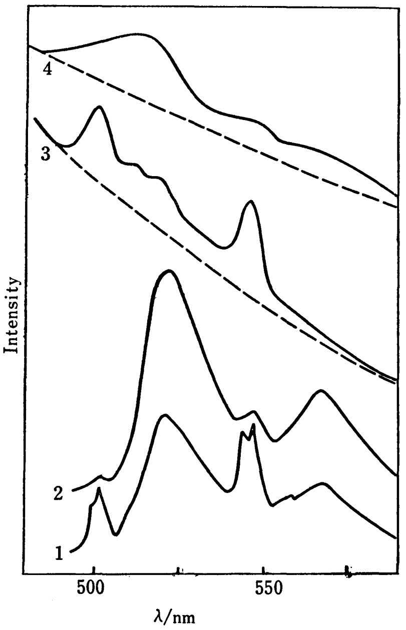

Fig. 1. Phosphorescence spectra of NQ in the heptane solution at 77 K.
1: 3×10^{-3} M, 313 nm ex., 2: 3×10^{-3} M, 365 nm ex., 3: 10^{-5} M, 313 nm ex., 4: 10^{-5} M, 365 nm ex. (In Figs. 1 and 5, ex. denotes excitation.)

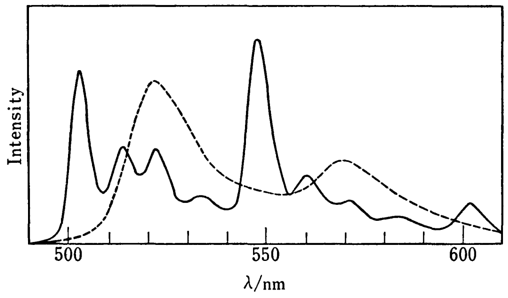

Fig. 2. Phosphorescence spectra of NQ in solutions at 77 K.
——: Methylcyclohexane, 1.6×10^{-3} M, ----: octane, 1.9×10^{-3} M.

case of the short-wavelength spectra. In NQ, the short-wavelength spectrum of the heptane solution also can not be observed using the phosphoroscope, but the corresponding phosphorescence spectrum of the hexane solution is barely observable using the phosphoroscope. The phosphorescence spectra of the hexane and toluene solutions of PDQ (Fig. 4) can be observed using the phosphoroscope; the observed lifetimes are 1.8 and 3.2 ms respectively. The observed lifetime of the short-wavelength phosphorescence spectrum of the benzene solution of PDQ (Fig. 5) is *ca.* 2 ms. The phosphorescence spectrum of PDQ crystals (Fig. 4) can not be observed using the phosphoroscope.

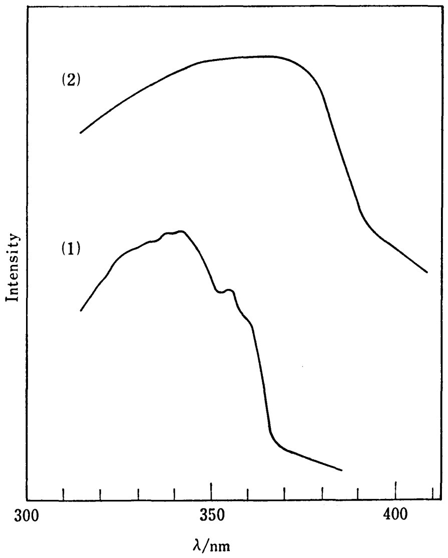

Fig. 3. Phosphorescence excitation spectra of NQ in solutions at 77 K.
(1) Methylcyclohexane, 1.6×10^{-3} M, 548 nm mon., (2) heptane, 1.5×10^{-3} M, 522 nm mon. (In Figs. 3 and 6, mon. denotes monitor.)

TABLE 1. PEAK WAVELENGTHS, λ, OF THE PHOSPHORESCENCE SPECTRA

Solvent		λ/nm	
		I[a]	II[a]
NQ	Heptane	498, 501.5	521
		544, 547.5	569
	Methyl-cyclohexane	501	
		547	
		602	
	Octane		521
			569
PDQ	Hexane	472	
		477	
		481	
		488	
		492	
		502	
		504.5	
		513	
		517.5	
		523	
		545	
		560.5	
	Benzene	472	495
		511.5	539.5
		558	591.5
	Toluene	461	
		497	
		540	

a) I and II denote the short- and long-wavelength spectra respectively.

Discussion

In normal paraffine solutions, such as pentane, hexane, and heptane solutions, a regular, broad phosphorescence spectrum appears at wavelengths longer by *ca.* 750 cm^{-1} than the sharp $n\pi^*$ phosphorescence spectrum,[1e] and the intensity of the former spectrum relative to the latter becomes weaker with decreases in the concentrations of the solutions, as may be seen from a comparison of the 1 and 3 spectra in Fig. 1.[3] The long-wavelength spectrum appears most strongly in the heptane solution, though it is relatively weak. In the heptane solution, it is observed even at the low concentration of NQ (10^{-5} mol/l), as may be seen in Fig. 1. In the octane solution, it appears alone, as may be seen in Fig. 2. The long-wavelength spectrum is clearly different from that of the NQ crystals.[5] Therefore, the long-wavelength spectrum is thought to be due to NQ aggregates. Since the lifetime of the short-wavelength spectrum of the heptane solution is thought to be close to that of the hexane solution, it may be longer than that of the long-wavelength spectrum. As the long-wavelength spectrum shows the C–O stretching vibrational structre and its lifetime is short, it may be assigned to the $n\pi^*$ phosphorescence spectrum. No such broad, long-wavelength spectrum has been observed in the other solutions of NQ studied.

In the phosphorescence excitation spectra of NQ in Fig. 3, the main broad spectra are assigned to the low-energy $\pi\pi^*$ absorption spectrum.[6] The correspondence between these excitation spectra and the $\pi\pi^*$ absorption spectra is qualitative, because the absorption in this wavelength region is very strong in the light of the NQ concentrations of the solutions used. Figure 3, however, proves that the $\pi\pi^*$ absorption spectrum in the heptane solution is at considerably longer wavelengths than that in the methylcyclohexane solution.[7] The spectra corresponding to the S–S $n\pi^*$ absorption spectra at the long wavelengths could not be accurately observed. However, the corresponding spectrum in the heptane solution is qualitatively observed to be at shorter wavelengths than that in the methylcyclohexane solution. As may be seen in Fig. 1, the intensity of the broad spectrum relative to that of the sharp spectrum is far larger at the 365 nm excitation than at the 313 nm excitation. This fact can reasonably be explained by the above results.

In Fig. 4, the phosphorescence spectra of the hexane and toluene solutions of PDQ are reasonably assigned to the $n\pi^*$ spectrum because of their C–O stretching vibrational structure and short lifetime. The spectrum of the toluene solution is at shorter wavelengths than that of the hexane solution; this is a result of the

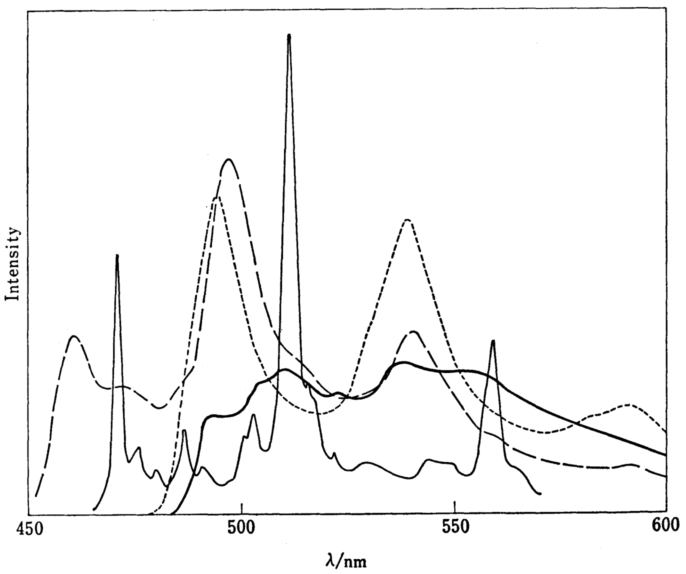

Fig. 4. Phosphorescence spectra of PDQ in solutions and the crystalline phase at 77 K.
——: Hexane, 2×10^{-5} M, ----: benzene, 10^{-3} M, — —: toluene, 10^{-3} M, ——: crystalline phase.

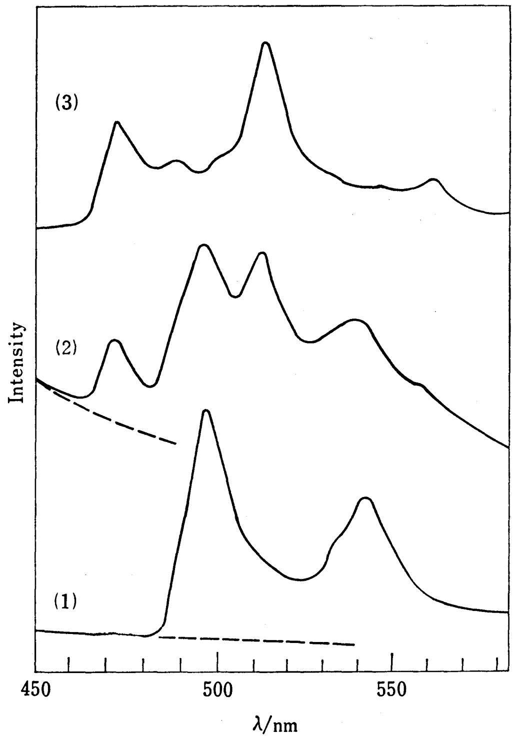

Fig. 5. Phosphorescence spectra of PDQ in the benzene solution at 77 K.
(1) 10^{-3} M, 365 nm ex., (2) 5×10^{-5} M, 365 nm ex., (3) 5×10^{-5} M, 365 nm ex.

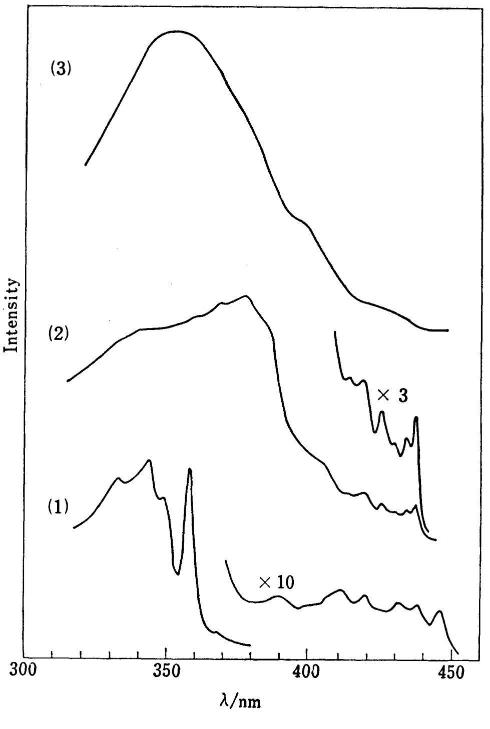

Fig. 6. Phosphorescence excitation spectra of PDQ in solutions at 77 K.
(1) Dodecane, 2×10^{-4} M, 513 nm mon., (2) benzene, 10^{-3} M, 540 nm mon., (3) toluene, 10^{-3} M, 498 nm mon.

charge-transfer interaction between toluene and PDQ, as in the cases of other quinones.[1e,1f] As may be seen in Fig. 4, PDQ[2] also shows a broad, long-wavelength phosphorescence spectrum, with the C–O stretching vibrational structure, in the benzene solution at 77 K. This spectrum is also different from that of the PDQ crystals. A similar phosphorescence spectrum has not been observed in other solutions. In the benzene solution, as may be seen in Fig. 5, a new phosphorescene spectrum appears at the wavelengths shorter by *ca.* 980 cm^{-1} than the above long-wavelength spectrum as the concentration of PDQ decreases; the former can be observed through the phosphoroscope. This short-wavelength spectrum is situated close to the phosphorescence spectrum of the hexane solution and is similar in shape to that of the toluene solution. From these results, the long- and short-wavelength spectra in the benzene solution are also assigned to the nπ* phosphorescence spectra of the quinone aggregates and isolated molecules respectively, as in the case of NQ.

In the phosphorescence excitation spectra[8] of PDQ in Fig. 6, the long-wavelength weak and structured spectra and the short-wavelength strong spectra are assigned to the S–S nπ* and $\pi\pi$* absorption spectra respectively.[2,9] In the benzene and toluene solutions, the correspondence between the short-wavelength spectra and the $\pi\pi$* absorption spectra is also thought to be qualitative, as in the case of NQ in Fig. 3. In the benzene solution, the $\pi\pi$* absorption spectrum is at considerably longer wavelengths than those in other solutions studied, while the nπ* absorption spectrum is at shorter wavelengths than that in the dodecane solution as in the case of the heptane solution of NQ. At 77 K, since the S–S nπ* absorption spectrum in the benzene solution is, as has been mentioned above, at shorter wavelengths than that in the dodecane solution, the T–S nπ* absorption spectrum[10] in the benzene solution is also thought to be at shorter wavelengths than that in the dodecane solution, while the nπ* phosphorescence spectrum in the benzene solution is at considerably longer wavelengths than that in the hexane solution. A similar situation is also found in the case of NQ. It can, therefore, be concluded that, in the phosphorescence state, the geometry of the NQ and PDQ aggregates changes from that at the ground state in such a manner that the phosphorescent nπ* level of the aggregates becomes considerably lower than that of the isolated quinone molecules.

In the long-wavelength phosphorescence spectrum of the benzene solution of PDQ in Fig. 4, a very weak shoulder on the shorter-wavelength side of each peak is observed. This shoulder may be due to aggregates of another form, different from the aggregates showing the peaks. As for the temperature dependence of the long-wavelength phosphorescence spectrum in the benzene solution, it almost disappears at 100 K, while the phosphorescence spectrum in the dodecane solution can still be clearly observed at 200 K.

The shorter lifetimes of the phosphorescence spectra of these quinone aggregates relative to those of the isolated quinone molecules are thought to be due to the intermolecular interaction between the components of the aggregates. The aggregates of NQ and PDQ are thought to be favorably formed in the heptane and benzene crystals respectively. These host-guest combinations may correspond to that of key and keyhole. As for the structure of the aggregates of these quinones, it is thought probable that the aggregates consist of two quinone molecules, because large-sized aggregates can not be favorably formed in the solvent crystals, and that they take the form of a slipped sandwich-type dimer,[11] since the π-electronic exchange interaction between the component molecules of these quinone aggregates may not be very small, in view of the aforementioned large red-shift of the low-energy $\pi\pi$* absorption spectrum.

The aforementioned large red-shift of the nπ* phosphorescence spectra of these aggregates may be explained as follows. The three kinds of intermolecular interaction in the aggregates, the electrostatic, dispersion-force, and π-electronic exchange interactions, may affect the shift of the nπ* spectra. The electrostatic interaction usually brings about the blue-shift for the nπ* transition spectra. On the other hand, the dispersion-force interaction is thought to be too weak to bring about such a large red-shift as that. Therefore, the exchange interaction is thought to raise the above red-shift. In the ground-state geometry of the aggregates, the eletrostatic interaction, which is a long-range interaction, may be the predominant factor in the shift of the nπ* absorption spectra, resulting in the aforementioned blue-shift of the nπ* absorption spectrum of the PDQ aggregates. On the other hand, in the nπ* phosphorescent-state geometry of the aggregates, the exchange interaction, which is a short-range interaction, may become the predominant factor in the shift of the nπ* phosphorescence spectra, resulting from a decrease in the distance between the components of the aggregates, accompanied by the formation of a state corresponding to the nπ* triplet excimer state.[13] In this explanation, therefore, the phosphorescent state of the aggregates corresponds to the nπ* triplet excimer state.

This red-shift of the nπ* phosphorescence spectra which is brought about by the π-electronic exchange interaction may be explained using a simple one-electron model as follows. In the nπ* phosphorescent state of the aggregates, in comparison with the case of the isolated quinone molecules, the degenerate π*-levels will split to some extent through the intermolecular π-electronic exchange interaction, while the degenerate n-levels will remain almost unchanged, because the overlap between the π*-orbitals of the component molecules may not be small, while that between the n-orbitals is very small. Threfore, the nπ* phosphorescence spectra of the aggregates may shift considerably to the red in comparison with that of the isolated quinone molecules. Such a long-wavelength nπ* phosphorescence spectrum as is studied in this work can be expected to be found in other *p*-quinones.

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