

## Luminescence from Upper Electronic Excited States of Phthalocyanines

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It has been demonstrated that certain features of the electronic structure in complex molecules can force departure from Kasha's rule, e.g. [1]. The extensively studied azulene system whose principal emission originates from the second singlet state rather than from the first state [2, 3]. Examples of such departures are of value since they extend our comprehension of the processes involved in the energy degradation from electronic excited states.

We are reporting, to our knowledge for the first time in phthalocyanines, the observation of a visible luminescence,  $\lambda_{\text{max}} \sim 470$  nm, which can be traced to states of energy greater than the lowest lying  $\pi\pi^*$  vibronic states\*\*. Such assignment can be justified if the excitation energy is trapped in a state which achieves a significant population because transitions to the lowest lying  $\pi\pi^*$  state are forbidden. Gouterman's calculations indicate the existence of several excited states in the phthalocyanines with the required properties for such emission [5]. Moreover, while several of the long lived excited states of phthalocyanines have been observed by flash photolysis, further clarification of the energy level scheme may be obtained by assignment of the luminescent states reported here.

We have investigated the luminescence of the chlorophthalocyaninerhodium(III),  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Cl}$  in deaerated solutions†. Excitation with monochromatic light in the ultraviolet region ( $\lambda_{\text{excit}} \leq 400$  nm) induces a broad visible emission with  $\lambda_{\text{max}} \sim 420$  nm, Fig. 1. The quantum yield for this emission may be seen to be independent of the solvent used; see Table I. The emission spectrum was measured at 77 K in glassy solution as well as at room temperature. From the Fig. 1, it is apparent

TABLE I. Quantum Yield for the Emission of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Cl}$  in Various Solvents at Room Temperature.

Solvent <sup>a</sup>	$\phi_{\text{emission}}^b \times 10^3$
$\text{CH}_3\text{CN}$	1.4
$\text{CD}_3\text{CN}$	1.5
$\text{CH}_2\text{Cl}_2$	1.3
Methanol	1.6
Ethanol + Methanol (9:1)	1.2
Benzene + Acetonitrile (4:1)	1.4

<sup>a</sup>Solvents were distilled in an all glass apparatus before the preparation of the solutions. All solutions were deaerated with Ar. <sup>b</sup> $\lambda_{\text{excit}} = 320$  nm. Quinine Sulfate in 1 N  $\text{H}_2\text{SO}_4$  was used as a standard.

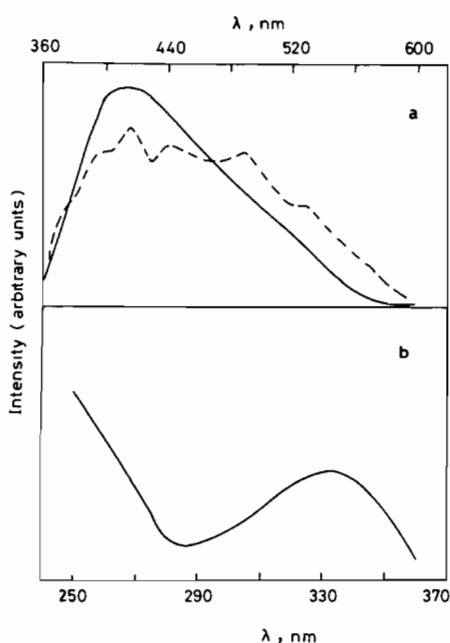


Fig. 1. Luminescence of  $\text{Rh}(\text{ph})(\text{CH}_3\text{OH})\text{Cl}$  in deaerated  $\text{CH}_3\text{CN}$ : (a) Emission spectra for  $\lambda_{\text{excit}} = 320$  nm at  $T = 298$  K (—) and  $T = 77$  K (---). (b) Excitation spectrum obtained with  $\lambda_{\text{emiss}} = 420$  nm at  $T = 298$  K.

that the spectrum at 77 K exhibits vibrational structure not evident at the higher temperature. The separation between vibrational levels,  $\Delta\epsilon \sim 1300$   $\text{cm}^{-1}$  approaches that measured for the vibrational levels in the first excited singlet [6],  $\Delta\epsilon \sim 1620$   $\text{cm}^{-1}$ , but is yet significantly smaller. All spectra given were obtained using an SLM spectrofluorimeter equipped with single photon counting and programmed correction of instrument response. That the

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\*\* The emission from the second excited singlet in porphyrins has been observed [4].

† The compounds used here were available from a previous work.

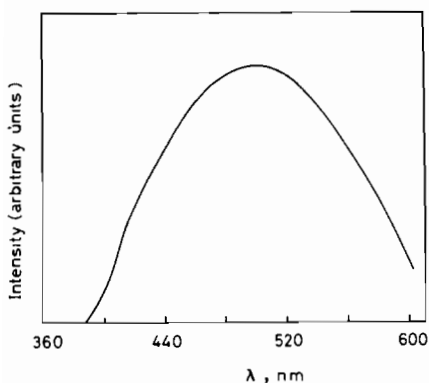


Fig. 2. Emission spectrum of Al(ph) in deaerated  $\text{CH}_3\text{CN}$  at  $T = 298 \text{ K}$ . Excitation at  $\lambda_{\text{excit}} = 320 \text{ nm}$ .

emission with  $\lambda_{\text{max}} \sim 420 \text{ nm}$  cannot be associated with emissions from high vibrational states of the lowest states of the singlet and/or triplet manifolds is demonstrated by the excitation spectrum. Indeed this spectrum suggests that the emissive state is populated from states that lie well above the lowest  $\pi\pi^*$  excited state.

The time dependent decay of the 420 nm emission at room temperature was monitored with a PRA single photon counting apparatus. Although the time profile did not correspond to that expected for a single exponential decay, the use of a double exponential function gives a relatively good fit with lifetimes of  $\tau \sim 4.0 \times 10^{-9} \text{ sec}$  for one component and  $\tau \sim 18.0 \times 10^{-9} \text{ sec}$  for the other. These lifetimes seem to be rather large for states with a singlet

multiplicity since subnanosecond life-times have been reported for the fluorescence of phthalocyanines [6, 7]. The consideration of the points indicated above suggest that the 420 nm emission must originate in triplet ligand centered states, e.g.,  $[3] \pi\pi^*$ . Insofar as Aluminium(III) phthalocyanine exhibits similar luminescence at 470 nm, Fig. 2, one cannot assign the emission to pure metal centered, namely dd, states.

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