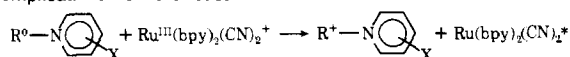


- (13) Potentials for the excited-state couples $\text{Ru}(\text{bpy})_2(\text{CN})_2^{+/0*}$ and $\text{Ru}(\text{phen})_2(\text{CN})_2^{+/0*}$ were estimated by subtracting the experimental emission energies (1.86 and 1.88 V) plus 0.05 V from the ground-state ($\text{Ru}(\text{III})/\text{Ru}(\text{II})$) potentials (0.83 and 0.84 V). The factor of 0.05 V has been estimated to be the difference between the emission energy and the free-energy content of the thermally equilibrated excited state for $\text{Ru}(\text{bpy})_3^{2+*}$.
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- (15) k_D was calculated using the Debye-Smoluchowski equation: $k_D = [4\pi M(D_A + D_B)(r_A + r_B)f]/1000$, where $f = 1.0$ for a diffusional process involving uncharged particles.¹⁶ The diffusion coefficients for $\text{Ru}(\text{bpy})_2(\text{CN})_2^{+/0}$ and $\text{Ru}(\text{phen})_2(\text{CN})_2^{+/0}$ were calculated from polarographic data in DMF¹⁷ and corrected for the viscosity difference between CH_3CN and DMF to give $D = 7.4 \times 10^{-6}$ cm²/s. For the pyridinium ions and radicals, the Stokes-Einstein equation $D = kT/6\pi\eta r_w$ was used.¹⁸ Values of r were calculated from van der Waals increments given in the literature.^{16a} The radii for $\text{Ru}(\text{bpy})_2(\text{CN})_2$ and $\text{Ru}(\text{phen})_2(\text{CN})_2$ were taken to be 6.0 and 6.2 Å, respectively.
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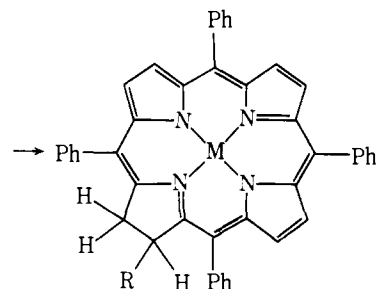
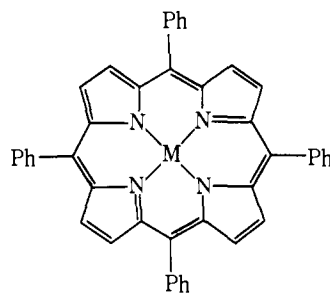
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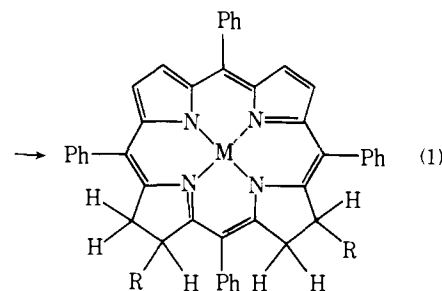
Exciplex Formation from Transition-Metal Complexes. Luminescent Nonpolar Exciplexes from Palladium(II) Porphyrin Triplets and *N,N*-Dimethylaniline

Sir:

Both photoredox reactions and exciplex emission have been observed upon irradiation of various chromophores in the presence of amines.¹⁻⁸ While exciplex emission has been observed for a variety of organic substrates, it has not been generally detected with transition-metal complexes,^{9,10} even though the latter frequently undergo photoreaction with amines and other substrates that give luminescent exciplexes with aromatic hydrocarbons.¹¹⁻¹⁵ One group of reactions that might be anticipated to involve exciplex intermediates is the photoreduction of metalloporphyrins. This reaction, which has been observed for a variety of different metal complexes,¹⁴⁻¹⁷ generally involves the consecutive conversion of the porphyrin to chlorin and isobacteriochlorin complexes (eq 1) under irradiation in the presence of a variety of reducing agents. In recent investigations we have examined photoreactions of the platinum(II) and palladium porphyrins.¹⁸ These complexes



- 1, M = Pd; R = H
3, M = Pd; R = $\text{CH}_2\text{N}(\text{-CH}_3)_2\text{C}_6\text{H}_5$



- 2, M = Pd; R = H
4, M = Pd; R = $\text{CH}_2\text{N}(\text{-CH}_3)_2\text{C}_6\text{H}_5$

show very weak fluorescence and prominent phosphorescence in fluid media at room temperature, and the long triplet lifetimes, particularly for the palladium complexes,¹⁸⁻²⁰ permit the observation in several cases of relatively slow and energetically uphill excited-state reactions.¹⁸ We felt that these properties should make these complexes especially useful for a study of metalloporphyrin excited-state interactions with amines and other reductants. In the present paper we report results that indicate the formation of luminescent exciplexes between amines and palladium porphyrin triplets. Our results indicate that the exciplex has little charge-transfer character and strongly resembles the uncomplexed porphyrin triplet in both lifetime and emission spectrum. The results observed here with luminescent triplets are apparently related to those obtained previously for nonemitting metalloporphyrin triplets with electron acceptors.^{21,22}

Palladium(II) porphyrin complexes were prepared as previously described.^{18,23} Our study has included several different porphyrins (e.g., octaethylporphyrin, $\alpha,\beta,\gamma,\delta$ -mesotetraphenylporphine (TPP), and mesotetra($\alpha,\alpha,\alpha,\alpha$ -hexadecylamidophenylporphine)), as well as a number of potential donors (triethylamine, *N,N*-dimethylaniline (DMA), and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$); however, the present report will deal only with the system PdTPP-DMA, which shows typical behavior and has been studied in greatest detail. Irradiation of degassed solutions of PdTPP in the presence of 0.5-5 M DMA in a number of solvents (e.g., benzene, pyridine, acetone, 2-propanol, or isobutyronitrile) with light absorbed only by the porphyrin leads to inefficient ($\phi \approx 0.001$ at 3.9 M DMA) formation of reductive adducts **3** and **4**. In addition to photoadduct formation, we find that DMA produces changes in

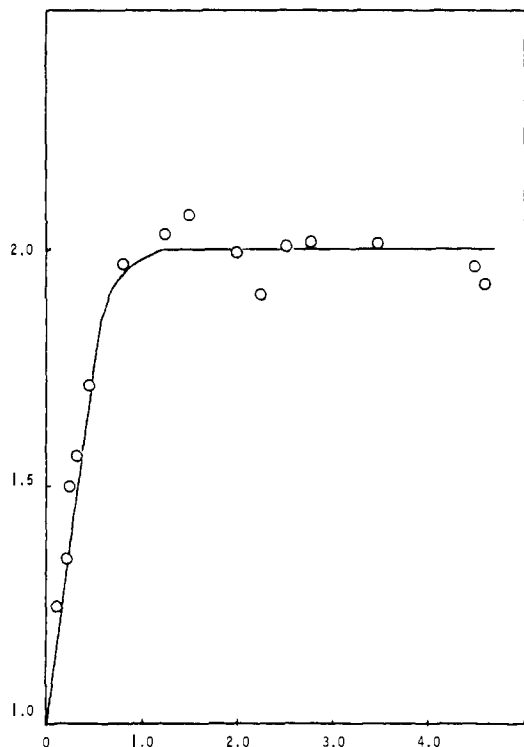
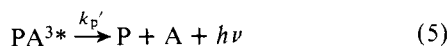
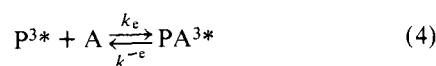
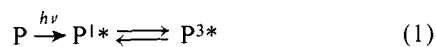


Figure 1. Stern-Volmer plot of phosphorescence quenching of PdTPP by DMA in pyridine. The ordinate is the ratio of intensity of the unquenched to quenched phosphorescence, I_0/I . The abscissa is the molar DMA concentration.

both the lifetime and intensity of the PdTPP luminescence. Figure 1 gives a plot of phosphorescence intensity quenching by DMA in pyridine. Although an apparent initial quenching is observed at low [DMA], it is clear that there is a leveling off at moderate concentrations of DMA such that no further quenching can be detected.²⁴ Phosphorescence lifetimes measured over the same range of concentrations show qualitatively similar behavior, although there is somewhat more scatter in the data. The weak fluorescence consists of prompt and delayed components;²⁰ the effect of DMA on this emission is less easy to measure, but the very limited quenching observed here compared to the phosphorescence suggests only the delayed portion is affected and that the effect is similar to that observed for the phosphorescence. The luminescence and transient absorption spectra obtained for PdTPP in the absence and presence of large amounts of DMA are identical within the limits of detection. The absorption spectrum of PdTPP is unaffected by addition of DMA, suggesting that there is little or no complex formation in the ground state.²⁵

The results obtained are most consistent with reaction of DMA with the excited triplet of PdTPP to form an exciplex as outlined in eq 1-6:^{25,26}



Since no change in the emission spectrum is observed at high [DMA], it is assumed that emission from the complex (eq 5) is nearly identical with that from the uncomplexed metalloporphyrin. A slight modification of previously derived kinetic treatments²⁷ leads to Stern-Volmer type expressions for situations where there is equilibration between P^{3*} and PA^{3*} ($K = k_c/k_{-c}$) (eq 7) or where the complex is formed irreversibly

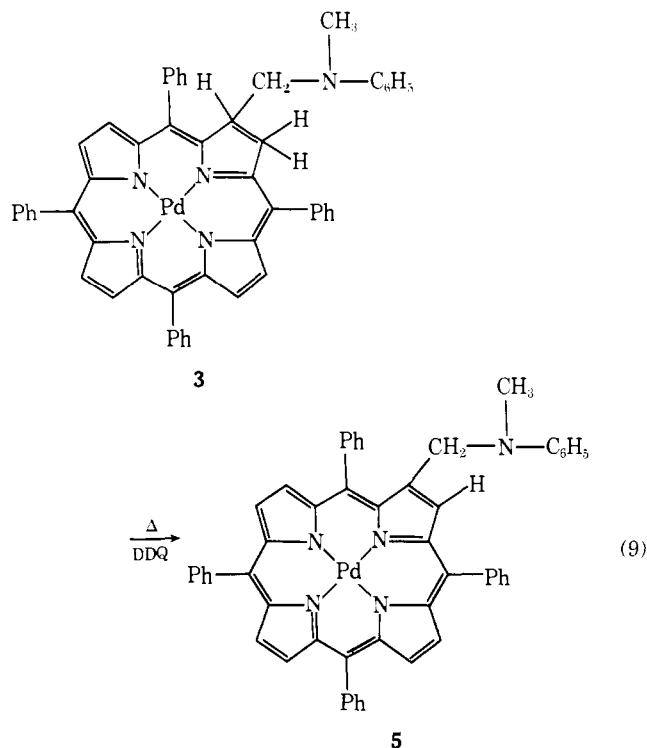
$$\frac{\phi^0}{\phi} = \frac{k_p}{k_p + Kk_p'[A]} \left(1 + K[A] \frac{\tau^0}{\tau_e} \right) \quad (7)$$

$$\frac{\phi^0}{\phi} = \frac{k_p}{k_p + k_p'k_c[A]\tau_e} (1 + k_c\tau^0[A]) \quad (8)$$

where τ^0 and τ_e are the lifetimes for the emission at zero and high DMA concentrations. Both expressions predict an increase in ϕ^0/ϕ at low concentrations of DMA and a leveling off at high concentrations. Since the limiting value $\phi^0/\phi = k_p\tau^0/k_p'\tau_e$ in both cases and τ^0 and τ_e are measurable, it is possible to generate plots from eq 7 and 8 for different values of K and k_q , respectively. Although both treatments lead to reasonable fits for the experimental data yielding best values of $K \approx 10 \text{ M}^{-1}$ and $k_q \approx 10^5 \text{ M}^{-1} \text{ s}^{-1}$, it seems unreasonable in view of the relatively long lifetimes for both P^{3*} and PA^{3*} to assume no reversibility in the quenching step. This would imply a large stabilization of the complex, which would almost surely result in altered emission and transient absorption spectra. The results seem much more compatible with a weak complex in which the equilibrium constant is small but equilibrium is rapidly established.

The low indicated value of K suggests that even with a moderately ordered system the stabilization of the complex can be no more than a few kilocalories per mole. Although the formation of reductive adducts suggests that interaction of excited states of PdTPP with DMA may involve charge-transfer interactions, the stabilization of the exciplex formed in the present process must involve these interactions to only a very limited extent, since from redox potentials the "pure" charge-transfer state, PdTPP-DMA⁺, can be estimated to lie about 6.5 kcal/mol above the PdTPP triplet. The present results are most satisfactorily explained by assuming eq 4 involves formation of a "nonpolar exciplex" in which the energy minimum may arise in part from charge-transfer interactions, but in which the excitation remains largely localized on the metalloporphyrin. This would then represent a limiting case of the range of exciplexes as recently outlined by Lewis and others.²⁸⁻³² Further evidence in favor of an emitting nonpolar exciplex is provided by the study of a linked porphyrin-DMA compound (5). This complex can be easily obtained by oxidation of 3 with 2,3-dichloro-5,6-dicyanoquinone (eq 9).³³ 5 has absorption and luminescence spectra nearly identical with those of PdTPP; however, 5 has a lower phosphorescence intensity (80%) and lifetime (84%) than PdTPP. That its excited triplet is largely a complex between PdTPP and the bound DMA is indicated by the finding that its phosphorescence is quenched by added (up to 1.2 M) DMA. The transient absorption spectrum for 5 is also nearly identical with those for uncomplexed PdTPP and PdTPP at high [DMA].

Although similar behavior has been observed with triethylamine and with DMA and other palladium porphyrins, a rather dramatic change occurs when PdTPP is excited in the presence of 4-methoxy-*N,N*-dimethylaniline (MDMA). Here the triplet is quenched efficiently to near completion with a rate constant $k_q = 2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, while the prompt fluorescence is unaffected. No products are detected on prolonged irradiation, and no transients are detected upon flash photolysis. Since MDMA is a better electron donor than DMA by ca. 5 kcal/mol, it is reasonable that charge-transfer interactions would play a much greater role in stabilizing any exciplex formed in this case and perhaps that actual electron transfer



provides a rapid channel for nonradiative decay in this system.²⁸

The results observed with the luminescent palladium porphyrins and DMA appear closely related to those previously obtained with long-lived but nonemitting triplets of zinc and magnesium porphyrins with acceptors such as aromatic nitro and halogen compounds.^{21,22} Here initial apparent quenching is followed by formation of relatively long-lived complexes having transient spectra very similar to the uncomplexed metalloporphyrin triplet. For these systems too it can be concluded that charge-transfer interactions play a limited role and that the exciplex is nonpolar. Since weak complex formation is a fairly general phenomenon in the ground state, there is no reason why phenomena similar to those reported in the present study should not occur for a variety of substrates having long excited-state lifetimes and that such very weak exciplexes could be frequent but masked precursors to photoproducts.

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- At high [DMA] (above 4 M) there is some indication of an increase in both phosphorescence intensity and lifetime. While this could be a "solvent effect", it could also be attributable to a higher order complex as has been previously determined.^{21,22}
- One could argue, however, that a very weak ground-state complex could be undetectable and that such a complex could play a role in the luminescence. The kinetics suggest this is not the case.
- This neglects product-forming steps that may occur in low efficiency from p_3^* .
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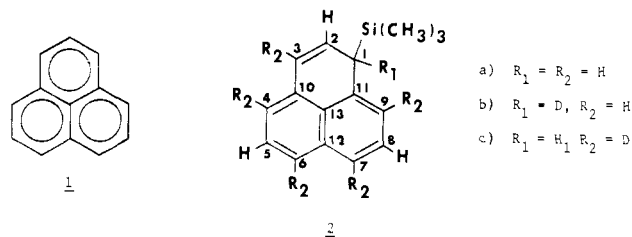
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Thermally and Photochemically Induced Shifts of Silicon on the Phenalene Ring System

Sir:

In recent years there has been a great deal of interest in the fluxionality and sigmatropic behavior associated with σ - and π -bonded metal derivatives of organic π ligands, among them being metal derivatives of cyclopentadienyl, indenyl, cycloheptatrienyl, cycloheptatriene, and cyclooctatetraene.¹ Su, in a theoretical paper describing the nature of several of these reactions, suggested that one could explore these reactions (metallotropic shifts) more deeply and in entirely new ways by using new organic π ligands.² We suggest that the phenalenylyl ring system (**1**) is an excellent choice for this purpose



because (1) it possesses high symmetry (D_{3h}); (2) both σ - and π -bonded metal complexes are possible;³ and (3) for a given derivative, several metal shifts, some of which are unique here, are possible. Consider, for example, the σ complex 1-trimethylsilylphenalene (**2a**). Here there are possibly three nonequivalent 1,3-silicon shifts, to C-3, -9, and -13,⁴ and two nonequivalent 1,2 shifts, to C-2 and -11. We wish to report our results pertaining to the thermally and photochemically induced sigmatropic shifts of silicon on **2**.

Silane **2a**,⁵ which was prepared by the reaction of the phenalenylyl anion with trimethylsilyl chloride, in C_6D_6 is non-fluxional on the NMR time scale at temperatures up to 185 °C,⁶ with studies at high temperatures being precluded by