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Electron-Transfer Quenching vs. Exciplex-Mediated Quenching of the Low-Lying Excited States in Phthalocyanines

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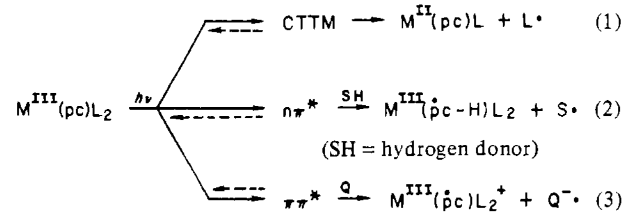
Oxidative electron-transfer quenching of the lowest ligand-centered $^3\pi\pi^*$ of Ru(pc)L_2, L = dmf or py, by a series of nitroaromatic compounds, viologen salts, and metal complexes has been investigated by laser and conventional flash photolysis. The quenching rate constants, treated according to Marcus–Hush and Rehm–Weller equations, gave self-exchange rate constants, $k_{\text{exch}} \sim 10^7$ M^{-1} s^{-1}, for the electron exchange between the $^3\pi\pi^*$ and the ruthenium(II) ligand radical. The excited states of a number of phthalocyanines, e.g. Ru(pc)$(Me_2SO)_2$, Ru(pc)(dmf)CO, Ru(pc)(py)CO, and Rh(pc)(CH_3OH)Cl, undergo quenching mediated by exciplex formation. The formation of exciplexes is discussed in terms of the related exciplexes of the porphyrins.

Introduction

The photochemistry of transition-metal phthalocyanines has recently received considerable attention.[1-9] Such a photochemistry is associated with the population of various excited states, namely charge transfer or $n\pi^*$ ligand-centered states, in the ultraviolet irradiation of monomeric phthalocyanines.[1,2,4-6]

These excited states can induce characteristic chemical transformations as is indicated in eq 1 and 2. The population of acido to metal charge-transfer states in cobalt(III) phthalocyanines, eq 1, induces the oxidation of axially coordinated ligands.[2] In addition, hydrogen abstraction from the solvent, eq 2, is a very common process in the ultraviolet photochemistry of the phthalocyanines, namely for excitations at wavelengths of the Soret band and below that band.[1-6]



(SH = hydrogen donor)

(Q = electron acceptor)

The low-lying $\pi\pi^*$ ligand-centered states that are populated by excitations in the red region, e.g. Q band, do not exhibit the kind of photoreactivity that is described above (eq 1, 2). However, these states experience oxidative quenching with appropriate electron acceptors (eq 3).[7-9] Previous results show that these quenching processes are outer-sphere electron-transfer reactions, which can be theoretically described by Marcus and Hush theoretical treatments.[9-11] This conclusion on the quenching of the low-lying $^3\pi\pi^*$ in ruthenium(II) phthalocyanines has been reinforced in this work. However, the departure of such outer-sphere electron-transfer quenching, namely in instances where the quenching is mediated by exciplex formation, is also reported and compared with similar processes in porphyrins.[12-15]

Experimental Section

Photochemical Procedures. The laser flash photolysis and conventional flash photolysis apparatus used in this work were described elsewhere.[4-16] A Quanta Ray neodymium yag pumped dye laser with a DCM dye for 640-nm excitations forms part of our laser flash setup. Transients were monitored with a focused 500-W xenon lamp pulsed to around 10^4 times the steady-state intensity. The data points were stored and digitized in a Tektronix R7912 transient digitizer and processed in a PDP-11 digital computer. The power of the laser was adjusted to values where neither the ground-state depletion nor biphotonic processes were detected. The duration of the laser pulse limits the time resolution to times longer than 5 ns. Conventional flash photolysis experiments were carried out by firing two xenon flash lamps, Xenon Corp. FP8-100C, at energies between 250 and 50 J/pulse. The time resolution of the conventional flash photolysis setup was limited to 30 μs.

The solutions for the photochemical experiments were deaerated with streams of Ar, and they were refreshed after each irradiation.

Materials. Ru(pc)$(py)_2$, Ru(pc)$(dmf)_2$, Ru(pc)$(Me_2SO)_2$, Ru(pc)(dmf)CO, and Ru(pc)(py)CO were prepared and purified according to reported procedures.[17] Rh(pc)(CH_3OH)Cl was available from a previous work.[5] The commercially available nitroaromatic derivatives were purified by recrystallization. The viologen salts were prepared by following literature procedures.[18] The various compounds were recrystallized as hexafluorophosphate salts.

Acetonitrile and dichloromethane, Aldrich Gold Label, were distilled in an all-glass distillation apparatus fitted with a 40-theoretical-plate fractionating column.

Results and Discussion

Previous studies on the quenching of the low-lying $^3\pi\pi^*$ excited state of various phthalocyanines reveal that this state acts as a reducing agent.[7-9] This behavior was also exhibited by $(^3\pi\pi^*)$Ru(pc)$(py)_2$ and $(^3\pi\pi^*)$Ru(pc)$(dmf)_2$ when they were quenched by nitroaromatic compounds and paraquat derivatives; see below.

This flash excitation of Ru(pc)$(dmf)_2$ at wavelengths of the Q band, namely $\lambda_{\text{excit}} \simeq 640$ nm, produces a transient spectrum with $\lambda_{\max} \simeq 500$ nm and a lifetime $\tau \simeq 165$ ns (Figure 1). Such a transient spectrum can be easily assigned to the lowest $^3\pi\pi^*$ by comparison with spectra reported for $^3\pi\pi^*$ excited states of phthalocyanines.[3-9] The quenching of the excited state by nitroaromatic compounds or paraquat derivatives produces the oxidized ligand radical Ru$(\dot{p}c)(dmf)_2^+$. Rate constants for the quenching reaction were obtained from the dependence

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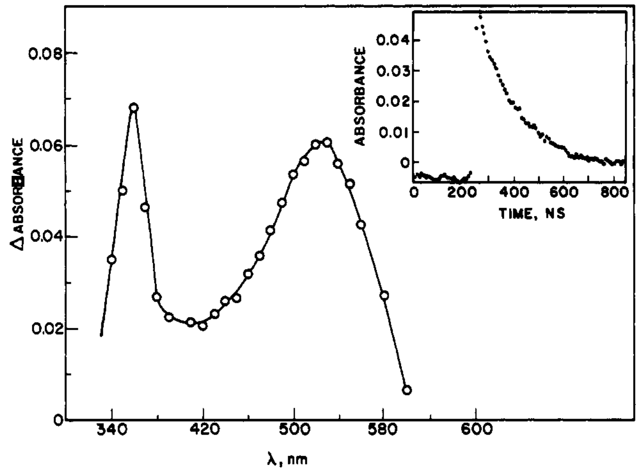

Figure 1. Difference spectrum of $(^3\pi\pi^*)Ru(pc)(dmf)_2$ obtained in laser flash photolysis of $Ru(pc)(dmf)_2$ in deaerated acetonitrile after the 640-nm irradiation. The inset shows a typical trace, λ_{ob} = 500 nm, with a 200-ns pretriggering delay.

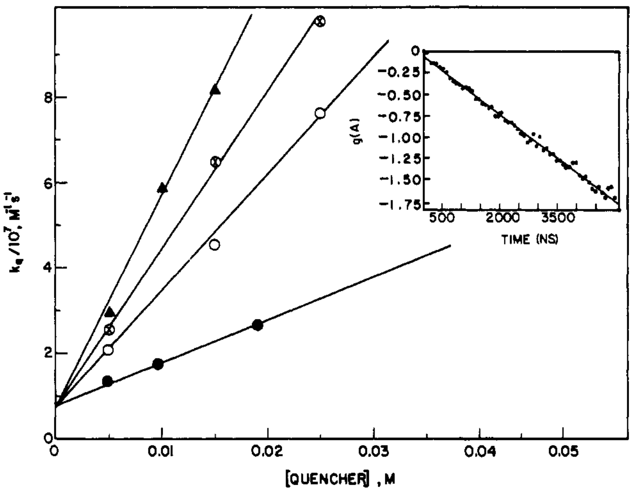

Figure 2. Typical dependence of the overall rate constant k_q on the quencher concentration of the quenching of $(^3\pi\pi^*)Ru(pc)(dmf)_2$ by (Δ) *p*-dinitrobenzene, (⊗) 4,4′-dimethyl-1,1′-diethyl-2,2′-bipyridinium (diaquat), (○) 1,1′-dimethyl-4,4′-bipyridinium (paraquat), and (●) ruthenium hexaammine chloride. The inset shows a characteristic first-order treatment (solid line) of an average of seven traces; dots represent the average data and $g(A) = \ln [(A_t - A_\infty)/(A_0 - A_\infty)]$.

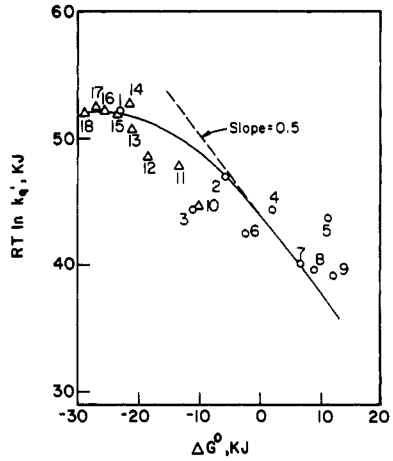

Figure 3. Dependence of the free energy of activation, $RT \ln k_q$, on the standard free energy, ΔG°, for the quenching of $(^3\pi\pi^*)Ru(pc)(dmf)_2$ by (1) *p*-dinitrobenzene, (2) *p*-nitrobenzaldehyde, (3) *o*-dinitrobenzene, (4) methyl *p*-nitrobenzoate, (5) methyl *m*-nitrobenzoate, (6) *m*-dinitrobenzene, (7) *o*-nitrobenzaldehyde, (8) *m*-nitrobenzaldehyde, (9) 1-iodo-4-nitrobenzene, (10) 1,1′-dimethyl-2,2′-bipyridinium, (11) 1,1′-dibutyl-2,2′-bipyridinium, (12) 1,1′-dipropyl-2,2′-bipyridinium, (13) 1,1′-ethylene-4,4′-dimethyl-2,2′-bipyridinium, (14) 4,4′-dimethyl-1,1′-diethyl-2,2′-bipyridinium, (15) 1,1′-dimethyl-4,4′-bipyridinium, (16) 1,1′-bis(hydroxyethyl)-4,4′-bipyridinium, (17) 1,1′-diethyl-2,2′-bipyridinium, and (18) 1,1′-dibenzoyl-4,4′-bipyridinium.

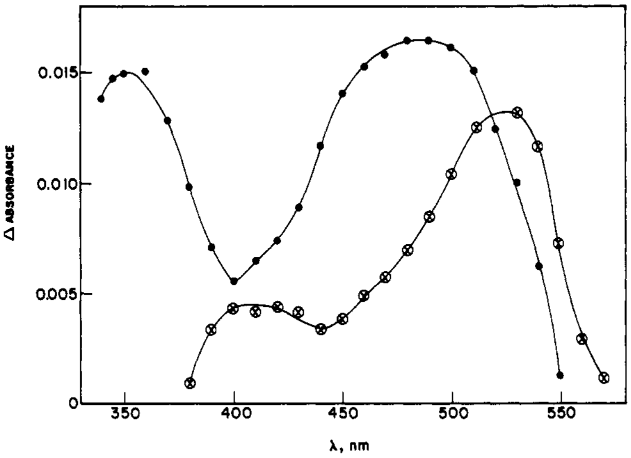

Figure 4. Comparison between the difference spectra of the $(^3\pi\pi^*)Ru(pc)(Me_2SO)_2$ (○) and the exciplex generated when this excited state is quenched by 0.1 M *p*-dinitrobenzene (⊗) (laser excitations at 640 nm and observations at 5 μs after the irradiation).

Table II. Self-Exchange Rate Constants for the Lowest Lying $^3\pi\pi^*$ in Ruthenium(II) Phthalocyanines

electron donor	electron acceptor[a]	k_{exch}, $M^{-1}\ s^{-1}$	medium
$(^3\pi\pi^*)Ru(pc)(py)_2$	Fe^{3+}	5.9×10^6	CH_3CN-H_2O (70:30)
	nitroaromatic quenchers[b]	1.9×10^7	CH_3CN
	paraquat derivatives[b]	8.1×10^6	CH_3CN
$(^3\pi\pi^*)Ru(pc)(dmf)_2$	paraquat derivatives[b]	1.9×10^7	CH_3CN
	nitroaromatic quenchers[b]	8.1×10^6	CH_3CN

[a] Electron acceptor(s) used for the determination of the self-exchange rate constant. [b] For a list of the quenchers see Figure 3.

of the overall rate constant on the quencher concentration (Figure 2). Such rate constants for redox quenching (Table I)[19] were analyzed according to treatments described by Marcus[10] and Hush[11] in order to obtain the self-exchange rate constants.[20] The application of these models to our results was limited to those rate constants that were far from the limiting values for highly exothermic redox processes (Figure

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(19) Supplementary material.

(20) Details of the mathematical treatment followed for the derivation of the self-exchange rate constants were reported elsewhere.[9] Self-exchange rate constants were obtained from the equation for the rate constant of the cross-reaction $k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$, where k_{11} and k_{22} are the self-exchange rate constants and k_{12} and k_{12} are the rate constant and equilibrium constant for the cross-reaction, respectively, and $\ln f = (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)]$[21] The values of K_{12} were obtained from the corresponding redox potentials of the quencher and $(^3\pi\pi^*)Ru(pc)L_2$.

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Table III. Overall Rate Constants for the Disappearance of Phthalocyanine Exciplexes

complex	quencher	k,[a] s^{-1}
$Ru(pc)(Me_2SO)_2$		2.40×10^6 [b]
$Ru(pc)(Me_2SO)_2$	*p*-dinitrobenzene	5.3×10^5
$Ru(pc)(Me_2SO)_2$	paraquat	5.5×10^5
$Ru(pc)(Me_2SO)_2$	diaquat	5.7×10^5
Ru(pc)(dmf)CO		2.31×10^6 [b]
Ru(pc)(dmf)CO	*p*-dinitrobenzene	1.27×10^6
Ru(pc)(py)CO		2.37×10^6 [b]
Ru(pc)(py)CO	*p*-dinitrobenzene	1.30×10^6
$Rh(pc)(CH_3OH)Cl$		3.1×10^6 [b]
$Rh(pc)(CH_3OH)Cl$	*p*-dinitrobenzene	2.6×10^6

[a] Rate constants determined at room temperature in acetonitrile.
[b] Rate constants for the $^3\pi\pi^*$ relaxation.

3). The self-exchange rate constants for the lowest $^3\pi\pi^*$ of the ruthenium(II) complexes (eq 4) are reported in Table II.

$$(^3\pi\pi^*)\mathrm{Ru(pc)L_2} + \mathrm{Ru}(\dot{p}\mathrm{c})\mathrm{L_2}^+ \rightarrow \mathrm{Ru}(\dot{p}\mathrm{c})\mathrm{L_2}^+ + (^3\pi\pi^*)\mathrm{Ru(pc)L_2} \quad (4)$$

$$\mathrm{L} = \mathrm{py,\ dmf}$$

The results in Table II are in agreement with a value of the self-exchange rate constant reported in a previous work.[9] Therefore, it is possible that the value of the self-exchange rate constant must be $k_{\mathrm{exch}} \sim 10^7\ M^{-1}\ s^{-1}$ for all ruthenium(II) phthalocyanines.

The redox behavior of $(^3\pi\pi^*)Ru(pc)L_2$, L = py or dmf, contrasts with that of the excited state of $Ru(pc)(Me_2SO)_2$, $Rh(pc)(CH_3OH)Cl$, Ru(pc)(py)CO, and Ru(pc)(dmf)CO. Laser flash irradiations of the carboxyl and Me_2SO complexes at wavelengths of the Q band produces the transient low-lying $^3\pi\pi^*$ (Figure 4). However, quenching of these excited states by various aromatic quenchers does not induce the electron-transfer process that is described above (eq 4); both nitroaromatic and poly(pyridine) quenchers produce new species whose absorption spectra are considerably red shifted with respect to the low-lying $^3\pi\pi^*$ (Figure 4). These species, which are longer lived than the $^3\pi\pi^*$ (Table III), can be assigned as exciplexes formed when the $^3\pi\pi^*$ react with aromatic quenchers. Since the lowest excited state of the quencher has a larger energy than the lowest excited states of the phthalocyanines, it is unlikely that the dissociation of the exciplex produces an excited state of the quencher. Moreover, the disappearance of the exciplex by a first-order process does not form the products expected from a redox dissociation, and it regenerates the phthalocyanine complex (eq 5).

$$(^3\pi\pi^*)\mathrm{Ru(pc)L_2} + \mathrm{Q} \rightleftarrows [\mathrm{Ru(pc)L_2{-}Q}]^* \rightarrow \mathrm{Ru(pc)L_2} + \mathrm{Q} \quad (5)$$

The formation of exciplexes with ruthenium(II) phthalocyanines is in agreement with the behavior exhibited by chlorophyll and some metalloporphyrins when their low-lying excited states are quenched by aromatic compounds.[12-15] If similar interactions were to stabilize these exciplexes, the charge-transfer interactions must play a limited role in such stabilization. However, these interactions must be sufficiently strong in order to induce the observed differences between the spectra of the exciplex and the $^3\pi\pi^*$ of the ruthenium(II) phthalocyanines. In this regard, it seems that the best description of the exciplex structure involves the mixing of the electronic densities of the phthalocyanine and the quencher in loosely overlapped molecular orbitals.

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Registry No. $Ru(pc)(py)_2$, 67588-46-9; $Ru(pc)(dmf)_2$, 74594-37-9; $Ru(pc)(Me_2SO)_2$, 74594-33-5; Ru(pc)(dmf)CO, 74594-32-4; Ru(pc)(py)CO, 67588-47-0; $Rh(pc)(CH_3OH)Cl$, 81725-25-9; Fe^{3+}, 20074-52-6; $Fe(CN)_6^{3-}$, 13408-62-3; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Co(NH_3)_5OH_2^{3+}$, 14403-82-8; $Co(NH_3)_6^{3+}$, 14695-95-5; *N,N*-dimethyl-*p*-nitrosoaniline, 138-89-6; *p*-dinitrobenzene, 100-25-4; *o*-dinitrobenzene, 528-29-0; *p*-nitrobenzaldehyde, 555-16-8; *m*-dinitrobenzene, 99-65-0; methyl *p*-nitrobenzoate, 619-50-1; *o*-nitrobenzaldehyde, 552-89-6; *m*-nitrobenzaldehyde, 99-61-6; methyl *m*-nitrobenzoate, 618-95-1; 1-iodo-4-nitrobenzene, 636-98-6; 1,1′-dibenzoyl-4,4′-bipyridinium, 83993-48-0; 1,1′-diethyl-2,2′-bipyridinium, 85294-11-7; 1,1′-bis(2-hydroxyethyl)-4,4′-bipyridinium, 33944-70-6; 1,1′-dimethyl-4,4′-bipyridinium, 4685-14-7; 4,4′-dimethyl-1,1′-diethyl-2,2′-bipyridinium, 85294-12-8; 1,1′-ethylene-4,4′-dimethyl-2,2′-bipyridinium, 16651-71-1; 1,1′-dipropyl-2,2′-bipyridinium, 85294-13-9; 1,1′-dibutyl-2,2′-bipyridinium, 85294-14-0; 1,1′-dimethyl-2,2′-bipyridinium, 41491-80-9.

Supplementary Material Available: Table I, electron-transfer quenching rate constants for $(^3\pi\pi^*)Ru(pc)(py)_2$ and $(^3\pi\pi^*)Ru(pc)(dmf)_2$ (2 pages). Ordering information is given on any current masthead page.

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