

Photochemical Formation of Ruthenium Phthalocyanine π -Cation Radical Species

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Abstract

Upon Q-band excitation (irradiation wavelength > 580 nm) ruthenium(II) phthalocyanine complexes can be quantitatively photooxidized to stable π -cation radical species. The photooxidation can be carried out at either room temperature using CH_2Cl_2 solutions containing CBr_4 as an 'irreversible' electron acceptor, or in low-temperature (79 K) 2-methyltetrahydrofuran solutions containing 2,3-dichloro-5,6-dicyanobenzoquinone as a 'reversible' acceptor. Absorption and magnetic circular dichroism (MCD) spectra indicate that there are two major, resolved transitions in the visible region, one at 510 nm and the other at 700 nm. The MCD spectra of the transition at 510 nm shows that it is non-degenerate, while the transition at 700 nm is seen to be degenerate in the case of photooxidized $\text{Ru(II)Pc}(-2)(\text{CO})\text{DMF}$ at room temperature.

Introduction

The photochemical properties of transition-metal phthalocyanines have been the subject of many investigations in recent years [1, 2]. Much of this interest is due to the prospect of the use of such macrocyclic ring compounds in photocatalytic processes. The pathway followed by photochemical reactions of phthalocyanines depends on the specific excited state involved [3–5]. It has been found [4, 5] that the lowest-lying triplet excited state of ruthenium(II) phthalocyanine, populated by excitation into the Q band (where the wavelength > 500 nm), can be quenched by electron transfer to a number of electron acceptors. The lowest energy, ligand-centered, triplet excited states of a number of ruthenium(II) phthalocyanine complexes, $\text{Ru(II)Pc}(-2)(\text{LL}')$, where L and L' are axially-coordinated species, can also undergo quenching by exciplex formation with no evidence of a redox dissociation of the exciplex [5]. The outer-sphere, electron-transfer quenching route has to date yielded the expected products from the redox reaction for a

number of metallophthalocyanines, but these species were very short-lived because there was an efficient back reaction [6–8]. The one-electron photooxidation reaction of $\text{Ru(II)Pc}(-2)(\text{LL}')$ species is expected to be centered on the phthalocyanine ring rather than on the metal, yielding an interesting class of complexes of the type of $[\text{Ru(II)Pc}(-1)(\text{LL}')]^+*$, which involve a bivalent transition metal and a phthalocyanine π -cation radical. It is expected that the highest occupied molecular orbital would be of $^2\text{A}_{1u}$ symmetry. For such complexes charge transfer interactions between the metal, the axial ligand and the ring can be anticipated. MCD spectroscopy [9, 10] can be used to obtain additional assignment criteria, in particular, it can be used to reveal the polarization of the electronic transitions in these complexes.

We report in this paper that a number of ruthenium phthalocyanine complexes undergo clean, one-electron, photooxidation reactions with appropriate electron acceptors, to form the corresponding, stable π -cation radical species in liquid solution at room temperature. In addition, we demonstrate conditions for long-range electron transfer from the excited ruthenium phthalocyanine to a 'reversible' electron acceptor; this results in the production of similar radicals in low temperature glassy solutions.

Experimental

The ruthenium phthalocyanine complexes were prepared by literature methods [11]. Dichloromethane (Fisher) and 2-methyltetrahydrofuran (MTHF, Sigma) were freshly distilled under nitrogen. CBr_4 (Kodak) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, Kodak) were recrystallised before use.

The ruthenium phthalocyanines were dissolved in nitrogen-purged solvents to which an appropriate electron acceptor was added. Published molar extinction coefficients [11] were used to determine the concentrations of the phthalocyanines in solution as follows: $\text{Ru(II)Pc}(-2)(\text{py})_2$, $\lambda = 622$ nm, $\epsilon = 74\,000$; $\text{Ru(II)Pc}(-2)(4\text{-methylpyridine})\text{CO}$, $\lambda = 640$ nm, $\epsilon = 152\,000$; $\text{Ru(II)Pc}(-2)(\text{DMF})\text{CO}$, $\lambda = 638$

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nm, $\epsilon = 120\,000$; $\text{Ru(II)Pc(-2)(DMSO)}_2$, $\lambda = 637$ nm, $\epsilon = 88\,000$. Absorption spectra were obtained with a Cary Model 219 spectrophotometer. For the low-temperature measurements an Oxford Instruments (U.K.) CF204 flow cryostat was used. The MCD spectra were obtained at room temperature with a Jasco J-500C spectropolarimeter controlled by an IBM Instruments S9001 computer using the program CDSCAN5 (R. Kitchenham and M. J. Stillman, unpublished), with a field of 5.5 T from an Oxford Instruments SM2 superconducting magnet. All data were digitized as recorded and the spectra presented here are redrawn plots of the original data.

The phthalocyanine solutions were irradiated with light from a 300 W tungsten-halogen projector lamp and excitation solely in the Q band was ensured by the use of a Corning CS 2-73 high energy (580 nm) cut-off filter.

Results and Discussion

Both chemical and electrochemical oxidation techniques are well-established as routes to the production of the π -cation radical species of porphyrins and phthalocyanines. However, photochemical oxidation with low energy light (of visible region energies) has only recently been utilized successfully [12–14] to form the π -cation radical species of porphyrins as stable products in high yield in room temperature solutions. The oxidative quenching of the phthalocyanine's excited states to yield the π -cation species, especially for those complexes involving a transition metal, seemed to be generally a much more difficult task. This is because only the lowest energy excited triplet states with the energy of the order of 1.1 to 1.3 eV have been found to undergo the one-electron oxidation reaction [4, 5], whereas, by comparison, both the excited triplet and singlet states of porphyrins with energies from 1.4 to 2.3 eV can be utilized in such a reaction.

We have found that when deoxygenated solutions of $\text{Ru(II)Pc(-2)(4-methylpyridine)CO}$, in CH_2Cl_2 containing CBr_4 (0.02 mol l^{-1}), were irradiated with light of wavelengths longer than 580 nm that photo-oxidation of the parent compound to the π -cation radical species, $[\text{Ru(II)Pc(-1)(4-methyl pyridine)CO}]^{+\bullet}$ occurred, as in Fig. 1. The sharp, isobestically-related changes in the optical absorption spectra that accompanied the photolyses clearly showed that only a single product was formed. Exhaustive photolysis results in a UV-Vis spectrum which is identical to that obtained by electrochemical or chemical (using Br_2) one-electron oxidation of the phthalocyanine [11].

The photochemical ligand exchange reaction which is well known for a number of phthalocyanines

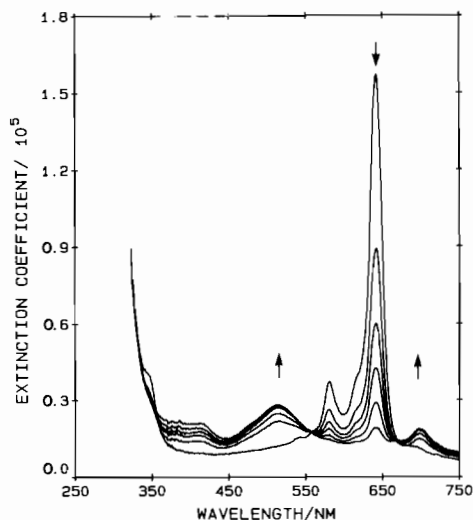


Fig. 1. Optical absorption spectrum changes during photolysis of $\text{Ru(II)Pc(-2)(4-methylpyridine)CO}$ in CH_2Cl_2 containing 0.02 mol l^{-1} of CBr_4 . The irradiation time was 0, 4, 7, 11, 16 and 25 min with the lamp in an arbitrary position relative to the sample. Light with wavelength > 580 nm was used for the irradiation. Extinction coefficient (ϵ) has units $\text{L mol}^{-1} \text{ cm}^{-1}$.

can be excluded since only radiation < 400 nm is effective in this type of reaction. We have carried out such reactions for Ru(II)Pc(-2)(L)CO in which the CO is removed by photolysis at 400 nm; the spectral characteristics observed for these reactions are quite different to those reported in this paper for the photolysis in the presence of the electron acceptor.

The photooxidation reaction demonstrated in Fig. 1 is general for several ruthenium phthalocyanine complexes and a number of different π -cation radical species of the form $[\text{Ru(II)Pc(-1)(LL')}]^{+\bullet}$, where $L = \text{CO, DMF or DMSO}$, can be produced in liquid solution.

The origins of the electronic transitions observed in the π -cation radical spectra of phthalocyanines have not been unambiguously identified to date unlike the transitions in the parent phthalocyanines. Recent theoretical studies of Edwards and Zerner [15], and Minor *et al.* [16] present the first attempts to rationalise spectral patterns for a number of the π -cation radical species of porphyrins and phthalocyanines, respectively. Figures 2 and 3 show the optical absorption and MCD spectra of $\text{Ru(II)Pc(-2)(DMF)CO}$ and its photooxidation product, and $\text{Ru(II)Pc(-2)(DMSO)}_2$ and its photooxidation product, respectively.

There are three main bands in the visible region of the spectra of $\text{RuPc}^{+\bullet}$ species at 710, 510 and around 400 nm. These bands are characteristic for the phthalocyanine π -cation radicals, $[\text{M(II)Pc(-1)}]^{+\bullet}$. The 710 nm and 400 nm bands have been

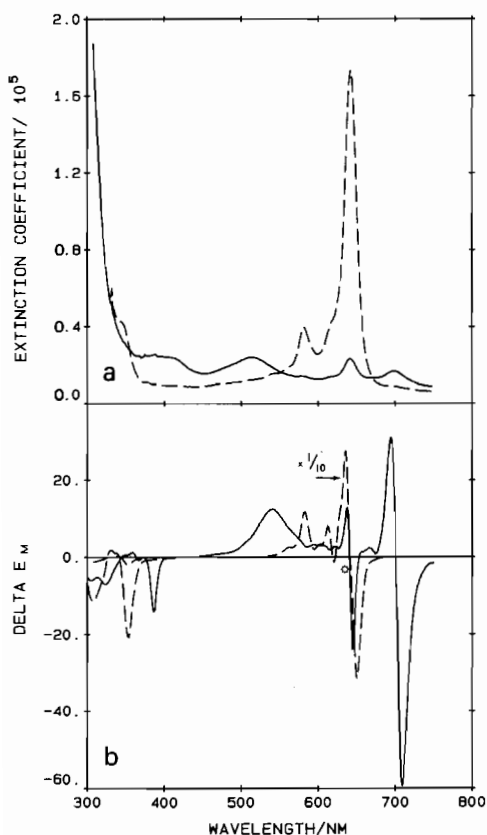


Fig. 2. Optical absorption (a) and MCD (b) spectra of Ru(II)-Pc(-2)(DMF)CO (broken line) in CH_2Cl_2 containing 0.02 mol l^{-1} of CBr_4 and the photolytic product (solid line) formed from this phthalocyanine. The solution photolysis was carried out under the same conditions as in Fig. 1. Extinction coefficient (ϵ) in (a) and $\Delta\epsilon_M$ in (b) have units $1 \text{ mol}^{-1} \text{ cm}^{-1}$ and $1 \text{ mol}^{-1} \text{ cm}^{-1} \text{ T}^{-1}$, respectively. A contributing, residual MCD signal from unreacted phthalocyanine ($\sim 1\%$) is marked by an asterisk.

associated by Minor *et al.* [16] with the electronic transitions $1e_g(\pi) \rightarrow 1a_{1u}(\pi)$ and $2e_g(\pi) \rightarrow 1a_{1u}(\pi)$, respectively, where the state transitions are ${}^2E_g \leftarrow {}^2A_{1u}$, while they assign the 510 nm band as the $\pi \rightarrow \pi^*$ Q band.

The MCD spectra shown in Figs. 2 and 3 for the ruthenium phthalocyanine radical species, clearly indicate that the main new band that is observed near 510 nm has B term character which signifies that the transition is non-degenerate; this is the case in the spectra of all the oxidized Pc complexes that we have studied. The band seen near 710 nm in Fig. 2 exhibits the characteristic of an MCD A term, a derivative-shaped band, indicating that the transition is of degenerate nature. The proposed assignments by Minor *et al.* [16] do not include any radical cation species of RuPc, however, we have measured quite similar characteristics in the MCD spectra of $[\text{Zn-Pc}(-1)]^{+\bullet}$ (T. Nyokong *et al.*, unpublished data) and consider that the $[\text{RuPc}]^{+\bullet}$ data are not atypical

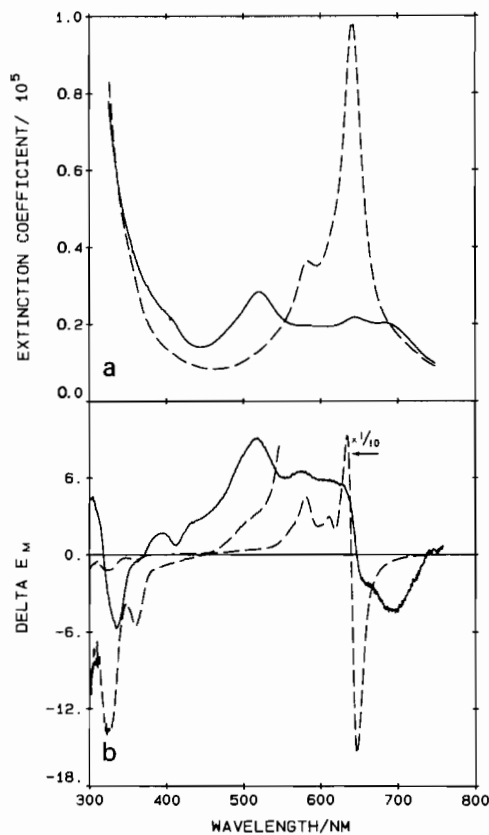


Fig. 3. Optical absorption (a) and MCD (b) spectra of Ru(II)-Pc(-2)(DMSO) $_2$ (broken line) in CH_2Cl_2 containing 0.02 mol l^{-1} of CBr_4 and the photolytic product (solid line) formed from this phthalocyanine. The solution photolysis was carried out under the same conditions as in Fig. 1. Extinction coefficient (ϵ) in (a) and $\Delta\epsilon_M$ in (b) have units $1 \text{ mol}^{-1} \text{ cm}^{-1}$ and $1 \text{ mol}^{-1} \text{ cm}^{-1} \text{ T}^{-1}$, respectively.

of the data for other metallophthalocyanine cation radical species. As both the one-electron transition assignments are based on a degenerate transition, we would not expect to observe such an intense B term if the 510 nm band had such an origin (ground-state degeneracies were also ruled out through the measurements of the MCD spectra for the $[\text{Zn(II)Pc}(-1)]^{+\bullet}$ π -cation radical species). The assignment by Minor *et al.* [16] of the 700 nm band as ${}^2E_g \leftarrow {}^2A_{1u}$ ($\pi-\pi$) is consistent with our data. We would expect that the spectrum of the ruthenium phthalocyanine radical species should also contain a contribution from metal to ligand charge transfer transitions; at present we are unable to assign the specific features observed below 510 nm to one of either ring-based or charge transfer origins.

Photochemical oxidation of ruthenium phthalocyanine complexes was also investigated in rigid glassy solutions at 79 K using polyhalogenated alkane and quinone acceptors. Figure 4 shows the changes in the optical absorption spectrum observed in the visible, Q band region during the photolysis

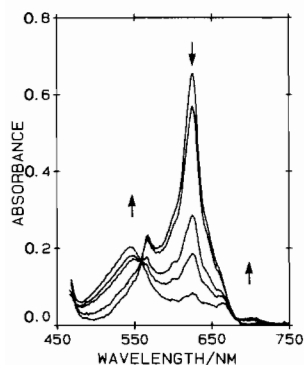
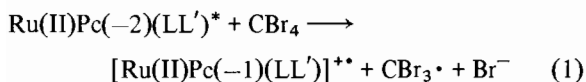


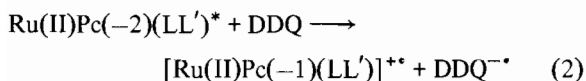
Fig. 4. Optical absorption spectrum changes during photolysis of Ru(II)Pc(-2)(py)₂ in MTHF containing 0.05 mol l⁻¹ of DDQ at 79 K. The irradiation time was 0, 1, 4, 7 and 12 min with the lamp in an arbitrary position relative to the sample cell. Light with wavelength > 580 nm was used for the irradiation.

of Ru(II)Pc(-2)(pyridine)₂ in the presence of 0.05 mol l⁻¹ of 2,3-dichloro-5,6-dicyanobenzoquinone in 2-methyl tetrahydrofuran at 79 K. The changes in the absorption spectrum during photolysis are consistent with the conversion of Ru(II)Pc(-2)(pyridine)₂ into the corresponding π -cation radical species, [Ru(II)Pc(-1)(pyridine)₂]^{•+}. Most of the parent compound can be recovered by careful warming of the photolysed sample to about 95 K, *i.e.*, about 30 K below the softening point of the solvent.

The experimental results can be explained using the following scheme for the reaction in liquid solution:



and for the reaction in the low temperature glassy solution:



where Ru(II)Pc(-2)(LL')^{*} represents the phthalocyanine in the lowest triplet excited state.

The redox potential of the [Ru(II)Pc(-1)(LL')]^{•+}/Ru(II)Pc(-2)(LL')^{*} couple can be estimated at about $E_{1/2} = -0.5$ to -0.7 V *vs.* standard calomel electrode, using, as a basis for the estimation, the ground state redox potential of the ruthenium phthalocyanines, $E_{1/2} = 0.7$ to 0.9 V *vs.* standard calomel electrode [11], and the energy for the triplet excited state, $E_T = 1.35$ eV [17]. The triplet excited state behaves as a reductant with enough strength to reduce substrates such as CBr₄, $E_{1/2} = -0.3$ V *vs.* standard calomel electrode [18], and DDQ, $E_{1/2} = +0.5$ V *vs.* standard calomel electrode [19]. It should be noted that quenching of the excited state of the carbonyl and DMSO complexes

by various aromatic quenchers does not induce the electron transfer process, but instead involves transient exciplex formation followed by regeneration of the phthalocyanine complex [5].

The irreversible character of reaction (1) allows for the accumulation of the relatively stable phthalocyanine cation radical species in quantities equimolar to that of the parent compound. The formation of cation radicals of ruthenium phthalocyanines when irradiated in polyhalogenated alkane-containing solutions is consistent with the behaviour exhibited by some metalloporphyrins when their low-lying excited states are quenched by alkyl chlorides [12–14]. On the other hand, the stabilization of the radical ions in the reaction (2) occurs as a result of a suppression of the back reaction in the low temperature glassy solution [20]. The thermodynamic grounds for this hindrance rests on the low values of the thermodynamic potential change for the back reaction, which can be shown to be about -0.2 eV in comparison to about -1.2 eV for the forward reaction.

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