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Photosensitization reactions of neodymium, dysprosium and lutetium diphthalocyanine

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Abstract—Photolysis, using a visible radiation, of diphthalocyanine complexes of Nd^{III}, Dy^{III} and Lu^{III} ($[Pc(\text{-}2)Nd^{III}Pc(\text{-}2)]^-$, $[Pc(\text{-}2)Dy^{III}Pc(\text{-}2)]^-$ and $[Pc(\text{-}2)Lu^{III}Pc(\text{-}2)]^-$, respectively) in the presence of pentachlorophenol (PCP) or SO_2 results in the one-electron oxidation of the diphthalocyanine species to $Pc(\text{-}1)Nd^{III}Pc(\text{-}2)$, $Pc(\text{-}1)Dy^{III}Pc(\text{-}2)$ and $Pc(\text{-}2)Lu^{III}Pc(\text{-}2)$, respectively. The PCP is reductively dechlorinated to tetra- and trichlorophenols. The quantum yields for the photosensitization reactions are of the order 10^{-4}. © 1997 Elsevier Science Ltd

Keywords: lanthanide; diphthalocyanine; pentachlorophenol; photosensitization; sulfur dioxide; dechlorination.

Polychlorinated phenols are used widely as pesticides, germicides and fungicidal agents [1]. These complexes are common environmental pollutants because of their halogen content. Chlorophenols are readily susceptible to breakdown through biological processes, but the chlorinated impurities are generally more stable to degradation than the parent compounds [1,2]. The toxicity of chlorophenols and their resistance to biodegradation increase with the increase in halogenation [3], hence dechlorination of these complexes could be an alternative approach to reducing their toxicity.

There are several reports on the purification of water containing chlorophenols by UV photolysis [1,4,5]. The products of such irradiations have been found to be more toxic than the parent complexes [4]. Photosensitized dechlorination of chlorophenols has been suggested as an alternative method for the reduction of the toxicity of these complexes [5–8]. There have been reports on the oxidation or reduction of chlorophenols in the presence of photosensitizers [5,6,9]. Mainly dimeric products were formed by riboflavin-sensitized photooxidation of dichlorophenol [5], whereas reductive dechlorination of pentachlorophenol (PCP) was observed in the presence of carbazole photosensitizer [6].

Metallophthalocyanines [MPc, Pc(-2) = phthalocyanine dianion] are efficient catalysts for many reactions [10,11]. Tetrasulfonated phthalocyanine complexes of Fe and Mn (FeTsPc and MnTsPc, respectively) have been used as catalysts during hydrogen peroxide oxidation of trichlorophenol [12–14]. MPc complexes are also known to act as photosensitizers for many reactions [15–22]. Photosensitization reactions involving MPc complexes occur *via* electron transfer from or to the triplet excited state of these complexes. Although a number of metal diphthalocyanine (Pc_2M) have been synthesized and characterized, their use as photosensitizers has not received much attention. Photolysis of the lanthanide diphthalocyanine (Pc_2Ln) in acetonitrile/dichloromethane solvent mixture resulted in an electron transfer from the Pc_2Ln species to dichloromethane [23]. We have recently reported on the electron transfer from the photoexcited $^*Pc_2Sn^{IV}$ to SO_2 [17]. It is expected that $^3\pi$–π^* states are populated by irradiation of lanthanide diphthalocyanine complexes in the visible region as was observed for the Pc_2Sn complex [24,25].

The cationic and anionic Pc_2M complexes are generally described in terms of their colour. The green Pc_2Ln species has the formula $Pc(\text{-}2)Ln^{III}Pc(\text{-}1)$ and the blue species is the reduced form with the formula $[Pc(\text{-}2)Ln^{III}Pc(\text{-}2)]^-$ [26]. We report in this work on the use of the blue forms of the diphthalocyanine

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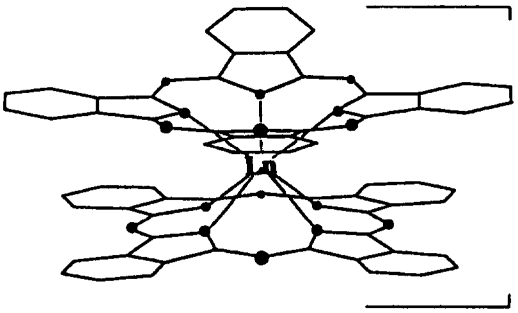
complexes of neodymium, dysprosium and lutetium, $[Pc_2Nd]^-$, $[Pc_2Dy]^-$ and $[Pc_2Lu]^-$, respectively (structure **1**), in the dechlorination of PCP.



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Electron-transfer reactions between SO_2 and MPc complexes could be useful in converting harmful sulfur complexes to their less harmful analogues. Recent reports have shown that photolysis of tin(IV) diphthalocyanine [Pc(-2)SnPc(-2)] complexes in the presence of SO_2 resulted in the oxidation of this species to $[Pc(-1)SnPc(-2)]^+$ [17]. We report in this work on the interaction of $[Pc_2Nd]^-$, $[Pc_2Dy]^-$ and $[Pc_2Lu]^-$, with sulfur dioxide and we compare these interaction with the interaction of these lanthanide diphthalocyanine species with pentachlorophenol.

EXPERIMENTAL

Materials

The blue forms of neodymium, dysprosium and lutetium diphthalocyanines were synthesized by reported procedures [27,28], by mixing 1 mol of the lanthanide acetate with 9 mols of 1,2 dicyanobenzene and heating the mixture in a crucible (with a lid) at 200°C for 3 h. The $[Pc_2In]^-$ complexes were purified as described before [28], by extraction of the complex with dimethylformamide (DMF), followed by chromatography on a silica column. Only fractions with a ratio of Soret to Q bands of less than 1.4 were retained. The samples gave satisfactory IR and UV–vis spectra. The cyclic voltammograms obtained for the $[Pc_2Ln]^-$ complexes were similar to those reported in the literature [26].

Pentachlorophenol (PCP, 99%) and 2,4,5-trichlorophenol (TCP, 99%) were purchased from Aldrich and used without further purification. Acetonitrile used for photolysis experiments was dried in phosphorous pentoxide and distilled before use. Dichloromethane and dimethylformamide (DMF) were freshly distilled. SO_2 gas was purchased from Messer Griesheim. Sulfur dioxide concentrations were determined by treatment with standardized iodine and titration with aqueous sodium thiosulphate.

Methods

Solutions to be photolysed were contained in a 1 cm pathlength UV–vis cell fitted with a stopper. Acetonitrile solutions of $[Pc_2Ln]^-$ contained in the cell were degassed, then known amounts of PCP dissolved in acetonitrile were added to the cell and the solution deoxygenated. For work involving SO_2 a solvent mixture consisting of DMF and dichloromethane was employed instead of acetonitrile. The electronic absorption spectra was recorded before photolysis and periodically during the photolysis with a 50 W tungsten lamp. Photolysis in the visible region was achieved by using a 590 nm filter to exclude the UV radiation. Extinction coefficients for $Pc(-2)Lu^{III}Pc(-1)$ [29], $Pc(-2)Dy^{III}Pc(-1)$ [29] and $Pc(-2)Nd^{III}Pc(-1)$ of $\varepsilon = 2\times10^5$, 1.8×10^5 and 2×10^5 $dm^3\ mol^{-1}\ cm^{-1}$, respectively, were used in estimating the concentration of these species in solution. Concentrations of the $[Pc_2Ln]^-$ species were in the range 2×10^{-6}–1×10^{-5} mol dm^{-3}, whereas concentrations of PCP were varied from 0.00004 to 0.0005 mol dm^{-3}. SO_2 concentrations ranged from 0.00003 to 0.05 mol dm^{-3}. The light intensity was determined, using Reinecke's salt actinometry [30] to be 1.1×10^{-8} einstein s^{-1}.

Products formed upon irradiation of the $[Pc_2Ln]^-$ species in the presence of PCP were also monitored with the HP 8310 gas chromatograph fitted with an electron capture detector and a Supelco SPB fused silica capillary column (15 m length, 0.53 mm inner diameter and 1.5 μm film thickness). The parameters for analysis were: carrier gas N_2 at 38.7 cm s^{-1}, injector temperature = 300°C, detector temperature = 280°C.

UV–vis absorption and IR (KBr disks) spectra were recorded with the Cary IE and Perkin–Elmer model 180 IR spectrophotometers, respectively.

RESULTS AND DISCUSSION

Interaction between lanthanide diphthalocyanines and pentachlorophenol

Electronic absorption spectra of phthalocyanines have been used successfully in characterizing the redox products of these species. Thus, absorption spectra was used in this work to characterize the lanthanide diphthalocyanine products formed following photosensitization reactions. The spectra of the Pc_2Ln species have been reported [31–41]. The blue form, $[Pc(-2)Ln^{III}Pc(-2)]^-$, shows a splitting in the Q band with an intense band observed near 600 nm and a weaker band near 700 nm [32]. The splitting of the Q band is due to the splitting of the molecular orbitals as a result of the coupling between the phthalocyanine rings in Pc_2M complexes. One-electron oxidation of the $[Pc(-2)Ln^{III}Pc(-2)]^-$ species gives the green species, $Pc(-2)Ln^{III}Pc(-1)$ and shows a strong absorption band near 670 nm and a weaker band due to the electronic

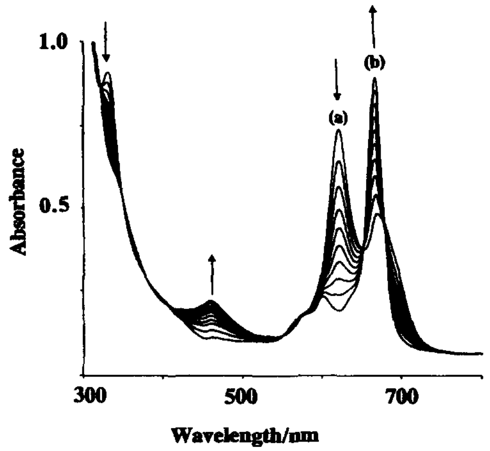

Fig. 1. Absorption spectral changes observed during the photolysis of $[Pc_2Dy]^-$ in CH_3CN containing pentachlorophenol. (a) Before and (b) at the end of photolysis. Starting $[Pc_2Dy]^-$ concentration = 5×10^{-6} mol dm^{-3} and [PCP] = 7×10^{-5} mol dm^{-3}.

transition into the semi-occupied molecular orbital (SOMO) near 470 nm [40]. One electron oxidation of the $Pc(-2)Ln^{III}Pc(-1)$ species results in the formation of the red $[Pc(-1)Ln^{III}Pc(-1)]^+$ species [28].

Figure 1 shows spectral changes observed on addition of solutions of PCP in acetonitrile to solutions of the $[Pc(-2)Dy^{III}Pc(-2)]^-$ species in the same solvent. The spectra observed before the addition of PCP is shown in Fig. 1(a). The spectra shown in Fig. 1(a) is typical [28] of the blue $[Pc(-2)Ln^{III}Pc(-2)]^-$ species and shows a relatively intense absorption band at 620 nm and a weaker band at 666 nm. When solutions containing $[Pc(-2)Dy^{III}Pc(-2)]^-$ and PCP were photolysed in the visible region, the 620 nm band decreased in intensity and the 666 nm band increased in intensity. The solution turned from blue to green. The new spectra is formed with isosbestic points at 347, 378, 548, 650 and 678 nm. The final spectra at the end of photolysis, Fig. 1(b), is typical of the spectra of the green $Pc(-2)Ln^{III}Pc(-1)$ species [28]. The weak absorption band formed after photolysis at 470 nm is due to the electronic transition into the SOMO energy level and is characteristic of the $Pc(-2)Ln^{III}Pc(-1)$ species. Thus, Fig. 1 gives spectroscopic evidence for the formation of $Pc(-2)Dy^{III}Pc(-1)$ following the photolysis of the $[Pc(-2)Dy^{III}Pc(-2)]^-$ species in the presence of PCP. Similar spectral changes were observed on addition of PCP to solutions of $[Pc(-2)Lu^{III}(-2)]^-$. The final green species could be reduced back to the blue $[Pc(-2)Dy^{III}Pc(-2)]^-$ by addition of chemical reductants such as sodium borohydride. The spectral changes shown in Fig. 1 were observed with or without excluding the UV light with the 590 nm filter. The spectral changes observed when PCP was added to solutions of $[Pc(-2)Nd^{III}Pc(-2)]^-$ were different from those shown in Fig. 1, in that the spectra due to the blue form decreased in intensity but only very minor changes occurred in the spectra of the green form.

The difference in the reactivity of $[Pc(-2)Nd^{III}Pc(-2)]^-$ towards PCP when compared with $[Pc(-2)Dy^{III}Pc(-2)]^-$ and $[Pc(-2)Lu^{III}Pc(-2)]^-$ may be explained in terms of the differences in the interactions between the π-electron systems of the phthalocyanine rings in these complexes. This interaction is stronger for metals with smaller radii. The higher the interaction between the rings, the lower the oxidation potential of the $[Pc_2Ln]^-$ [26]. Thus, $[Pc(-2)Lu^{III}Pc(-2)]^-$ is easier to oxidize than $[Pc(-2)Dy^{III}Pc(-2)]^-$, which in turn is easier to oxidize than $[Pc(-2)Nd^{III}Pc(-2)]^-$. The apparent low reactivity of the $[Pc(-2)Nd^{III}Pc(-2)]^-$ in the presence of PCP when compared with the other two $[Pc(-2)Ln^{III}Pc(-2)]^-$ complexes may thus be attributed to relative difficulty in oxidizing the $[Pc(-2)Nd^{III}Pc(-2)]^-$ complex.

PCP and other less chlorinated phenols show distinct absorption spectra in the UV region. Hence, absorption spectra have been successfully used in the analysis of PCP [1]. The absorption bands of PCP in CH_3CN are located at 291 and 302 nm. Spectral changes observed in the UV region following photolysis of a solution containing $[Pc_2Ln]^-$ species and PCP consisted of the reduction of the Soret band of the former at 330 nm and an increase in the intensity of the absorption band of PCP at 302 nm, Fig. 2. An increase in the PCP absorption spectral region was also observed when carbazole was employed as a photosensitizer for the dechlorination of PCP [6] and was assigned to the formation of tetrachlorophenols. It is thus quite likely that the increase in the absorption band at 302 nm, Fig. 2(b) following photolysis of solutions containing PCP and $[Pc(-2)Dy^{III}Pc(-2)]^-$ or $[Pc(-2)Lu^{III}Pc(-2)]^-$ is due to the formation of tetrachlorophenol following photoreduction of PCP.

Spectral changes observed on prolonged photolysis of solutions containing PCP and $[Pc_2Dy]^-$ resulted in the decrease of the 302 nm absorption band and the

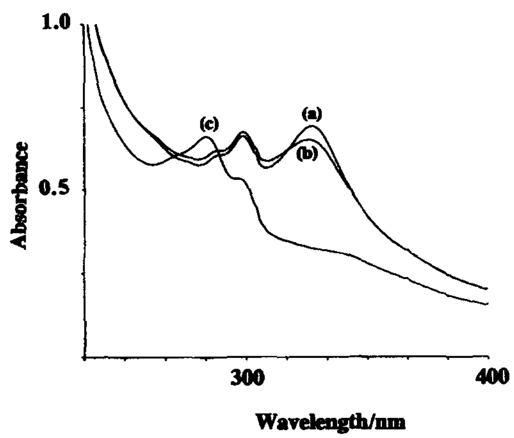

Fig. 2. Absorption spectral changes observed in the UV region during the photolysis of $[Pc_2Dy]^-$ in CH_3CN containing PCP. (a) Before photolysis, (b) after 3 h photolysis and (c) after 11 h photolysis. Same concentrations and conditions as in Fig. 1.

formation of a new band at 289 nm, Fig. 2(c). This absorption band is in the range of the absorption spectra of 2,4,5-trichlorophenol in acetonitrile. Thus, the final spectra in Fig. 2(c) is attributed to further dechlorination of the ring and the formation of trichlorophenols. The spectral changes shown in Fig. 2 were also observed for the prolonged photolysis of solutions containing $[Pc_2Lu]^-$ and PCP.

The spectral changes attributed to the dechlorination of PCP were not observed on photolysis of PCP in the absence of the Pc_2M complexes, hence confirming the involvement of the latter in the photochemical reaction. The spectral changes observed in Fig. 1 may thus be attributed to the electron transfer from the photoexcited $^*[Pc(\text{-}2)Dy^{III}Pc(\text{-}2)]^-$ species to PCP.

The photochemical reactions between PCP and $[Pc_2Ln]^-$ complexes were also followed with a gas chromatograph (GC) equipped with an electron capture detector, as explained in the experimental section. Figure 3 shows GC traces before and after irradiation of the solution containing $[Pc_2Ln]^-$ and PCP in acetonitrile. New peaks, at shorter retention times, were observed after photolysis. This observation is characteristic of the formation of chlorophenols containing fewer chlorine substituents [6] and is thus clear evidence for the dechlorination of PCP. Figures 3(b) and (c) show that the retention times of some of the products coincided with the retention time of trichlorophenol (TCP), giving evidence for the formation of the latter following photolysis. The presence of small amounts of chlorophenols with less chlorine substituents than PCP before photolysis, Fig. 3(a), is not surprising since commercial PCP is usually contaminated with tri- and tetrachlorophenols [1].

Kinetic data was collected by keeping the concentration of the $[Pc(\text{-}2)Dy^{III}Pc(\text{-}2)]^-$ or $[Pc(\text{-}2)Lu^{III}Pc(\text{-}2)]^-$ species constant at 5×10^{-6} mol dm^{-3} and varying the concentration of PCP, then photolysing the solutions. The formation of the green form was monitored spectrophotometrically at 666 nm. Plots of the logarithm of absorbance of the green Pc_2Ln species *vs* time were linear, showing a first-order dependence on the diphthalocyanine complexes. The slopes of these plots gave the observed rate constant, k_{obs} and plots of k_{obs} *vs* the concentration of PCP were also linear, Fig. 4(a), confirming a first-order dependence of the photolysis reaction on PCP.

Irradiation of metallophthalocyanine dimers, $(MPc)_2$, at wavelengths of the Q band produce the low-lying $^3\pi$–π^*, but irradiation in the Soret region generally induces photoredox reactions of the type [24]:

$$(M^{II}Pc)_2 \xrightarrow{h\nu} [M^{I}Pc(\text{-}2)]^- + [M^{III}Pc(\text{-}2)]^+ \quad (1)$$

OR

$$(M^{II}Pc)_2 \xrightarrow{h\nu} [M^{II}Pc(\text{-}3)]^- + [M^{II}Pc(\text{-}1)]^+ \quad (2)$$

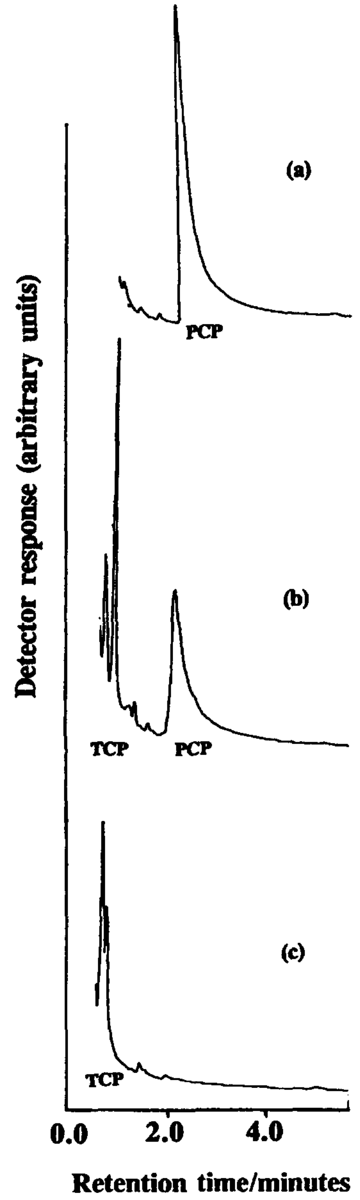

Fig. 3. Gas chromatograph traces for (a) before (0 hr) and (b) after (11 h) photolysis of solutions containing $[Pc_2Lu]^-$ and PCP in CH_3CN. (c) Corresponds to the GC trace for 2,4,5-trichlophenol. GC conditions are as set out in the experimental section. GC traces due to the acetonitrile solvent have been left out.

In comparison with the photosensitization reactions of Pc_2Sn [17], we suggest that the $(^3\pi$–$\pi^*)[Pc_2Ln]^-$ state is formed by excitation in the visible region and that this state may then be quenched by PCP or other electron donors or acceptors. Thus, the mechanism for the dechlorination of PCP may be represented by eqs (3)–(5). The first step is the excitation of the $[Pc_2Ln]^-$ species to the excited singlet state followed by intersystem crossing (isc) to the triplet state. The excited $(^3\pi$–$\pi^*)[Pc_2Ln]^-$ then transfers an electron to PCP with the formation of the $PCP^{-\cdot}$

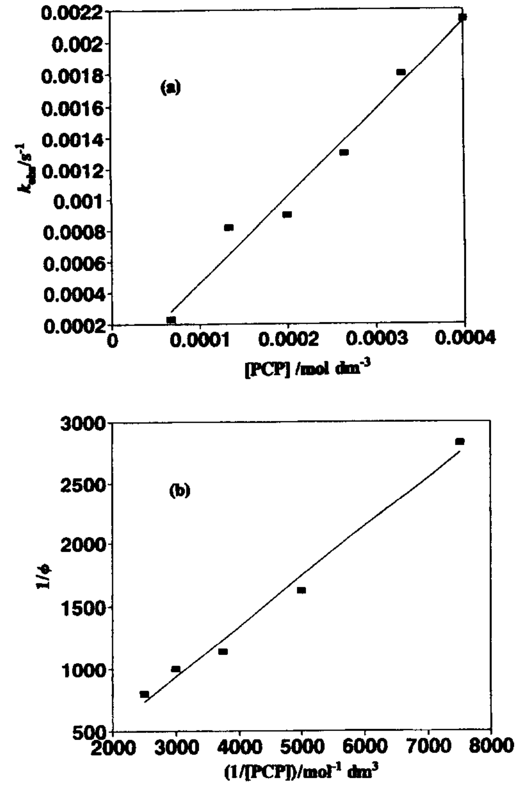

Fig. 4. (a) Plots of k_{obs} (s^{-1}) *vs* [PCP] (mol dm^{-3}) and (b) plots of the reciprocal of quantum yield *vs* the reciprocal of PCP concentration for the photooxidation of $[Pc_2Dy]^-$ in the presence of PCP. Concentration of $[Pc_2Dy]^- = 5 \times 10^{-6}$ mol dm^{-3}.

radical anion, which then abstracts hydrogen ions from the media, followed by dechlorination and the formation of tetra- and trichlorophenols.

$$[Pc_2Ln]^- \xrightarrow{h\nu} (^1\pi\text{–}\pi^*)[Pc_2Ln]^- \xrightarrow{isc} (^3\pi\text{–}\pi^*)[Pc_2Ln]^- \quad (3)$$

$$(^3\pi\text{–}\pi^*)[Pc_2Ln]^- + PCP \rightarrow Pc_2Ln + PCP^{-\cdot} \quad (4)$$

$$PCP^{-\cdot} \rightarrow \text{trichlorophenols and tetrachlorophenols} \quad (5)$$

Earlier work gave spectroscopic evidence for the formation of small quantities of monomeric $Sn^{IV}Pc$ species on photolysis of Pc_2Sn in the presence of SO_2 [17]. This was evidenced by the occurrence of a weak band to the low energy side of the spectra of the Pc_2Sn species. There was no evidence of formation of species other than the Pc_2Ln on photolysis of the $[Pc_2Ln]^-$ species in the presence of PCP. Monomeric lanthanide phthalocyanine have not been characterized.

The quantum yields for the reaction between the excited $(^3\pi\text{–}\pi^*)[Pc_2Ln]^-$ and PCP were determined and the inverse of quantum yields were plotted *vs* the inverse of PCP concentration. Fig. 4(b), linear Stern–Volmer plots were obtained showing that PCP does quench the excited $(^3\pi\text{–}\pi^*)[Pc_2Ln]^-$ species. The quantum yields obtained for the photosensitized dechlorination of PCP by $[Pc_2Dy]^-$ and $[Pc_2Lu]^-$ were 1.2×10^{-4} and 9.1×10^{-4}, respectively, for a PCP concentration of 4×10^{-4} mol dm^{-3}. The slightly higher quantum yield for the photolysis reactions involving the $[Pc_2Lu]^-$ complex may be explained in terms of the relative ease of oxidation of the $[Pc_2Ln]^-$ complexes. Although electrode potentials of the excited $^*[Pc_2Ln]^-$ may differ from the ground state reduction potentials, the relative magnitudes of these ground-state reduction potentials may give an approximation of the relative ease of oxidation of the excited states. The relatively higher quantum yields observed for the lutetium complex could be a result of the ease of oxidation of this complex as compared with the dysprosium complex [26]. Factors such as the relative lifetimes and quantum yields of the excited states of the Pc_2M species will also determine the reactivity of the excited states.

Interaction between lanthanide diphthalocyanine and sulfur dioxide

Figure 5 shows the spectral changes observed when solutions of SO_2 in DMF/CH_2Cl_2 were added to solutions of $[Pc(-2)Lu^{III}Pc(-2)]^-$. Similar spectral changes were observed for the photolysis of $[Pc(-2)Dy^{III}Pc(-2)]^-$ and $[Pc(-2)Nd^{III}Pc(-2)]^-$ in the presence of SO_2. Previous studies have shown that photolysis (at $\lambda > 320$ nm) of lanthanide or tin diphthalocyanine in the CH_2Cl_2/CH_3CN solvent mixture resulted in the electron transfer from the photoexcited $^*Pc_2Ln$ to the CH_2Cl_2 [17,23]. When the solutions of $[Pc(-2)Lu^{III}Pc(-2)]^-$, $[Pc(-2)Dy^{III}Pc(-2)]^-$ or $[Pc(-2)Nd^{III}Pc(-2)]^-$ were photolysed in the DMF/CH_2Cl_2 solvent mixture in the absence of SO_2, there were no significant spec-

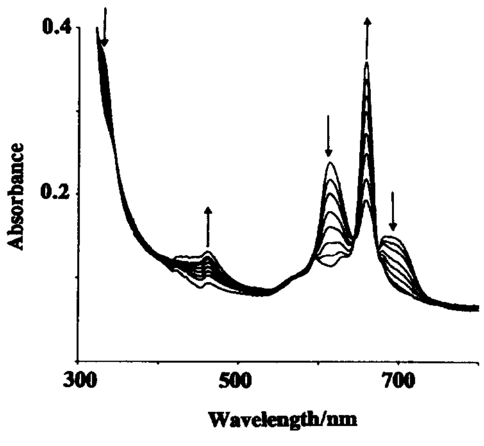

Fig. 5. Absorption spectral changes observed during the photolysis of $[Pc_2Lu]^-$ in DMF/CH_2Cl_2 containing SO_2. (a) Before and (b) at the end of photolysis. Starting $[Pc_2Ln]^-$ concentration $= 2 \times 10^{-6}$ mol dm^{-3} and $[SO_2] = 1 \times 10^{-4}$ mol dm^{-3}.

tral changes observed, hence showing that dichloromethane plays an insignificant role in the electron transfer process when the DMF/CH_2Cl_2 solvent mixture is employed. The spectral changes in Fig. 5 are quite similar to those shown in Fig. 1 in that the green Pc(-1)Lu^{III}Pc(-2) species is formed by one-electron oxidation of [Pc(-2)Lu^{III}Pc(-2)$]^-$, as discussed above. The absorption bands of the blue, [Pc(-2)Dy^{III}Pc (-2)$]^-$ complex, observed at 613 and 688 nm, decreased in intensity on photolysis of this species in the presence of SO_2 and the absorption bands of the green Pc (-1)DyPc(-2) species were observed at 657 and 459 nm. These spectral changes occurred with isosbestic points at 346, 550, 643 and 674 nm. It has been shown before [17] that photolysis of tin(IV) diphthalocyanine (Pc(-2)Sn^{IV}Pc(-2)) in dichloromethane containing SO_2 resulted in the one-electron oxidation of this species to [Pc(-2)Sn^{IV}Pc(-1)$]^+$. The difference between the interactions of the Pc(-2)Sn^{IV}Pc(-2) and the [Pc(-2) Ln^{III}Pc(-2)$]^-$ species with SO_2 is that the latter is negatively charged, hence electron transfer to SO_2 may occur more readily. The formation of the Pc(-1) Ln^{III}Pc(-2) species in the presence of SO_2 is attributed to the photoredox processes that occur following the excitation of the [Pc(-2)Ln^{III}Pc(-2)$]^-$ species and the quenching of the excited state by electron transfer to SO_2, as discussed above for the interaction of these species with pentachlorophenol. The quantum yields for the formation of the Pc(-1) Ln^{III}Pc(-2) species increased with the increase in the concentration of SO_2, Fig. 6, confirming the involvement of SO_2 as a quencher in these photoredox reactions. In comparison with the reactions between PCP and the lanthanide diphthalocyanine complexes, we suggest that the $(^3\pi\text{–}\pi^*)[Pc_2Ln]^-$ state is populated by excitation in the visible region and is quench by SO_2 according to equation (6):

$$(^3\pi\text{–}\pi^*)[Pc_2Ln]^- + SO_2 \rightarrow SO_2^- + Pc_2Ln. \qquad (6)$$

Kinetic data for the reaction between [Pc(-2)Ln^{III} Pc(-2)$]^-$ and SO_2 were collected by keeping the concentration of the former constant at 2×10^{-6} mol dm^{-3} and varying the concentration of SO_2, then photolysing the solutions and monitoring the formation of the oxidized product at 657 nm. Plots of the logarithm of absorbance of the oxidized species *vs* time were linear, again showing a first-order dependence on the diphthalocyanine complexes, as was observed above for the reactions with PCP. Plots of k_{obs} *vs* the concentration of SO_2 were also linear, Fig. 7, confirming a first-order dependence on SO_2. The relative slopes of the plots in Fig. 7 were 2.8, 0.4 and 0.02 s^{-1} mol^{-1} dm^3 for [Pc(-2)Lu^{III}Pc(-2)$]^-$, [Pc(-2)Dy^{III}Pc (-2)$]^-$ or [Pc(-2)Nd^{III}Pc(-2)$]^-$ photosensitizers, respectively. The observation of a higher slope for the photosensitization reactions involving [Pc(-2)Lu^{III}Pc(-2)$]^-$ implies that this species is a better photosensitizer for the reactions involving SO_2 than the other two complexes.

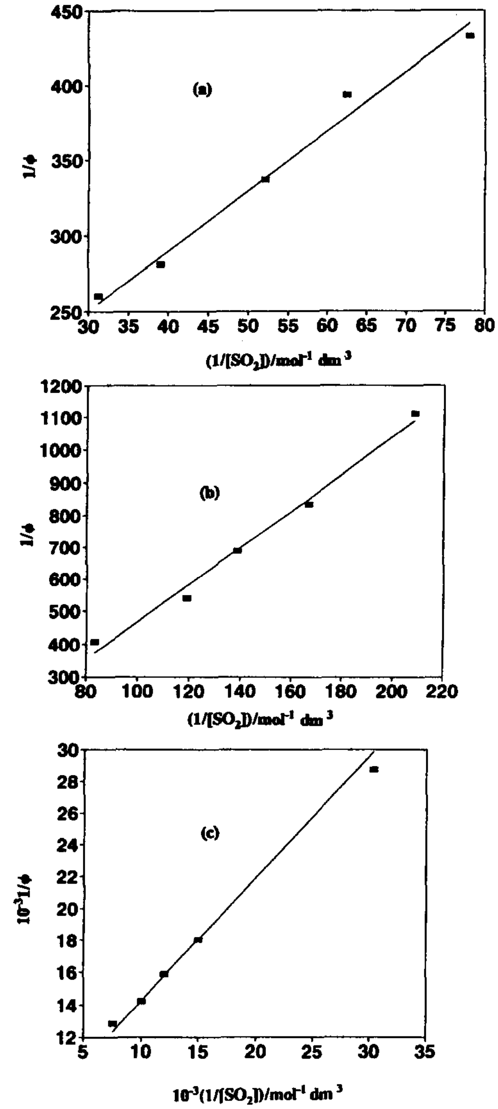

Fig. 6. Plots of reciprocal quantum yields *vs* the reciprocal concentration of SO_2, for the photooxidation of 2×10^{-6} mol dm^{-3} of (a) $[Pc_2Nd]^-$, (b) $[Pc_2Dy]^-$ and (c) $[Pc_2Lu]^-$ in the presence of SO_2.

CONCLUSIONS

Photolysis of the diphthalocyanine complexes [Pc (-2)Lu^{III}Pc(-2)$]^-$ and [Pc(-2)Dy^{III}Pc(-2)$]^-$ in the presence of pentachlorophenol results in the oxidation of these complexes to the Pc(-1)Lu^{III}Pc(-2) and Pc (-1)Dy^{III}Pc(-2) species, respectively, and the reductive dechlorination of pentachlorophenol, with evidence for the formation of tetra- and trichlorophenols. There was no evidence of the degradation of the benzene ring during the photolysis. The electron transfer between the lanthanide diphthalocyanine complexes and pentachlorophenol is preceded by the population of the excited triplet states of the $[Pc_2Ln]^-$ complexes. Dechlorination of polychlorophenols is of environmental importance since the toxicity of these species

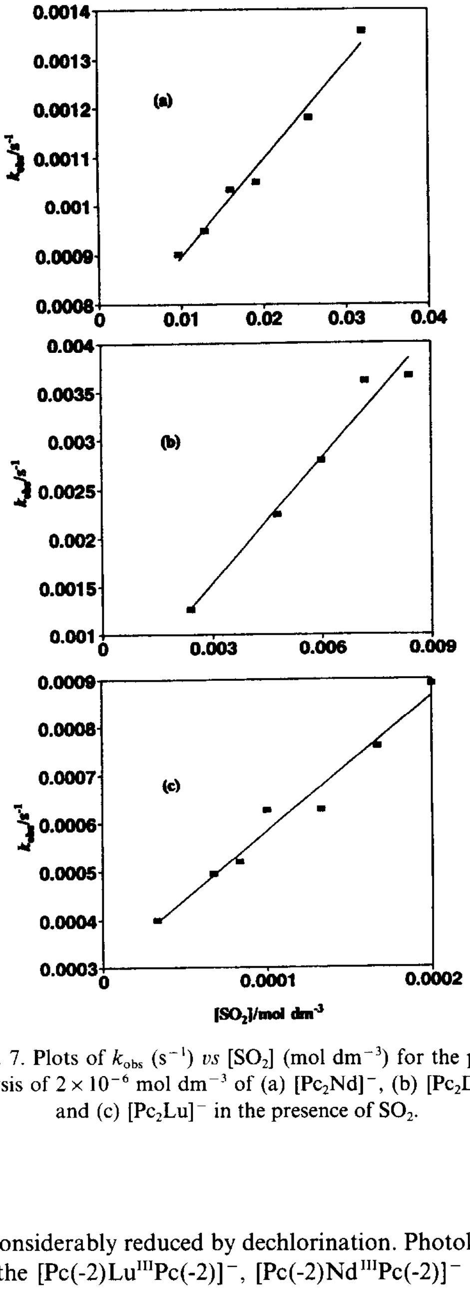

Fig. 7. Plots of k_{obs} (s^{-1}) *vs* $[SO_2]$ (mol dm^{-3}) for the photolysis of 2×10^{-6} mol dm^{-3} of (a) $[Pc_2Nd]^-$, (b) $[Pc_2Dy]^-$ and (c) $[Pc_2Lu]^-$ in the presence of SO_2.

is considerably reduced by dechlorination. Photolysis of the $[Pc(-2)Lu^{III}Pc(-2)]^-$, $[Pc(-2)Nd^{III}Pc(-2)]^-$ and $[Pc(-2)Dy^{III}Pc(-2)]^-$ species in the presence of SO_2 resulted again in the one-electron oxidation of the diphthalocyanine complexes and the possible reduction of SO_2. The quantum yields for the reaction between SO_2 and photoexcited lanthanide diphthalocyanine complexes ($\phi \simeq 10^{-5}$–10^{-3}) are generally of the same order of magnitude as the quantum yields observed for the reaction between SO_2 and tin(IV) diphthalocyanine ($\phi \simeq 10^{-4}$–10^{-3}). The quantum yields for the reaction of the lanthanide diphthalocyanine with SO_2 are of the same magnitude as those observed for the reductive dechlorination of pentachlorophenol.

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