

## PHOTOREDUCTION OF TIN(IV) PHTHALOCYANINES

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**Abstract**—Photolysis of  $\text{Sn(IV)Pc(OH)}_2$  (Pc = phthalocyanine dianion) and  $\text{Sn(IV)Pc(Cl)}_2$  using a tungsten lamp, and in the presence of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as an electron donor results in the reduction of these complexes to  $\pi$  anion radical species. The reduction shows second order dependence on the concentration of the  $\text{Sn(IV)Pc}$  complexes and a first order dependence on  $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ .

In photosynthetic processes, light-harvesting complexes capture sunlight and transfer the energy to the reaction centres. Understanding light-harvesting phenomena at the molecular level is a major objective of photosynthesis research and might provide the basis for the design of synthetic molecular devices.

There is a considerable interest in the photochemically induced electron-transfer reactions in metallophthalocyanines (MPc).<sup>1-10</sup> Both photo-oxidation and photoreduction can be achieved by irradiation of the MPc complexes in the presence of electron acceptors or donors.

Photoredox activity in MPc complexes may be centred at the metal, *e.g.*  $\text{Fe(II)Pc}^{11}$  and  $\text{Mo(V)Pc}^{12}$  or at the phthalocyanine ligand, *e.g.*  $\text{RuPc}^{6,11}$  and  $\text{ZnPc}^{11}$  MPc complexes where the central metal can exist in more than one stable oxidation state tend to show redox activity at the metal. The ability of the phthalocyanine ligand to undergo photoredox activity depends on a number of factors, including the properties of the central metal, the medium, other ligands in the coordination sphere and on the radiation wavelength.

UV irradiation of monomeric MPc complexes results in processes that originate from the  $n\pi^*$  states such as the abstraction of hydrogen from the solvent or appropriate hydrogen donors. Excitation in the Q band region results in the population of the lowest-lying  $^3\pi\pi^*$  states with a possible transfer of electrons between these states and electron donors or acceptors.<sup>11,13,14</sup>

There have been several reports on the photo-oxidation properties of MPc complexes,<sup>6,11,12</sup>

however, very little is known about the photoreduction of these complexes. Up to six successive one-electron reductions into the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ligand may occur in the MPc complex. The reduction products have distinct colours and spectral characteristics. The colour change exhibited by MPc complexes on oxidation or reduction may lead to the applications of these complexes in visual display systems.

Previous studies have shown that excitation of  $\text{Sn(IV)Pc(Cl)}_2$  at wavelengths of the visible region generates the  $^3\pi\pi^*$  state of this complex.<sup>7</sup> Quenching this state with electron acceptors resulted in the formation of the  $\pi$  cation radical species. There has, however, been no report on either the electrochemical reduction or the photolysis of SnPc complexes in the presence of electron donors.

This work reports on the photolysis of  $\text{Sn(IV)Pc(OH)}_2$  and  $\text{Sn(IV)Pc(Cl)}_2$  complexes in the presence of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The electronic absorption spectral properties of the photoreduction product are compared with those of the species generated by the electrochemical reduction of the  $\text{Sn(IV)Pc}$  complexes.

### EXPERIMENTAL

#### Materials

The tin(IV) phthalocyanine complexes,  $\text{Sn(IV)Pc(OH)}_2$  and  $\text{Sn(IV)Pc(Cl)}_2$  were prepared and purified by literature methods.<sup>15,16</sup> The purity of these complexes was established by comparison