



Photochemical studies of binuclear phenoxysubstituted phthalocyanines containing catechol bridges

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ABSTRACT: Binuclear ZnPc complexes covalently bridged by catechol units have been synthesized and their absorption and photochemical properties examined. The complexes studied are 1,2-bis-2',9',16',23'-triphenoxyphthalocyaninatozinc benzene (**6a**), 1,2-bis-2'-9',16',23'-tri-4-carboxyphenoxyphthalocyaninatozinc benzene (**6b**), 1,2-bis-2',9',16',23'-tri-4-nitrophenoxyphthalocyaninatozinc benzene (**6c**) and 1,2-bis-2'-9',16',23'-tri-4-*tert*-butylphenoxyphthalocyaninatozinc benzene (**6d**). Larger intramolecular coupling was observed for **6b** and **6c**, containing the carboxyphenoxy and nitrophenoxy substituents, respectively, than for **6a** and **6d**. A single Q band peak was observed for the fluorescence spectra of **6b** and **6c**, whereas **6a** and **6d** showed a split Q band. The absence of the high energy fluorescence peaks corresponding to absorbance peaks in the 640 nm region, suggests that the intramolecular coupling is broken by excitation for complexes **6b** and **6c**. Copyright © 2003 Society of Porphyrins & Phthalocyanines.

KEYWORDS: binuclear phthalocyanines, phenoxyphthalocyanine, singlet oxygen quantum yield, photobleaching, fluorescence, zinc phthalocyanine.

INTRODUCTION

Binuclear porphyrin complexes capable of four electron reduction of oxygen to water have been extensively investigated [1-4]. Binuclear porphyrin catalysts however tend to decompose with time. Metallophthalocyanine (MPc) complexes are more robust and show better electrocatalytic behavior than porphyrins. Synthesis of binuclear phthalocyanine complexes for use in oxygen reduction is of interest. Binuclear MPc complexes containing two to five atom linkages have been reported [5-9]. Peripheral substituents have been attached to these binuclear complexes in order to improve solubility. Binuclear MPc complexes are of interest as possible photosensitisers for photodynamic therapy (PDT) which may mimic hematoporphyrin derivatives (HpD). The latter has been used successfully as a

photosensitiser for PDT. HpD contains ester, ether and carbon-carbon linkages between porphyrin rings. HpD has a disadvantage in that it is a mixture containing monomers, dimers and oligomers. Synthesis of pure binuclear MPc complexes could lead to enhanced PDT activity.

We report on the fluorescence, photobleaching and singlet oxygen studies of binuclear MPc complexes covalently bridged by catechol units. The complexes synthesized are 1,2-bis-2',9',16',23'-triphenoxyphthalocyaninatozinc benzene (**6a**), 1,2-bis-2'-9',16',23'-tri-4-carboxyphenoxyphthalocyaninato zinc benzene (**6b**), 1,2-bis-2',9',16',23'-tri-4-nitrophenoxyphthalocyaninatozinc benzene (**6c**) and 1,2-bis-2'-9',16',23'-tri-4-*tert*-butylphenoxyphthalocyaninatozinc benzene (**6d**, Scheme 1). The synthesis of catechol linked MPc complexes has been reported [6, 9]. This work reports on the binuclear complexes substituted with phenoxy and phenoxy derivatives in addition to the Pc rings being

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