



Synthesis, characterization and photodynamic therapy properties of an octa-4-*tert*-butylphenoxy-substituted phosphorus(V) triazatetrabenzcorrole

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Dedicated to Professor Nagao Kobayashi on the occasion of his 65th birthday

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ABSTRACT: A novel octa-4-*tert*-butylphenoxy-substituted phosphorus(V) triazatetrabenzcorrole (P^VTBC), has been synthesized and characterized by MALDI-TOF MS and NMR, FT-IR and MCD spectroscopy. The fluorescence emission spectrum was used to determine the fluorescence quantum yield and the quantum yield for singlet oxygen generation was calculated by using 1,3-diphenylisobenzofuran as a scavenger. The photocytotoxicity against U87MG cells was measured. The results indicated that P^VTBC is potentially useful as an NIR region photosensitizer for photodynamic therapy (PDT).

KEYWORDS: triazatetrabenzcorrole, TD-DFT calculations, MCD spectroscopy, photocytotoxicity.

INTRODUCTION

There has been considerable interest in phthalocyanines (Pcs) because of their diverse potential applications in a wide range of different fields such as nonlinear optics [1], thin films [2], organic solar cells [3], and photodynamic therapy (PDT) [4–6]. The Pc complexes of the metalloids and nonmetals of Group IVA and VA, such as silicon, germanium and phosphorus have been the focus of a great deal of research interest, since two different oxidation states are readily accessible [7]. When complexes are prepared with phosphorus as the central atom in the presence of a reducing agent, the phthalocyanine ligand can lose an aza-nitrogen atom so that a triazatetrabenzcorrole (TBC) complex is formed instead as a low-symmetry Pc structural analog [8]. The first example of a phosphorus

TBC complex was reported by Gouterman and coworkers in 1981 [9], but was incorrectly reported to be a P^{III}Pc complex. Subsequently, Fujiki in 1986 demonstrated that this complex was actually a P^{III}TBC [10]. The structure and properties of P^VTBC were later elucidated by Liu *et al.* [11] and Goldberg and coworkers [12], while those of P^{III}TBCs in cold concentrated H₂SO₄ have been investigated by Jianbo *et al.* [13]. The optical properties of TBCs differ markedly from those of Pcs. There is a marked narrowing and red shift of the B-band to *ca.* 450 nm and three intense bands are observed in the Q-band region between 580–700 nm, which can be used to monitor the formation of the compound [14]. Since the Q-band lies at the edge of the optical window for tissue penetration [15], TBC complexes are potentially suitable for use as photosensitizers in photodynamic therapy (PDT). P^VTBC derivatives have been reported to have significant fluorescence yields and moderately high singlet oxygen quantum yields [11, 13]. Oxophosphorus triazatetrabenzcorroles have also been shown to possess good photodynamic efficiency toward HeLa cells [16].

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