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Syntheses and photophysical properties of diaminotetraphenylporphyrins and their corresponding polyimides

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ABSTRACT

Two free base porphyrins, 5,10-bis(4-aminophenyl)-15,20-diphenylporphyrin (*cis*-DATPP), 5,15-bis(4-aminophenyl)-10,20-diphenylporphyrin (*trans*-DATPP), and their zinc metalated analogues (*cis*-ZnDATPP and *trans*-ZnDATPP) were synthesized. A series of their corresponding polyimides were obtained by the condensed polymerization of the respective monomeric isomer DATPP with a 1:1 ratio of 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB) and 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA). The inclusion of PFMB and 6FDA into the polymeric backbone causes the polymers to be moderately to highly soluble in organic polar solvents. The molar content of the respective DATPP monomer varied between 5 and 30%. All compounds were structurally characterized by ^{1}H NMR and ATR-IR spectroscopy and the porphyrin content in the polyimides was determined by UV–Visible absorption spectroscopy. Photophysical properties consisted of measuring both the UV–Visible (ground state) absorption and fluorescence (excited state) spectra, fluorescence quantum yields (Φ_f), and fluorescence lifetimes (τ_f) in dichloromethane and N,N-dimethylacetamide. Fluorescence quenching was also measured and observed by the Stern-Volmer relationship, using 9,10-anthraquinone (AQ) as the quencher molecule. Both the bimolecular rate constant of fluorescence quenching (k_q) and the Stern-Volmer constant (K_Q) were calculated from this relationship. Furthermore, deviations from linearity depicted in the Stern-Volmer plots for TPP and ZnTPP at higher concentrations of AQ were also measured as a means of examining and explaining the simultaneous occurrence of dynamic (collisional) quenching and static quenching in the mechanisms of fluorescence quenching. It was found in this work that the significantly larger values in the static quenching constant (K_S) than in the dynamic quenching constant (K_D) are indicative that static quenching and ground state complex formation between the fluorophore and quencher is the dominant mechanism of fluorescence quenching of these systems at higher quencher concentrations.

1. Introduction

Porphyrins and polyimides are two classes of organic compounds that have attracted much interest in a wide variety of applications, ranging in their use as photosensitizers in different types of electron and energy transfer processes, water purification, novel chemical synthesis and catalysis, artificial solar energy conversion (photovoltaic) systems, and many more [1–28]. Much attention has been focused on the synthesis of aromatic polyimides containing porphyrin moieties within the polymer backbone chain for studying their fundamental spectroscopic and photophysical properties in applications of artificial solar energy conversion systems [22,23], catalysts [24], photoresponsive materials [25], molecular wires [26], and photoinduced intramolecular electron transfer properties [19–21,27]. The presence and covalent attachment of porphyrin units in the polyimide backbone chain introduces the following three chemical characteristics: (1) higher degree of aromaticity, (2) extended π-conjugation, and (3) higher degree of electron donating behavior. These three characteristics are expected to result in an

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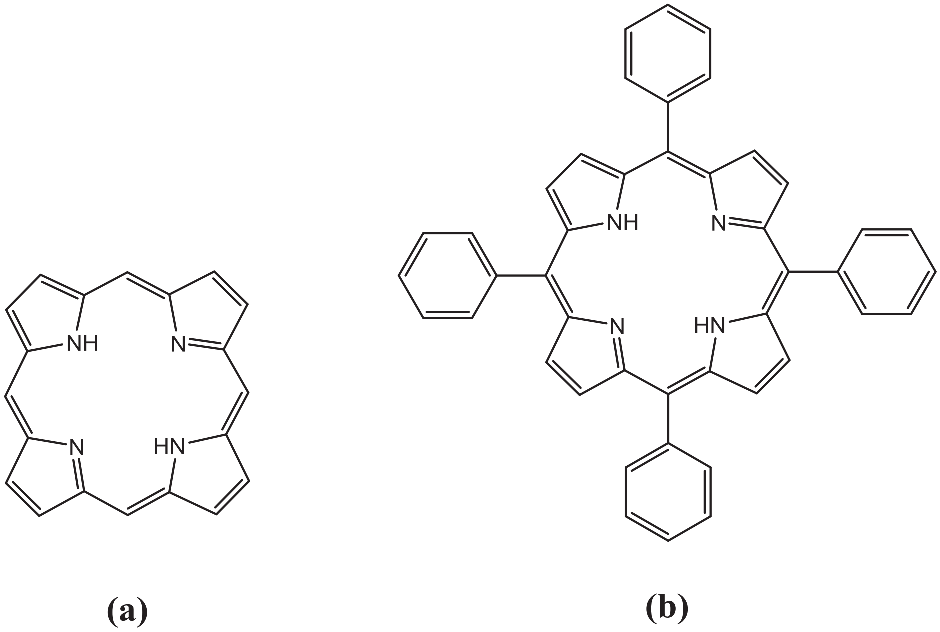
enhancement in the photoinduced intramolecular charge transfer properties of these compounds, in that photon absorption results in the transfer of electronic charge from the electron donor end of the molecule (porphyrin moiety) to the electron acceptor end of the molecule (electron withdrawing moieties along the polyimide backbone chain). Furthermore, in addition to the characteristics mentioned, the presence of electron donating porphyrin groups introduces unique absorbance and fluorescence spectral properties in the visible region of the electromagnetic spectrum.

Porphyrins are tetrapyrrolic macrocyclic compounds that belong to the family of organic compounds called porphyrinoids. Fig. 1 shows the chemical structures of porphyrin and meso-5,10,15,20-tetraphenylporphyrin (TPP). A single porphyrin macrocycle is nominally composed of 22 π electrons, 18 of which belong to the π-conjugated delocalization framework. A generic porphyrin backbone is structurally composed of four ‘pyrolle-type’ rings covalently linked together by four methine bridging groups to give an aromatically conjugated macrocyclic ring consisting of a sp^2 hybridized framework [1,2]. Porphyrins are known for their characteristic red and purple colors both in their solid and solution states and are efficient chromophores. Free base (or nonmetallated) porphyrins generally show four weak absorption bands, known as Quasi, or Q, bands in the visible absorption spectrum at an approximate wavelength range between 500 and 650 nm and a strongly intense absorption band in the near-UV region called the Soret, or S, band appearing at a wavelength of around 400 nm, characteristic with the π-conjugation of the macrocyclic ring [2,3]. Porphyrins are also recognized for their strongly intense fluorescence properties and their higher degree of π-conjugation makes them more red shifted fluorophores [4–11].

Porphyrins have been used in a wide variety of applications ranging in their use as photosensitizers for different types of electron, electron energy transfer, and energy storage processes, water purification, novel chemical synthesis, and decontamination of chemical and biological materials [12–14]. In particular, porphyrins are commonly used photosensitizers for singlet state oxygen ($^1\Delta_g$), a reactive oxygen species that has found widespread attention as a cytotoxic agent in photodynamic therapy (PDT) in destroying targeted tumor and cancerous cells in living organisms [15]. Additionally, singlet oxygen has been used as a reactive intermediate in the photooxidation of organic compounds in solution because of its high chemical energy content and its low lying excited states [16,17]. Aromatic polyimides are a class of organic compounds traditionally synthesized by the treatment of an aromatic diamine with an aromatic tetracarboxylic acid dianhydride [18] known for their thermal stability, high softening temperatures, chemical resistance, and mechanical properties [19–21,28]. Dianhydrides are reported as good electron acceptor groups and diamines are good electron donor groups, which thereby cause polyimides to easily form a charge transfer complex between the electron donor and acceptor groups [28].

The work presented in this manuscript reports on the direct syntheses of two free base monomeric porphyrin isomers, namely 5,10-bis(4-aminophenyl)-10,20-diphenylporphyrin (*cis*-DATPP) and 5,15-bis(4-aminophenyl)-10,20-diphenylporphyrin (*trans*-DATPP), their zinc metalated analogues, and their corresponding polyimides (see Fig. 2 for the chemical structures of *cis*-DATPP and *trans*-DATPP). The photophysical properties of these compounds were investigated, which involved measuring the UV–Visible (ground state) absorption spectra, fluorescence (excited state) spectra, fluorescence quantum yields (Φ_f), and fluorescence lifetimes (τ_f) in N,N-dimethylacetamide and dichloromethane. The fluorescence quenching of these classes of organic compounds were investigated in the presence of 9,10-anthraquinone (see Fig. 3) as the quencher compound using the Stern-Volmer relationship. The effects that polymerization, polymer molecular weights, and weight percent of porphyrin content in the polymers have on the photophysical properties of these class of compounds are discussed in the manuscript. Furthermore, the work presented in this manuscript will provide important information into the syntheses and photophysical properties of these classes of organic compounds. A thorough understanding of the properties of these compounds is pertinent to examining their applications.



(a) (b)

Fig. 1. Chemical structures of (a) porphyrin (porphine) and (b) meso-5,10,15,20-tetraphenylporphyrin (TPP).