

# Energy transfer in zinc porphyrin–phthalocyanine heterotrimer and heterononamer studied by fluorescence resonance energy transfer (FRET)

M. Durmuş<sup>a,b</sup>, J.Y. Chen<sup>c</sup>, Z.X. Zhao<sup>a</sup>, T. Nyokong<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

<sup>b</sup> Department of Chemistry, Gebze Institute of Technology, Gebze 41400, Turkey

<sup>c</sup> Department of Physics, State Key Laboratory for Advanced Photonic Materials and Devices, Fudan University, Shanghai, China

Received 9 February 2007; received in revised form 6 July 2007; accepted 10 July 2007

## Abstract

Two or eight zinc triphenyl porphyrins were conjugated with Zn-phthalocyanine or H<sub>2</sub>-phthalocyanine to form ZnPc–(ZnTPP)<sub>2</sub>, ZnPc–(ZnTPP)<sub>8</sub>, H<sub>2</sub>Pc–(ZnTPP)<sub>2</sub> and H<sub>2</sub>Pc–(ZnTPP)<sub>8</sub>. Energy transfers from the porphyrin moiety to phthalocyanine part were quantitatively studied with the modality of fluorescence resonance energy transfer (FRET). By measuring the fluorescence increment from the phthalocyanine moiety and the decrease from porphyrin part under selective excitation at the B band of the porphyrin part in those conjugated compounds and their equimolar mixture of compositions, energy transfer efficiencies were estimated to be 90% for H<sub>2</sub>Pc–(ZnTPP)<sub>8</sub> and ZnPc–(ZnTPP)<sub>8</sub>, and 60%, 30% for ZnPc–(ZnTPP)<sub>2</sub> and H<sub>2</sub>Pc–(ZnTPP)<sub>2</sub>, respectively.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Zinc porphyrin; Zinc phthalocyanine; Fluorescence; Energy transfer

## 1. Introduction

Phthalocyanines are an important class of organic compounds, which have a number of applications in different fields such as xerographic photoreceptors [1], infrared sensors [2], optical recording [3], organic photoelectronic devices [4], nonlinear optics [5] and as photosensitizers in photodynamic therapy (PDT) of cancer [6]. Phthalocyanines are stable and rigid compounds with a high quantum yield to emit red fluorescence, and can photo-induce singlet oxygen to destroy cancer cells when used in PDT. Phthalocyanines have two absorption bands, a strong Q band in the red region (600–700 nm) and a medium-strength Soret band in UV region (350 nm). Due to the attractive property of high fluorescence efficiency in red wavelength region, phthalocyanines are potentially useful as wavelength transfer devices absorbing the short wavelength and emitting longer red wavelengths. However, their poor absorption in the other visible region (except red region) limits these types of

applications. Furthermore, phthalocyanines such as Pc 4 have been used in clinical trials for photodynamic therapy of cancer [7], thus expanding the range of absorption (excitation) wavelengths in the visible region is of importance. With the aim of effectively capturing a wide region of visible light and efficiently emitting red light, porphyrin–phthalocyanine conjugates have been synthesized. Porphyrins have an intense B band in violet region [8], and successful energy transfer from porphyrin to phthalocyanine has been achieved [9]. To conjugate porphyrin with phthalocyanine, several links have been tested, such as ether [10], alkoxy [11], piperazinyl [12], phenylethynyl [13] and ethynyl groups [8]. However, among those linked porphyrin–phthalocyanines only a few conjugates, such as the phenylethynyl-linked dyad [13] and the meso- and  $\beta$ -position connected compounds [9], accomplished a remarkable energy transfer. The edge-to-edge distances for above conjugates are all similar (about a few nm). However, the results of energy transfer are different for different linkages, and no good explanation for such difference has been given. So far, no clear rule has been reported for energy transfer in linked porphyrin–phthalocyanine molecules. Thus searching a dominating rule in energy transfer would involve not only extending applications of phthalocya-

\* Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.  
E-mail address: [t.nyokong@ru.ac.za](mailto:t.nyokong@ru.ac.za) (T. Nyokong).