

Photo-induced intra-molecular energy transfer of tetra-{3,5-di-(4-nitro benzyloxy) benzyloxy} zinc (II) phthalocyanine

Zhenzhen Chen^{1,a}, Keqin Wu^{1,b}, Junri Wen^{1,c}, Hongqin Yang^{2,d}, Yiru Peng^{1,e*}

¹College of Chemistry and Engineering, Fujian Normal University, Fuzhou 350007, China

²Key Laboratory of Optoelectronic Science and Technology for Medicine of Ministry of Education, Fujian Provincial Key Lab for Photonics Technology, Fujian Normal University, Fuzhou 350007, China

^a773860502@qq.com, ^b334196650@qq.com, ^c1021764601@qq.com, ^dhqyang@fjnu.edu.cn
^{e,*}yirupeng@fjnu.edu.cn

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Abstract. The photophysical properties of a novel dendrimer tetra-{3,5-di-(4-nitro benzyloxy) benzyloxy} zinc phthalocyanine (DZnPc) was studied by steady-state, time-resolved fluorescence and UV/Vis spectroscopy. DZnPc mainly existed as a monomer in DMF. Intra-molecular energy could be transferred from peripheral dendrons, as donors, to the phthalocyanine core, as an acceptor, during a photo-induced process. The intra-molecular energy transfer quantum yield was as high as 65% for this dendritic phthalocyanine. The study suggests that this novel dendritic phthalocyanine could be used as an efficient energy transfer system.

Introduction

Light trapping in photosynthetic antenna refer to series of fast and efficient transfer of energy transfers between spectroscopically different chlorophylls [1]. Several methods have been applied to imitate this natural energy transfer process, for emample by self-assembly[2]. Therefore, dendrimeric phthalocyanine received extensive attention. Ng study terminal ester functionalities exhibits an intramolecular singlet-singlet energy transfer from the excited aryl-containing dendrons to the phthalocyanine core, and its quantum yield is about 33%[5]. Li et al reported energy transfer of tetrakis(perylenediimide zinc phthalocyanine[6]. Their studies both showed that the skeleton rigidity of dendrimers could significantly affect the intra-molecular energy transfer quantum yield. Recently, we have synthesized a series of poly (aryl benzyl ether) dendritic zinc (II) phthalocyanines, and these molecules have exhibited an absence of aggregation among other interesting photophysical properties[7]. However, the energy transfer of this dendritic zinc (II) phthalocyanines have still not been investigated. In the paper, the intra-molecular energy transfer of this series phthalocyanine was studied by UV/Vis spectroscopy, and steady-state, time-resolved fluorescence .

Materials and methods

Materials

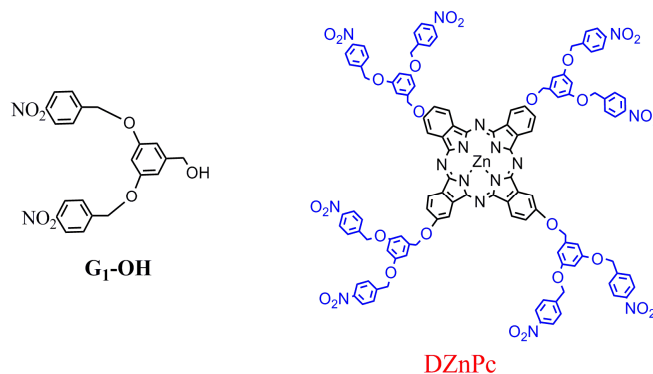


Fig.1 Chemical structure of G₁-OH and DZnPc

Tetra-{3,5-di-(4-nitro benzyloxy) benzyloxy} zinc phthalocyanine (DZnPc) was successfully synthesized via a convergent approach[8]. Its chemical structure was characterized by IR and ¹HNMR. Its structure was shown in Figure 1. Other solvents involved in this experiment, including dimethylsulfoxide (DMSO), dimethyl formamide (DMF), and chloroform were purchased from Sino-pharm Chemical Reagent Co. Ltd.

Methods

UV/Vis absorption spectra were measured using a UV/Vis spectrophotometer (Cary50, Varian, USA), steady-state and time-resolved fluorescence spectra were measured on a FL900/FS920 fluorescence spectrophotometer. Fluorescence quantum yields were determined according to Eq.1[9],

$$f_x = f_{\text{ZnPc}} \frac{F_x}{F_{\text{ZnPc}}} \times \frac{A_{\text{ZnPc}}}{A_x} \quad (1)$$

Where Φ_{ZnPc} is the fluorescence quantum yield of ZnPc in DMF ($\Phi_{\text{ZnPc}} = 0.20$), F_x is the fluorescence of integral of substituent zinc phthalocyanine, F_{ZnPc} is the fluorescence of integral of ZnPc, A_{ZnPc} is the absorbance of ZnPc, and A_x is the absorbance of substituent ZnPc.

The intra-molecular energy transfer quantum yield (Φ_{ENT}) can be determined through steady-state fluorescence spectroscopy approach. Φ_{ENT} can be calculated by the following equation [10]:

$$\Phi_{\text{ENT}} = 1 - F/F_0 \quad (2)$$

where F is the donor's integral fluorescence intensity in the presence of an acceptor, and F_0 is the donor's integral fluorescence intensity in the absence of an acceptor.

Results and discussion

The photo-physical properties of DZnPc were measured by UV/Vis, steady-state, and time-resolved fluorescence spectroscopic method. The absorption spectrum of DZnPc in DMF is shown in Fig.2. It exhibited typical spectra for non-aggregated phthalocyanine, with a B band at 360 nm and a Q band at about 685 nm. Moreover, there is a UV band ranging from at 290 nm, which was assigned to the absorption of dendritic ligand [11]. As it mainly existed as a monomer in DMF, therefore, the steric effect of dendritic substitution at the peripheral position of phthalocyanine can reduce its aggregation behavior efficiently.

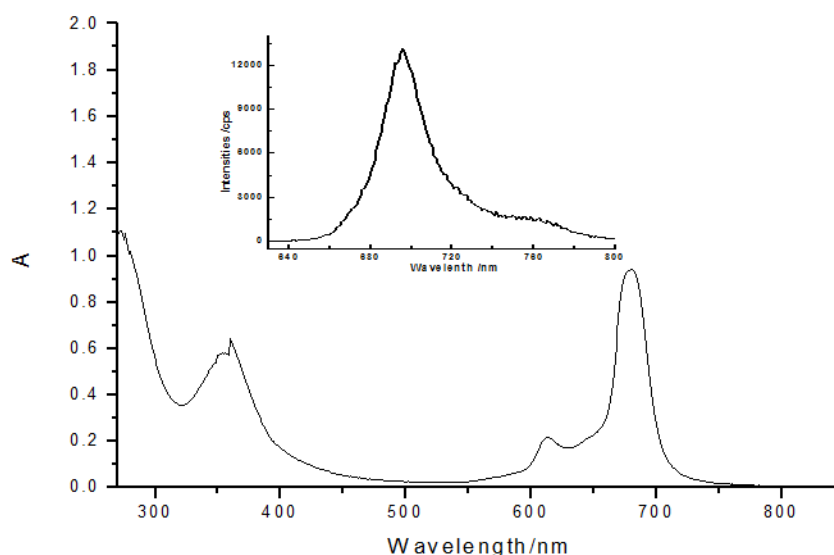


Fig.2 UV/Vis spectrum of DZnPc in DMF with $C_{\text{DZnPc}} = 2 \times 10^{-5}$ mol/L, the inset figure is the fluorescence spectrum of DZnPc in DMF ($C_{\text{DZnPc}} = 2 \times 10^{-5}$ mol/L)

Figure.2 shows the fluorescence spectrum of DZnPc in DMF. Upon excitation at 610 nm, DZnPc exhibited fluorescence emissions at 692 nm, with the fluorescence quantum yield of 0.22.

Intra-molecular energy transfer of this novel dendritic phthalocyanine was studied. When a G_1 -OH dendron (hydroxyl terminal), equivalent to the dendron subunits in DZnPc, was excited at the peak of its absorption band at 297 nm (see the inset in Fig. 3A), it emitted fluorescence at 340 nm, as shown with a dashed curve in Fig. 3. The emission of G_1 -OH dendron is partially overlapped with the B absorption band of the DZnPc (Fig. 3A(a)). The overlapping of the emission and absorption spectra indicated that the dendron on the peripheral of dendritic phthalocyanine could have a chance to communicate photo-chemically with the phthalocyanine core via energy transfer [12].

When DZnPc was excited at 297 nm in DMSO, it emitted a strong fluorescence from the dendron at 350 nm as well as a fluorescence from the phthalocyanine core at 696 nm (Fig. 3B(a)). The ratio of fluorescence intensity ($I_{696 \text{ nm}}/I_{480 \text{ nm}}$) was about 1.914, indicating a lower probability of the dendron-to-phthalocyanine intra-molecular energy transfer.

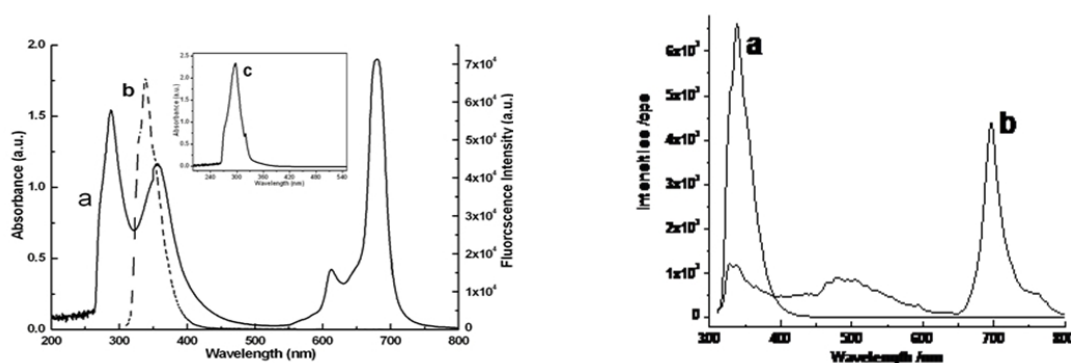


Fig. 3(A) UV-Vis absorption spectrum of DZnPc (a) and G_1 -OH (c) (inset); fluorescence spectrum (b) of G_1 -OH with $\lambda_{\text{ex}} = 297$ nm; (B) Fluorescence spectrum of G_1 -OH (a) and DZnPc (b) $\lambda_{\text{ex}} = 297$ nm

Conclusions

Photoinduced intra-molecular energy transfer in tetra-{3,5-di-(4-nitro benzyloxy) benzyloxy} zinc phthalocyanine (DZnPc) was demonstrated. Intra-molecular energy transfer could occur effectively from the peripheral excited dendron subunits to the phthalocyanine core, and its energy transfer quantum yield is about 65%. This study suggests that a new and efficient light-harvesting system can be developed based on this novel dendritic phthalocyanine system.

Acknowledgments

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