Synthesis, Characterization and Photophysical Properties of Tetra-(hydroxypheny-hexfluoropropyl) Zinc(II) Phthalocyanine

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Abstract. Tetra-(hydroxypheny-hexfluoropropyl) zinc(II) phthalocyanine was synthesized and its structure was characterized by elemental analysis, IR, MALDI-TOF mass, and 1HNMR methods. Its photophysical properties was measured by UV/Vis, steady-state, and time-resolved fluorescence spectroscopy. The bulky fluorinated substituents enhanced the solubility of macrocycle and reduced aggregation effectively.

Introduction

Phthalocyanines (Pcs) and their derivatives are well-developed organic materials that have been applied in different technology and medical areas such as liquid crystal, chemical sensors, solar cells, and photodynamic therapy (PDT) of cancer [1-4]. However, owing to their low solubility in common organic solvent and aggregation easier in aqueous medium through hydrophobic π–π stacking interactions between planar Pc ring, which limit their applications in many fields. Numerous studies have been carried out to overcome these drawbacks via modifying this macrocyclic compounds. Among them, fluorinated metallophthalocyanines are receiving a great deal of attention due to fluorine substituents exhibit interesting electron-transporting characteristics, increased its thermal stability, enhanced solubility, and decreased intermolecular interaction[5,6]. In this paper, we synthesized a novel tetra-(hydroxypheny-hexfluoropropyl) zinc(II) phthalocyanine. The bulky fluorinated substituents could not only enhance the solubility of zinc phthalocyanine but also lower their aggregation tendency, resulting in superior photophysical properties.

Experimental

Materials and equipment. Solvents for organic synthesis were reagent grade, and dried according to standard procedures. All other compounds were purchased from commercial sources and used as received. Infrared spectra in KBr pellets were recorded on a Perkin-Elmer PE-983G FT-IR Spectrophotometer. 1HNMR spectra were recorded with a Varian 400MHz spectrometer using TMS as an internal standard. Matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) spectra were performed on a Bruker bench TOF mass spectrometer. UV/Vis spectra were obtained on a Varian Cary 50 spectrophotometer. Elemental analyses were carried out on Vario Elementar EL III. Steady-state and time-resolved fluorescence spectra were measured on a FL900/FS920
fluorescence spectrophotometer.

Synthesis

Synthesis of 4-(4-hexfluoropropyl-4-hydroxypheny-phenoxy) phthalonitrile (1). A mixture of 2,2-bi(4-hydroxyphenyl)hexafluoropropane (4.58 g, 13.6 mmol), 4-nitrophthalonitrile (2.60 g, 14.96 mmol), and anhydrous K$_2$CO$_3$ (1.88 g, 13.6 mmol) in acetone (30 mL) was refluxed under nitrogen at 55 °C for 48 h. The reaction mixture was cooled to room temperature, and then the solvent was evaporated to dryness under reduced pressure. The crude product was purified by silica gel column chromatography eluting with PE/CH$_2$Cl$_2$ (v/v=1:100). A white powder was obtained. Yield: 2.56 g (40.7%). $^1$HNMR (400 MHz, CDCl$_3$, ppm): 7.89 (d, $J=8$ Hz, 1H), 7.53 (d, $J=8$ Hz, 2H), 7.36 (d, $J=16$ Hz, 2H), 7.31 (d, $J=8$ Hz, 2H), 7.09 (d, $J=12$ Hz, 2H), 6.88 (d, $J=8$ Hz, 2H). IR (KBr, $\nu_{max}$/cm$^{-1}$): 3420, 2232, 1608, 1583, 1252, 1167, 828. MS (MALDI-TOF)(m/z), 462.1. Found: 461.6 [M]$. Anal. Calc. for C$_{23}$H$_{12}$N$_2$O$_2$ (%): C, 59.75; H, 2.62; N, 6.06. Found: C, 59.70; H, 2.59; N, 6.10.

Synthesis of tetra-(hydroxypheny-hexfluoropropyl) zinc(II) phthalocyanine (ZnPcF) (2). The mixture of (1) (0.26 g, 0.57 mmol) and Zn(OAc)$_2$·2H$_2$O (0.033 g, 0.15 mmol) in n-pentanol (10 mL) was heated at 110 °C, and then a few drops of DBU were added. The mixture was heated at 150 °C with vigorously stirred 48 h under nitrogen. After cooling to room temperature, the reaction mixture was filtered and the filtrate was poured into n-hexane (50 mL). After that, precipitated green-blue solid was filtered off. The crude product was accomplished by column chromatography on silica gel with PE/CH$_2$Cl$_2$ (v/v=1:200) as the eluent. A green-blue powder was obtained. Yield: 0.07 g (26.6%). $^1$HNMR (400 MHz, DMSO-d$_6$, ppm): 8.28 (d, $J=8$ Hz, 4H), 7.95 (d, $J=8$ Hz, 4H), 7.54 (d, $J=16$ Hz, 16H), 7.26 (d, $J=8$ Hz, 8H), 6.90 (d, $J=12$ Hz, 8H), 5.31 (d, $J=8$ Hz, 4H). IR (KBr, $\nu_{max}$/cm$^{-1}$): 2934, 1608, 1583, 1252, 1167, 829. MS (MALDI-TOF)(m/z), 1912.3. Found:1912.34 [M]$^+$. Anal. Calc. for C$_{92}$H$_{48}$F$_{24}$N$_8$O$_8$Zn (%): C, 57.71; H, 2.53; N, 5.85. Found: C, 57.68; H, 2.52; N, 5.83.

Results and discussion

The synthetic pathway was listed in Scheme 1.

Scheme 1  The synthetic route of tetra-(hydroxypheny-hexfluoropropyl) zinc(II) phthalocyanine
Fig. 1 gives the UV/Vis spectra of ZnPcF in DMF. It displays typical B band at 354 nm, and Q band at 676 nm, respectively. In addition, the UV band at 277 nm was assigned to hexfluoropropyl functional ligands. As the concentration of ZnPcF increased, the intensity of the Q band also increased, but the shape and position of Q band remained unchanged. Thus, compound ZnPcF was essentially monomeric species in DMF. This suggested that the bulky fluorinated substituents can reduce interactions between phthalocyanine molecules, lowering their aggregation tendency.

The fluorescence spectra of ZnPcF in DMF was showed in Fig.2. Upon excitation at 610 nm, ZnPcF exhibited fluorescence emissions at 685 nm. The fluorescence decay curve of ZnPcF in DMF was showed in Fig.3. The singlet excited lifetimes ($\tau_s$) were determined by time-resolved experiments in which the fluorescence decay profiles were found to fit to a mono-exponential function $\text{Fit} = A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} + B_3 e^{-t/\tau_3} + B_4 e^{-t/\tau_4}$. The singlet excited lifetime of ZnPcF was calculated to be 3.43 ns.
Conclusions
A novel tetra-(hydroxyphenyl-hexfluoropropyl) zinc(II) phthalocyanine was synthesized and characterized. The peripheral fluorine substitutions on the macrocyclic ring increase the solubility of ZnPcF in DMF, which are essentially non-aggregated phthalocyanines by UV/Vis spectroscopy. The bulky fluorinated substitutions can prevent aggregation effectively. Besides, the fluorescence lifetime of ZnPcF was 3.43 ns.

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References