



Ultrafast excited-state dynamics of Ni-contained covalently bonded phthalocyanine–porphyrin conjugates



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ABSTRACT

Two covalently bonded phthalocyanine–porphyrin conjugates metalated with nickel were synthesized and spectroscopically characterized. The nonlinear optical responses and excited-state dynamics of these compounds were investigated via picosecond and femtosecond Z-scan and femtosecond pump-probe measurement, respectively. Both samples exhibited saturable absorption on picosecond regime and large reverse saturable absorption on femtosecond regime, which is attributed to the energy transfer from excited porphyrin unit to phthalocyanine ligand. The excited-state decay kinetics of both compounds were fit with a tri-exponential model with fast (~500 fs), medium (~10 ps), and slow (~200 ps) components. Our results revealed the photo-physical mechanism of the metal contained covalently bonded phthalocyanine–porphyrin conjugates, demonstrating the effect of intra-molecule energy transfer process on nonlinear optical properties.

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1. Introduction

Porphyrins and phthalocyanines are tetrapyrrole derivatives with large π -conjugation system. Phthalocyanines are widely investigated for prominent application in electro-catalyst, infrared sensors and as photosensitizers in photodynamic therapy agents. Porphyrins are extensively considered as biomimetic models for biological redox processes, nonlinear optics and used in electro-chemical and photochemical analyses. Over the past few decades, a lot of efforts have been done to successfully modulate excited state properties of porphyrin and phthalocyanine through metal coordination, substituent effects, π -conjugation length, and macrocycle modification [1–3].

Recently, conjugates of porphyrins (Pors) and phthalocyanines (Pcs) are regarded as good choices for usage in molecular photonics, catalysis and light harvesting architectures [4]. Various porphyrin–phthalocyanine arrays have been prepared by different synthetic strategies based on electrostatic interactions in molecules

with opposite charges, host–guest interactions, the axial coordination and covalent linked with functional groups [5,6]. In general, the Q band spectrum of porphyrins are located in blue–green portion of the visible region, where phthalocyanines have low extinction coefficients. The occurrence of efficient intramolecular energy transfer from excited porphyrin to phthalocyanine core can be contributed to good overlaps between the Q band absorption of phthalocyanine and the fluorescence of porphyrin in most phthalocyanine–porphyrin conjugates [7–9]. Photo-induced energy and electron transfer are important processes of photosynthesis and act as an key role in preparing artificial photosynthetic systems, energy harvesting photovoltaic devices [10,11]. Moreover, among various metal complexes, the nickel complexes are considered as excellent system for examining electronic deactivation dynamics, photothermal therapy (PTT) of cancer and photo-induced axial ligation/delegation dynamics [12–15].

In this paper, two Ni-contained phthalocyanine–porphyrin conjugates (Ni-TCPP-Pc and Ni-TCPP-Pc-TCPP) linked with oxy-bridges shown in Fig. 1 were synthesized. And their nonlinear optical (NLO) properties were investigated by picosecond and femtosecond Z-scan measurements. The energy transfer from excited porphyrin to ground state phthalocyanine and charge transfer process from excited phthalocyanine to metal state

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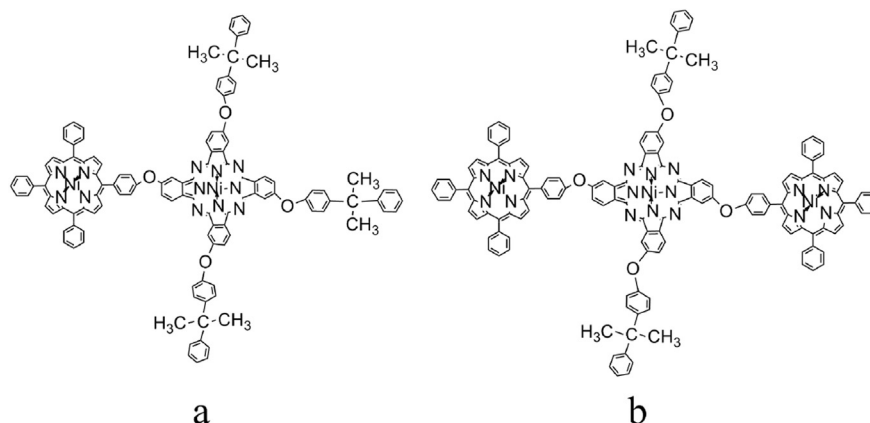


Fig. 1. (a), (b) represents molecular structure of Ni-TCPP-Pc and Ni-TCPP-Pc-TCPP compound, respectively.

undergoing ligand-metal interaction were investigated via ultrafast pump-probe technique. According to the results of ultrafast pump-probe technique, the photo-physical parameters of Ni-TCPP-Pc and Ni-TCPP-Pc-TCPP were extracted from pump-probe curves through numerical simulation. These findings are highly useful in fabricating promising artificial photosynthetic system, nonlinear optical materials and optoelectronic devices.

2. Experimental section

2.1. Materials and instrumentation

All the reagents were commercially available and used without further purification. The UV–Vis absorption spectra were measured through a scanning spectrophotometer (Shimadzu UV-1800), Fourier transform infrared (FTIR) spectra were determined by measuring samples in KBr disks on a Shimadzu IR-8400S spectrometer and ^1H NMR spectra were carried out on a Bruker Advance 400 MHz spectrometer at room temperature, using CDCl_3 as solvent.

The third-order nonlinear optical properties of two phthalocyanine–porphyrin conjugates solution were measured using Z-scan technique. The light sources for ps and fs Z-scan were a mode-locked Nd: YAG laser (21 ps, 532 nm, 10 Hz) and an Yb: KGW based fiber laser (190 fs, 515 nm, 20 Hz), respectively. The experimental apparatus has been described in detail elsewhere [16]. The sample solution was injected into 2 mm thickness quartz cell. And the cell was placed on a translation stage manipulated by a personal computer that moved along the z-axis with respect to the focal point of a 400 mm focal lens. The laser pulses adjusted by an attenuator were separated into two beams by using a splitter: one beam was focused on the sample through a lens of 400 mm focal distance and another beam regarded as the reference beam. The two beams were simultaneously measured by using two energy detectors (Rjp-765 energy probe) linked to an energy meter (Rj-7620 ENERGY RATIONETER, Laser probe). A personal computer was used to collect data originating from energy meter through a GPIB interface. The benchmark Kerr liquid CS_2 was used to calibrate our experimental systems.

In the pump-probe measurement, the laser source was a mode-locked Yb: KGW based fiber laser (190 fs, 515 nm, 20 Hz). The 2 mm sample cell was the same one used in the Z-scan experiment. The pump-probe setup was a standard one [17]. The laser pulse was separated into two beams through a splitter: a probe beam and a pump beam. In order to remove the nonlinear effect caused by the probe beam in the sample, the probe peak

irradiance was modulated as approximately 8% of the pump irradiance through the system of half plate and polarizer. The polarization of pump and probe beam was at magic angle to avoid anisotropic effect. The probe waist (22 μm) was smaller than the pump waist (152 μm) and the two pulses were recombined at the sample cell at a small angle (4°). The small angle between the beams and the fact that the probe spot size was considerably smaller than the pump ensure that the probe could experience a uniformly excited region of material in the 2 mm cell. A variable delay was introduced into the pump path and the variation of the probe beam intensity versus the delay time was recorded by an energy detector after the pump beam.

2.2. Preparation of Ni-TCPP-Pc and Ni-TCPP-Pc-TCPP

The synthesis route of Ni-TCPP-Pc and Ni-TCPP-Pc-TCPP involved a multistep procedure as outlined in Fig. 2: Firstly, through Alder method [18], p-hydroxybenzaldehyde (1.17 g, 9.57 mmol), benzaldehyde (2.67 mL, 26.3 mmol) and pyrrole (2.43 mL, 35 mmol) were added in a 250 mL RB flask containing 100 mL of propionic acid and whole mixture was refluxed for 4 h. After removing the solvent by distillation, the purple crude compound was purified by silica column. 5-(4-Hydroxy phenyl)-10, 15, 20-Triphenylporphyrin (THPP, $\text{C}_{44}\text{H}_{30}\text{N}_4\text{O}$, $M = 630.24$) was obtained as a second fraction eluted by dichloromethane. Secondly, THPP (200 mg, 0.26 mmol) was dissolved in DMF (10 mL) in a 50 mL RB flask, and then nickel(II) chloride hexahydrate puratrem (306.5 mg, 1.29 mmol) was added and whole mixture was refluxed until free base porphyrin was metalated which was checked by the thin layer chromatography. After evaporation of solvent, the crude compound was purified by silica column, and Ni-5-(3,4-Cyanide phenoxy)-10,15,20-Triphenylporphyrin (Ni-TCPP) was eluted by Petroleum ether: dichloromethane (1:3 v/v). Finally, Ni-TCPP (100 mg, 0.122 mmol), 4-(4- α -Cumylphenoxy) phthalonitrile (206 mg, 0.610 mmol), nickel(II) chloride hexahydrate puratrem (144.8 mg, 0.610 mmol) and catalyst DBU (0.5 mL) was dissolved in 15 mL of n-amyl alcohol in a 100 mL RB flask. The whole mixture was heated at 160 $^\circ\text{C}$ under N_2 and refluxed for 6 h. After cooling the mixture at room temperature, the solvent was evaporated to get the bluish violet crude compound purified by silica column. The desired compound Ni-TCPP-Pc ($\text{C}_{129}\text{H}_{103}\text{N}_8\text{O}_4\text{Ni}_2$, $M = 1957.62$) was obtained as a second fraction eluted by Petroleum ether: dichloromethane (1:1 v/v) and another desired compound Ni-TCPP-Pc-TCPP ($\text{C}_{158}\text{H}_{115}\text{N}_{12}\text{O}_4\text{Ni}_3$, $M = 2438.36$) was obtained as a fourth fraction eluted by dichloromethane: ethyl acetate (150:1 v/v). For Ni-TCPP-Pc, ^1H NMR (400 MHz, CDCl_3): $\delta = 8.56$ (m, 8H), 8.45

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