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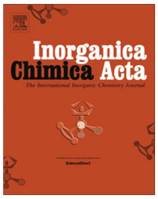

Research paper

The optical limiting of blue and green ytterbium double-decker phthalocyanines in solution and in poly(acrylic acid) as thin films

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Bis{1(4), 8(11), 15(18), 22(25)-tetra(4-*tert*-butylphenoxy)phthalocyaninato} ytterbium(III) (**2a**) (the green form) was synthesized and reduced to form **2b** (the blue form). Nonlinear optical parameters for complex **2** in green and blue forms were determined using the Z-scan technique and the values of third-order imaginary susceptibility (Im[$\chi^{(3)}$]) and second-order hyperpolarizability (γ) of the order of 10^{-9} (for **2b**) and 10^{-27} esu, respectively, were obtained in solution. In poly(acrylic acid) as a thin film, complex **2a** showed extremely high Im[$\chi^{(3)}$] and γ values of the order 10^{-8} and 10^{-25} respectively. A low optical limiting threshold value of 0.075 J cm^{-2} was obtained for the thin film **2a**.

1. Introduction

Double- or triple-decker phthalocyanines exhibiting characteristic optical and electronic properties can be employed in fields that include as electronic materials [1], sensors [2], electronic displays [3,4], organic field-effect transistors [5–7], single molecule magnets [8–11], self-assembly [12] and nonlinear optics [13]. Lanthanide bisphthalocyanine (LnPc$_2$) complexes exist as green (neutral) or blue (reduced) forms. Neutral LnPc$_2$ complexes exist as stable radicals with an unpaired electron on an orbital delocalized over two phthalocyanine (Pc) rings [14]. This is usually referred to as the "green" form, Pc^{1-}Ln^{3+}Pc^{2-}. One-electron reduction leads to the formation of the so called blue form, [Pc^{2-}Ln^{3+}Pc^{2-}]$^{-}$. There has been extensive studies on the extent of hole delocalization in green (neutral) forms in order to understand the nature and extent of interactions in these molecules [15–18]. LnPc$_2$ complexes show improved optical nonlinearities due to their expanded electron π system and the presence of the heavy lanthanide central metal [19–21] which enhances the rate of intersystem crossing (ISC) to the triplet state. We have recently reported on the improved nonlinear optical (NLO) behavior of the blue (reduced) form of bis{2,3,9,10,16,17,23,24-octa(4-*tert*-butylphenoxy)phthalocyaninato}lutetium(III) complex compared to the green form [22]. While the reported complex contains the diamagnetic lutetium(III) central metal cation, the complex studied in the current work contains Yb(III) ion which is paramagnetic. This means that the reduced form of a Pc ring will still contain a paramagnetic central metal which may affect the NLO behavior. Thus, we continue our studies on the effect of reduction on NLO of LnPc$_2$, this time using a paramagnetic central metal. The NLO properties of Pcs have been shown to be based on reverse saturable absorption (RSA) mechanisms [23]. RSA depends on the differences in the excited state absorption (ESA) of the singlet and triplet states, where ESA in the triplet state has to be larger. Paramagnetism shortens triplet state lifetimes hence reducing ESA. This work explores the effect of the paramagnetic central metal on the NLO behavior of a LnPc$_2$ derivative.

This manuscript presents the synthesis of bis{1(4), 8(11), 15(18), 22(25)-tetra(4-*tert*-butylphenoxy)phthalocyaninato} ytterbium(III) (**2a**) (Scheme 1) and its NLO properties in comparison with those of its blue form. Complex **2b** was obtained by reduction of **2a** using hydrazine. Only the ring is expected to be reduced from Pc^{1-}Ln^{3+}Pc^{2-} (for **2a**) to [Pc^{2-}Ln^{3+}Pc^{2-}]$^{-}$ (for **2b**). The central ytterbium will remain paramagnetic. The tetrasubstituted derivatives are employed in this work since they show improved solubility compared to the symmetrically octasubstituted derivatives (employed in the previous work [22]) due to the presence of four positional isomers in the former [24]. For practical purposes in NLO applications, Pc complexes are embedded in thin films of polymers such as poly(methyl methacrylate) (PMMA) [25] or poly(bisphenol A carbonate) (PBC) [26] resulting in improved optical limiting behavior compared to when in solution. Recently, poly(acrylic acid) (PAA) [27] was shown to result in improved optical limiting behavior when compared to PMMA, hence the employment of the former in this work.

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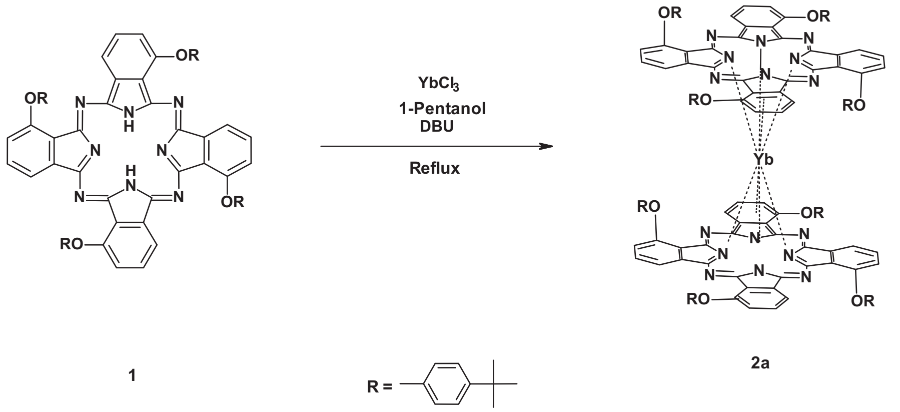

Scheme 1. Representation for the preparation of bis{1(4), 8(11), 15(18), 22(25)-tetra(4-*tert*-butylphenoxy)phthalocyaninato} ytterbium(III) (**2a**).

2. Experimental

2.1. Materials

Dimethyl formamide (DMF) was purchased from SAARCHEM. Deuterated chloroform ($CDCl_3$), ytterbium(III) chloride, 1-pentanol and poly(acrylic acid) (PAA) were purchased from Sigma–Aldrich. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and alpha-cyano-4-hydroxycinnamic acid were purchased from Fluka. Compound **1** was synthesized according to the literature method [28].

2.2. Synthesis of bis{1(4), 8(11), 15(18), 22(25)-tetra(4-tert-butylphenoxy) phthalocyaninato} ytterbium(III) (2a)

Compound **1** (100 mg, 0.090 mmol) and ytterbium(III) chloride (23.00 mg; 0.082 mmol) were transferred into a round bottom flask. 1-Pentanol (15 mL) and DBU (0.5 mL) were added into the reaction vessel. The reaction mixture was heated at reflux temperature for 21 h and then cooled down to room temperature. The green product was eluted as a second band from a column chromatography packed with silica, using chloroform and *n*-hexane (*v*/*v*; 3:2) as a solvent mixture, and dried in vacuum. Yield: (13%). IR: [KBr, ν, cm^{-1}] 747, 776, 802, 826, 878, 933, 958, 969, 999, 1011, 1044 (Pc skeleton), 1072, 1108, 1173, 1247, 1290, (C–O–C), 1318 ($Pc^{\cdot-}$ IR marker), 1360, 1391, 1411, 1477, 1504, 1588, 1729 (benzene, pyrrole, isoindole and aza), 2866, 2927, 2954 (C–H, aromatic or CH_3, *tert*-butyl). UV–Vis (DMF): λ_{max} nm ($\log\varepsilon$), 324 (4.78), 631 (4.54), 701 (4.96). Anal. Calc. for $C_{144}H_{128}N_{16}O_8Yb$: C, 72.56; H, 5.41; N, 9.40. Found: C, 72.27; H, 5.15; N, 9.15%. ^1H NMR ($CDCl_3$): δ, ppm: 6.86–6.85 (28H, m, Ar), 6.29–6.28 (28H, m, Ar), 1.72–1.58 (72H, m, t-Butyl). MS (MALDI-TOF): (*m*/*z*): Calc. 2384 amu. Found: 2390 amu [$M+6H^+$].

2.3. Preparation of PAA thin films

PAA (200 mg) was added to DMF (2.5 mL) and the mixture stirred at room temperature in an airtight vial. Complex **2a** (2.02 mg, 0.86 μmol) was transferred to the well dissolved PAA solution and stirred for another 24 h. The mixture was then transferred onto a clean thin glass slide and dried in the oven at 110 °C as reported previously [27]. Complex **2a** was then reduced to form **2b**. The latter was not isolated from solution since it readily oxidized back to **2a**. Hence, no thin films were prepared for **2b**. The thin film (TF) prepared from **2a** is represented as **2a-TF**. Film thickness (~8 μm) was determined by utilization of the knife edge attachment of the Bruker D8 Discover X-ray diffraction (XRD) following removal of the films from the glass slides.

2.4. Equipment

Infrared spectra were recorded on a Perkin Elmer 100 ART FT-IR spectrometer. Ultraviolet–visible spectra (UV–Vis) were recorded on a Shimadzu UV–Vis 2550 spectrophotometer. ^1H NMR nuclear magnetic resonance signals were recorded on a Bruker AMX 300 NMR spectrometer. Elemental analyses were carried out on a Vario EL III MicroCube CHNS Analyzer. Mass spectral data were collected with a Bruker AutoFLEX III Smart beam TOF/TOF Mass spectrometer. The spectra were acquired using α-cyano-4-hydroxycinnamic acid MALDI matrix, and a 355 nm Nd:YAG laser as the ionizing source.

All *Z*-scan experiments described in this study were performed using a frequency-doubled Nd:YAG laser (Quanta-Ray, 1.5 J/10 ns fwhm pulse duration) as the excitation source, as described before [27].

2.5. The nonlinear optical parameters

Using nonlinear regression technique, all open aperture *Z*-scan data were fitted with Eqs. (1)–(3), where the normalized transmittance (T_{Norm} (z)) is defined as a function of position [29–31] as described by Sheik-Bahae and co-workers.

$$T_{Norm}(z) = \frac{1}{\sqrt{\pi}q_0(z)}\int_{-\infty}^{\infty} \ln[1 + q_0(z)e^{-\tau^2}]d\tau \quad (1)$$

In Eq. (1),

$$q_0(z) = \frac{\beta_{eff} I_0 L_{eff}}{1 + (z/z_0)^2} \quad (2)$$

where, β_{eff} and I_0 are the effective intensity dependent nonlinear absorption coefficient and the intensity of the beam at focus, respectively. L_{eff} is the effective thickness of the sample and is given by Eq. (3) [31,32]. z and z_0 are sample position with respect to the input intensity and Rayleigh length (defined by $\pi w_0^2/\lambda$; λ = wavelength of the laser beam and w_0 = beam waist at the focus ($z = 0$)), respectively.

$$L_{eff} = \frac{1 - e^{-(\alpha L)}}{\alpha} \quad (3)$$

where α and L are the linear absorption coefficient and the thickness of the sample respectively.