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Enhanced nonlinear optical properties of octa-substituted lead and cadmium phthalocyanines when embedded in poly(bisphenol A carbonate) as thin films

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ABSTRACT

This work presents photophysical and nonlinear optical properties of a novel Cd 2,3-[octakis{4-tert-butylphenoxyphthalocyanine}] (CdOtBPPc) and compare them with those of Pb 2,3-[octakis{4-tert-butylphenoxyphthalocyanine}] (PbOtBPPc). For both the CdOtBPPc and PbOtBPPc, third order imaginary susceptibility and second order hyperpolarizability values were found to be within the limit set for good optical limiters. The Pcs were embedded in poly (methyl methacrylate) (PMMA) and poly(bisphenol A carbonate) (PBC) as thin films. The optical limiting values of the Pcs once embedded in film were found to be greatly improved and the limiting fluence of each film was well below the maximum threshold. Both PbOtBPPc and CdOtBPPc showed better optical limiting when embedded in PBC compared to PMMA. CdOtBPPc shows better nonlinear optical behavior than PbOtBPPc in solution and as thin films, even though the former is aggregated in solution.

1. Introduction

Optical limiting (OL) materials have become a subject of much research due to the need to protect sensitive optical devices, especially human eyes from high intensity light sources such as lasers [1]. When exposed to very intense light, OL materials limit the output energy of the emerging beam [1]. Molecules which exhibit this property do so due to the fact that their excited triplet state becomes more populated than their ground state. This phenomenon is known as reverse saturable absorption (RSA), as opposed to saturable absorption (SA) seen in most molecules [2].

Phthalocyanines (Pcs) have shown potential applications as optical limiters, optical switches and optical signal-processing devices [3–13]. Pcs are tunable by changing peripheral or non–peripheral substituents or the central metal [14–16]. MPcs containing heavy central metals exhibit better optical limiting due to the heavy metal effect, which enhances the intersystem crossing through spin orbit coupling, leading to a higher triplet state population [17].

In this work, we report on the nonlinear optical (NLO) properties of Pb (PbOtBPPc) and Cd (CdOtBPPc) octa-tert butyl phenoxy phthalocyanines. The synthesis of PbOtBPPc has been reported before [18], while that of CdOtBPPc is reported here for the first time. It has been reported before that using phenoxy substituents at the peripheral (β) positions of the Pc ring, results in better optical limiting behavior than non-peripheral (α) substitution, and also that octasubstitution shows better optical limiting than the tetra-substitution [19]. Hence peripherally octasubstituted PbPc and CdPc derivatives are employed in this work. The past work has shown that Pcs that are asymmetrically substituted at the ring show better optical limiting behavior than symmetrically substituted ones [20]. PbPc derivatives are known to be of C_{4v} geometry, due to the central metal being out of the plane of the ring in a "shuttle-cock" arrangement [20]. This lowering of symmetry is expected to enhance nonlinear optical behavior. The NLO data previously reported for PbOtBPPc were obtained through calculations using triplet absorption [18]. The data reported in this work are obtained from Z-scan analyses at 532 nm. NLO behaviour of CdPc derivatives (also containing a heavy metal Cd) has not received much attention hence is reported in this work.

Practical optical limiting devices require the casting of the optically active compounds in the solid state. The NLO behavior of PbPcs has been reported in solution [21,22]. In this work both PbOtBPPc and CdOtBPPc are embedded in polymer to form thin films for NLO studies. Poly (methyl methacrylate) (PMMA) has been the preferred polymer for embedding Pcs for OL [23,24] and was employed in this work and compared with when poly(bisphenol A carbonate) (PBC) is employed, the structures of the polymers

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are shown in Fig. 1. Thus, PbOtBPPc and CdOtBPPc complexes are separately embedded in PBC or PMMA. PBC has been used as a material for making safety visors in the past and has great affinity for modification [25]. This is the first time PBC is used to embed phthalocyanines for NLO applications.

2. Experimental

Details of the equipment employed in this can be found in the Supplementary information.

2.1. Materials

N,N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO), dichloromethane (DCM), methanol, ethanol and 1-octanol were purchased from Merck. Poly(bisphenol A carbonate) (PBC, average molecular weight ~28 200 g/mol), poly(methyl methacrylate) (PMMA, average molecular weight ~120 000 g/mol), Cd chloride hemi(pentahydrate), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and urea were from Sigma Aldrich. DMF, DMSO and DCM were dried using molecular sieves (0.4 nm, rods). Pb 2,3-[octakis{4-tert-butylphenoxyphthalocyanine}] was synthesized according to literature methods [18]. 4,5-Bis(4-t-butylphenoxy) phthalonitrile was synthesized according to literature [26].

2.2. Fabrication of films

Solutions of CdOtBPPc (5.6×10^{-4} M) and PbOtBPPc (6.6×10^{-4} M) in dichloromethane were prepared. To 5 mL of each of these solutions, 0.3 g of PBC or 0.6 g of PMMA were added to form PBC/PbOtBPPc, PBC/CdOtBPPc, PMMA/PbOtBPPc and PMMA/CdOtBPPc solutions. The film was prepared by placing 1 ml of solution in a small glass petri dish, and placing it under vacuum (~10^{-3} Torr) until the solvent was completely removed. The NLO activity of the film was determined using the Z-scan set up and the film thickness was determined using scanning electron microscopy.

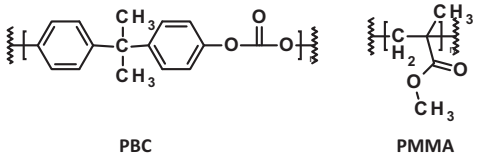
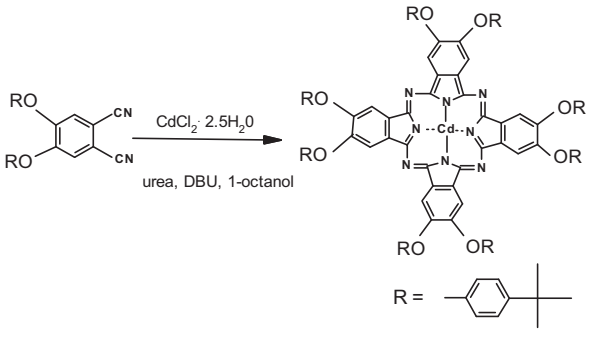


Fig. 1. Structure of a unit of poly(Bisphenol A Carbonate) (PBC) and poly(methyl methacrylate) (PMMA).



Scheme 1. Synthesis of Cd 2,3-[octakis{4,5-tertbutylphenoxy phthalocyanine}].

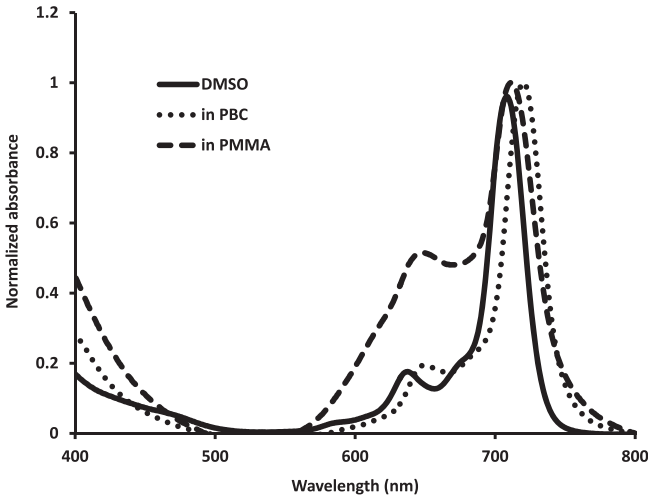


Fig. 2. Ground state absorption spectra for PbOtBPPc in DMSO, PBC and PMMA.

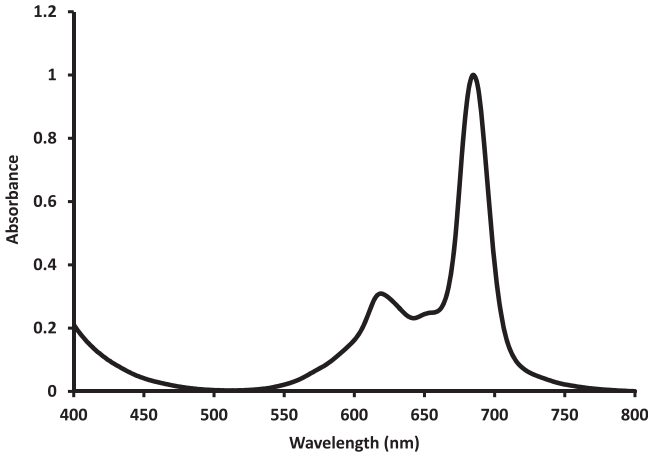


Fig. 3. Ground state absorption spectra of CdOtBPPc in DMSO (concentration: ~9×10^{-5} M).

2.3. Synthesis of CdOtBPPc

Under a blanket of argon, 4,5-bis(4-t-butylphenoxy) phthalonitrile (0.30 g, 0.71 mmol) was dissolved in 1-octanol (7 ml). Cadmium chloride hemi(pentahydrate) (0.046 g, 0.19 mmol) was then added to the solution along with urea (0.043 g, 0.7 mmol) and the reaction mixture refluxed at 180 °C overnight under argon. After cooling, the product was refluxed in ethanol for an additional 2 h. The final product was sequentially washed with methanol and water using a centrifuge. A silica column was employed to further purify using tetrahydrofuran as the eluent.

Yield: 0.18 g (56%). UV–Vis (DMSO): λ_{max} nm (log ε) 684 (4.84), 624 (4.09), 345 (4.40), IR [ν_{max}/cm^{-1}]: 1244 (C–O–C), 1013, 991, 890, 865, 826, 740, 722 (Pc skeletal), 1307 (C–N), 1391, 1363 (–C–H), 1599 (C=C), 2958 (C–H). ^{1}H NMR (DMSO-d^6): δ, ppm 7.26–8.02 (16H, m, Phenyl–H), 7.01–7.22 (12H, m, Phenyl-H), 6.46–6.98 (12H, m, Phenyl-H), 0.97–1.08 (72H, m, methyl-H). *Anal.* Calc. for $C_{112}H_{112}N_8O_8Cd{\cdot}8H_2O$: C, 68.82; H, 6.60; N, 5.73. Found: C, 68.50; H, 7.41; N, 5.56%. MS (Maldi-TOF) *m*/*z*: Calcd. 1814.7; Found: 1811.7 [M−3H]$^+$.

2.4. Photophysical parameters

Triplet ($_T$) and fluorescence ($_F$) quantum yields were determined using the comparative methods as described before [27–29]. ZnPc