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Nonlinear optical behavior of neodymium mono- and bi-nuclear phthalocyanines linked to zinc oxide nanoparticles and incorporated into poly acrylic acid

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ABSTRACT

Syntheses of bis{23-(3,4-di-yloxybenzoic acid)-(2(3), 9(10), 16(17), 23(24))-(hexakis-pyridin-3-yloxy phthalocyaninato)} dineodymium (III) acetate (**3**) and 2(3), 9(10), 16(17), 23(24)-(tetrapyridin-3-yloxy phthalocyaninato) neodymium (III) acetate (**4**) as well as their conjugates with ZnO nanoparticles (conjugates **6**, **7** and **8**) are presented. Thin films of conjugate **6** (where complex **3** is linked to ZnO nanoparticles via an amide bond) gave the best third-order susceptibility (5.89×10^{-8} esu), second-order hyperpolarizability (2.53×10^{-25} esu) and the lowest limiting threshold values ($0.12\ J\ cm^{-2}$). The nonlinear behavior is enhanced in solid state when compared to solution.

1. Introduction

Phthalocyanines (Pcs) are synthetically interesting molecules because of their structural flexibility. Due to their possible linkage to other molecules, and coordinating nature of their rings, Pcs can be modified into multinuclear forms which include dimers and trimers [1–10] and multi-decker forms [11,12]. In this work, we present binuclear phthalocyanines (Bi-Pcs) where the Pc molecules are held together by an organic molecule acting as a bridge. Such Pc structures are unsymmetrical. Lack of symmetry is known to improve nonlinear optical behavior [13,14]. However, solubility of Pcs remains a challenge, and can be enhanced by bulky substituents [15,16]. To the best of our knowledge, the nonlinear optical (NLO) behavior has been studied only for indium-based Bi-Pcs [13], using a Z-scan technique. Due to limited data on NLO behavior of binuclear Pcs, we study the optical limiting potential of neodymium based binuclear Pc (**3**, Scheme 1B) in comparison with its monomer derivatives (**4**, Scheme 1C) in solution and thin films. Enhanced NLO behavior is expected for **3** due to its low symmetry [13,14].

For practical applications, phthalocyanine complexes are embedded in thin films of polymers such as poly (methyl methacrylate) (PMMA) [17,18] or poly (bisphenol A carbonate) (PBC) [19] resulting in improved optical limiting behavior compared to solution. Recently [20], poly acrylic acid (PAA) was shown to result in improved optical limiting behavior when compared to PMMA, hence the former is employed in this work. The Pc complexes are linked to ZnO nanoparticles (ZnO NPs) since the latter show good NLO [21]. Hence the combination of the two NLO materials (Pc and ZnO NPs) is expected to improve NLO behavior. The ZnO NPs are linked to the Pc complexes using different strategies in order to compare the effects of different linkages on the photophysical and NLO behavior.

Bi-Pcs of the type shown in Scheme 1B are known for Zn as the central metal (with different substituents and linkers) and often referred to as clam shell [22,23]. But the derivatives containing lanthanide central metals are non-existent, and are reported in this work for the first time. Photophysical and NLO behavior of the neodymium based Pcs (alone or linked to ZnO NPs) are studied in solution or when embedded in thin films of PAA.

2. Experimental

2.1. Materials

Dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and ethanol were purchased from SAARChem. (3-Aminopropyl) triethoxysilane (APTES) and neodymium (III) acetate hydrate, deuterated dimethyl sulfoxide (DMSO-d_6), dicyclohexylcarbodiimide (DCC), 1-pentanol, poly acrylic acid (PAA), 3-nitrophthalonitrile, p-toluenesulfonic acid (*p*-TSA), potassium carbonate and

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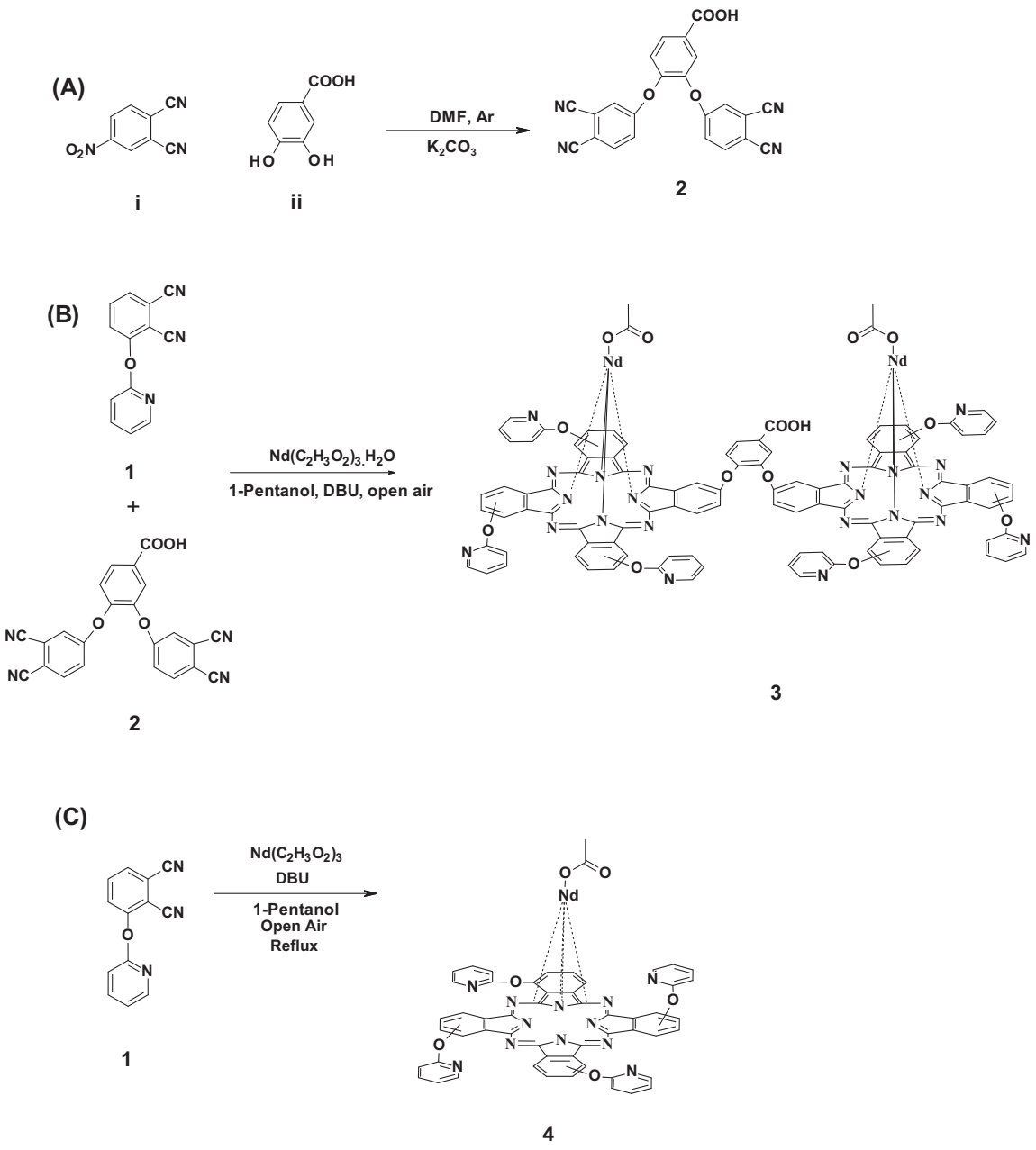

Scheme 1. Synthesis of complexes (A) **2**, (B) **3** and (C) **4**.

trifluoroacetic acid (TFA) were purchased from Sigma–Aldrich. Tetrahydrofuran (THF) was purchased from MINEMA. 3,4-Dihydroxybenzoic acid and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Fluka. 3-(Pyridine-2-yloxy)-phthalonitrile (**1**) was synthesised according to a literature method [24]. The synthesis of ZnO NPs containing APTES (represented as **5** in Scheme 2A) has been reported before [25].

2.2. Synthesis

2.2.1. Synthesis of 3,4-bis-(3,4-dicyano-phenoxy)-benzoic acid (*2*) (Scheme 1A)

3-Nitrophthalonitrile (**i**, 2.00 g; 9.75 mmol), 3,4-dihydroxybenzoic acid (**ii**, 751 mg; 4.87 mmol) and DMF (25 mL) were added together in a round bottom flask (250 mL). The reaction mixture was purged with argon for 10 min before the addition of potassium carbonate (20.00 g; 144.71 mmol), followed by constant stirring under inert atmosphere at room temperature for 48 h. The product was then poured into ice water, followed by addition of concentrated hydrochloric acid. The precipitate was washed several times with water and methanol and dried at 60 °C in the oven.

Yield: 17%. IR: [KBr, υ, cm^{-1}] 776, 804, 844, 860, 881, 904, 921, 950, 961, (benzene ring) 1092, 1110, 1171, 1197, 1242, 1273, 1372, 1414, 1436, 1482, 1497, 1568, 1592 (C—O—C), 1722, 1740 (C═O), 2232 (C≡N) 3033, 3078 (C—H, aromatic), 3247 (OH). ^{1}H NMR (DMSO-d_6): δ, ppm 13.44 (1H, s, COOH), 8.09–8.05 (2H, q, Ar-H), 7.97–7.97 (1H, d, Ar-H), 7.87–7.83 (3H, m, Ar-H), 7.50–7.45 (3H, m, Ar-H).

2.2.2. Synthesis of bis{23-(3,4-di-yloxybenzoic acid) (2(3), 9(10), 16 (17), 23(24)-(hexakis-pyridin-3-yloxy phthalocyaninato)} dineodymium (III) acetate (*3*) (Scheme 1B)

Complex **3** was synthesized by refluxing compounds **1** (400 mg; 1.95 mmol) and **2** (132 mg; 0.325 mmol) in 1-pentanol (15 mL) and DBU (0.5 mL) in the presence of neodymium acetate hydrate (229 mg; 0.713 mmol) for 21 h in open air. The green solution