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Optical limiting response of multi-walled carbon nanotube-phthalocyanine nanocomposite in solution and when in poly (acrylic acid)

Kutloano Edward Sekhosana, Tebello Nyokong*

Department of Chemistry, Rhodes University, PO Box 94, Grahamstown 6140, South Africa

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ABSTRACT

Bis{23-(3,4-di-yloxybenzoic acid)-(2(3), 9(10), 16(17), 23(24)-(hexakis-pyridin-3-yloxy phthalocyaninato)} dineodymium (III) acetate (**3**) is linked to amino-functionalized multi-walled carbon nanotubes (MWCNT) to form **3**-MWCNT. Z-scan technique was employed to experimentally determine the nonlinear absorption coefficient from the open-aperture data. The limiting threshold values as low as 0.045 J cm^{-2} were found in solution. The conjugate (**3**-MWCNT) gave better optical limiting behavior than complex **3** alone.

1. Introduction

Carbon nanotubes (CNTs) have appealing properties such as tunable surface functionalities, well-defined hollow interiors, and biocompatibility with living systems [1–3]. CNTs may be either metallic or semiconducting [4]. These properties are the backbone of many applications of CNTs, including in electronics [5–7], optical limiting [8,9], drug delivery systems, electronic devices, sensors and actuators [10,11]. Multi-walled carbon nanotubes (MWCNTs) are a subject of this work. Since the investigation of optical limiting mechanism of carbon based materials including MWCNTs by Sun et al. [12], many researchers have followed up by chemically modifying MWCNTs for optical limiting purposes [13–21].

Phthalocyanines (Pcs), on the other hand, are well known as optical limiting materials [22–25] due to their highly conjugated π–electron system. MWCNTs have been non-covalently functionalized with different metal phthalocyanines by π-π stacking method for NLO studies [26–28]. Covalent attachment of Pcs to MWCNTs for NLO studies is not known even though single walled carbon nanotubes (SWCNT) have been covalently attached to Pcs for this application [29]. Depending on the solvent, an increase or decrease on the NLO parameters of the phthalocyanines was observed in the presence of SWCNT [29]. In this work, we present the optical liming properties of phthalocyanine covalently attached to MWCNTs in solution and when embedded in poly (acrylic acid) thin films. A binuclear phthalocyanines (Bi-Pcs, **3** in Scheme 1) where the Pc molecules are held together by an organic molecule acting as a bridge is employed. Such Pc structures are unsymmetrical. Lack of symmetry is known to improve nonlinear optical behavior [30]. Even though both MWCNTs and Pcs are optical limiting materials, their combination does not always lead to improved NLO behavior [31]. It has been reported that since CNTs solutions are in the form of a dispersion, their optical limiting behaviour is due to scattering combined with possible electronic absorption contributions [31,32]. The aim of this work is to elucidate the mechanism used for NLO for complex **3** in the presence of MWCNTs.

For practical applications, phthalocyanine complexes are embedded in thin films of polymers. Recently [33], poly (acrylic acid) (PAA) was shown to result in improved optical limiting behavior when compared to other polymers such as poly (methyl methacrylate) (PMMA), hence the former is employed in this work. Diaminomaleonitrile is used for surface modification of MWCNTs for linkage to carboxyphenoxy-substituted Pcs.

* Corresponding author.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

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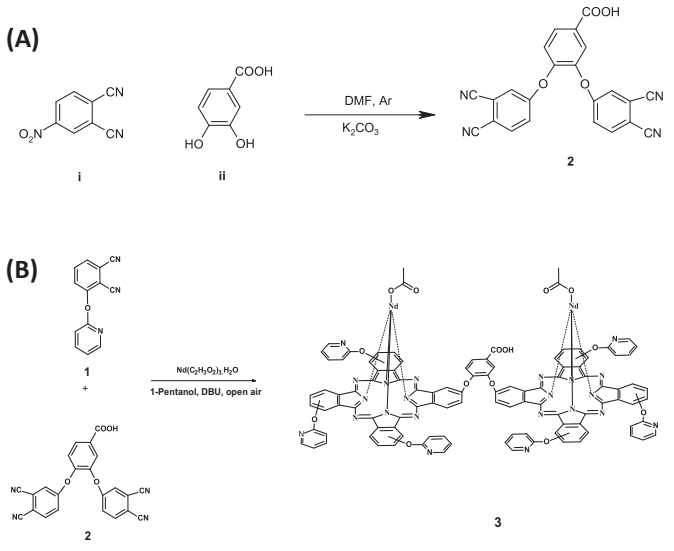
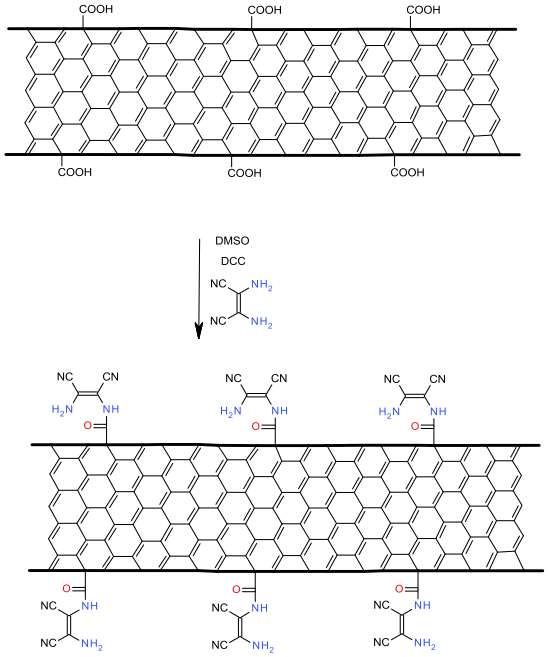


Scheme 1. Synthesis of complexes (A) **2** and (B) **3**.



Scheme 2. Synthesis of diaminomaleonitrile-functionalized MWCNTs.

2. Experimental

2.1. Materials

Dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dimethyl formamide (DMF) and ethanol were purchased from SAARCHEM. Neodymium (III) acetate hydrate, deuterated dimethyl sulfoxide (DMSO-d_6), dicyclohexylcarbodiimide (DCC), 1-pentanol, poly (acrylic acid) (PAA), trifluoroacetic acid (TFA), diaminomaleonitrile, 3-nitrophthalonitrile, and multi-walled carbon nanotubes (MWCNT, 110–170 nm length), were purchased from Sigma–Aldrich. Ethyl acetate was purchased from MINEMA. 3,4-Dihydroxybenzoic acid and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Fluka. All chemicals used were of analytical grade and were used as received without any further purification. 3-(Pyridine-2-yloxy)-phthalonitrile (**1**) was synthesised according to a literature method [34]. Acid (COOH) functionalization of MWCNT was performed as reported in literature [29,35].

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 to obtain a white powder.

Yield: 17%. IR: [KBr, ν, cm^{-1}] 776, 804, 844, 860, 881, 904, 921, 950, 961, (benzene ring) 1092, 1110, 1171, 1197, 1242, 1273, 1372, 1414, 1436, 1482, 1497 (C– O– C), 1568, 1592 (C═O), 1722, 1740 (–C═N–), 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) in the presence of DBU (0.5 mL) and neodymium acetate hydrate (229 mg; 0.713 mmol) for 21 h in open air. The green solution was cooled to room temperature and centrifuged several times at 3000 rpm in THF and methanol to obtain a green solid. After drying at 100 °C, the product was subjected to Soxhlet extraction using THF as a solvent. The Soxhlet extraction vessel was cooled to room temperature to obtain a green solid which was dried in open air. Further purification was achieved by subjecting the green product to a reverse phase column using THF and DMSO solvent system (4:1; v/v) which helped to obtain a green band. The remaining band in the column was further eluted with DMSO to which TFA (5 drops at a time) was added. Ice water was added to the obtained green solution and neutralized with ammonia to get a green precipitate which was washed in water and methanol respectively. On drying at 110 °C, a blue product was obtained.

Yield: 60%. IR: [KBr, ν, cm^{-1}] 747, 810, 837, 872, 888, 900, 953, 974 (Pc skeleton), 1038, 1080, 1123, 1213, 1236, 1269, 1287, 1325, 1374, 1388, 1481, 1553, 1573 (C– O– C), 1655 (C═O), 1712, 1773 (-C═N-), 2850, 2924 (C– H, aromatic), 3326 (OH). UV–Vis (DMSO): λ_{max} nm (log ε) 336 (4.66), 564 (3.82), 656 (4.60). Anal. Calc. for $C_{105}H_{58}N_{22}O_{12}Nd_2$. C, 58.93; H, 2.73; N, 14.45. Found: C, 59.35; H, 3.4; N, 15.12%. ^{1}H NMR (DMSO-d_6): δ, ppm 8.21 (1H, s, COOH), 8.03 (3H, s, Ar– H), 7.90 (16H, s, Ar– H), 7.66–6.64 (16H, m, Ar– H), 7.58–7.56 (16H, m, Ar– H), 1.36–1.19 (6H, m, methyl). MS (MALDI-TOF): (m/z): Calc. 2140 amu. Found: 2144 amu [M+4H$^+$].

2.2.3. ***Functionalization of MWCNTs with*** *diaminomaleonitrile (amino-MWCNTs, Scheme 2)*

MWCNTs were functionalized with acid as reported before for SWCNTs [29]. Acid functionalized MWCNTs were linked to diaminomaleonitrile for further attachment to complex **3** as follows: