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Synthesis and characterization of tetra phenoxy-substituted halogen-rich metallophthalocyanine derivatives: A study on their LCD color filter requirements

Palanisamy Muthukumar [a, b], Hak-Soo Kim [a], Jong Woo Jeong [a], Young-A. Son [a, *]

[a] Department of Advanced Organic Materials Engineering, Chungnam National University, Daejeon, 305-764, South Korea
[b] Department of Physical Sciences, Bannari Amman Institute of Technology, Sathyamangalam, 638 401, Erode Dt, Tamil Nadu, India

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ABSTRACT

This study addresses the synthesis and characterization of new tetra phenoxy-substituted halogen-rich metallophthalocyanine derivatives (MPcs) **4**–**7** (M = Co, Ni, Cu and Zn). The synthesized new compounds were characterized using UV–Vis, FT-IR, MALDI-TOF, ^{1}H NMR and elemental analyses. In addition, the basic requirements such as aggregation behavior, thermal stability, transmittance and solubility in propylene glycol monomethyl ether acetate (PGMEA) of MPcs **4**–**7** were investigated for their usage as a green color filter in Liquid Crystal Displays (LCDs). All of the MPcs showed thermal stability and sufficient solubility in PGMEA. However, the addition of binder into PGMEA solution of MPcs **5** and **6** leads to precipitation. Among the four MPcs, zinc phthalocyanine (**7**) showed higher transmittance. The higher transmittance of zinc phthalocyanine (**7**) along with its thermal stability and sufficient solubility in PGMEA are promising for its application as a green color filter in LCDs.

1. Introduction

Phthalocyanine (Pc) derivatives are synthetic analogs of porphyrins, which composed of N-fused four diimidazole rings and delocalized with 18 π electrons. Since the first synthesis of metal-free and metal-inserted Pcs by Linstead and co-workers in 1930s, many studies have been devoted to the exploration of their synthesis and properties [1,2]. Due to their unique color, optical and electronic properties [3] along with their chemical and thermal stability [4], metallophthalocyanine derivatives (MPcs) attracted much attention in various fields such as liquid crystal displays (LCDs) [5], sensors [6,7], dye-sensitized solar cells [8], photodynamic therapy [9], semiconductors [10] and dye stuffs [11]. The physical and chemical properties of MPcs can be tuned by changing the substituents and metal ions on the Pc ring. When electron-releasing groups are attached to the four α-positions of the Pc ring, the B and Q bands shift to longer wavelength. The introduction of electron-releasing groups at the β-positions of the Pc ring generally shifts the Q band to a shorter wavelength. The effect of electron-withdrawing groups is exactly the opposite with respect to the α- and β-positions [12]. Generally, Pc molecules are referred to as planar aromatic macrocycles; however, some metal ions larger or smaller than the phthalocyanine inner core can deform the planarity of these derivatives [13,14]. The UV–vis spectra of monomeric Pc derivatives showed two typical absorption bands, the B and Q-bands, which can be explained by Gouterman's four orbital model [15].

Due to their very compact, lightweight, low power consumption and inexpensive, LCD modules are widely used in a variety of electronic display devices. The LCD is composed of red, green and blue color filters. Copper phthalocyanine without any substituents on peripheral and non-peripheral positions know as pigment blue. The peripheral and non-peripheral positions of copper phthalocyanine substituted with halogen atoms known as pigment green. MPcs, such as C.I. Pigment green 36, C.I. pigment blue 15:6, 15:3, 15:2, have been widely used as colorants for the fabrication of blue and green pixels of LCD color filters [16–19]. Most of the MPcs are green in color, which transmits the light within the range of 520–560 nm. Since green color is most sensitive to human eyes, it posses greatest contribution to the optical property of color filters [20,21]. The strong green color of pigment green arises from the large red shift of the Q band due to the presence of strongly

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* Corresponding author.
E-mail address: yason@cnu.ac.kr (Y.-A. Son).

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electronegative chlorine atoms [22]. The problem associated with this pigment is its solubility. Hence, it is necessary to find out the suitable material to replace the green pigment. The poor solubility of MPcs restricts their application in several fields [23,24]. To increase the solubility of these derivatives, several solubilizing substituents, such as alkyl, alkoxy and phenoxy groups, have been introduced at the α- and β-positions of the Pc core [25–30]. Unfortunately, most of the substituted Pcs are not as stable as the unsubstituted compounds, and their electronic properties are different from those of the unsubstituted derivatives [31,32].

The Pc derivatives tend to form aggregates. The aggregates in solution exhibit distinct changes in the Q band compared with the monomeric species. The blue shift in the Q band indicates the presence of H-type aggregates, whereas the red shift in the Q band indicates the presence of J-type aggregates [33,34]. To control aggregation, several methods of Pc preparation have been adopted, such as the introduction of substituents at α- and β-positions and the octahedral co-ordination of the central metal ion [35,36]. It is well documented that solvents affect the aggregation behavior of MPcs. Organic solvents reduce the aggregation behavior of MPcs compared with an aqueous medium. However, many MPcs showed aggregation even in organic solvents [37–41].

In order to use a dye as color filter in LCD, the prepared dye should possess qualities such as stability at high temperatures (~250 °C), low aggregation, high transmittance and high solubility in industrial solvents, such as propylene glycol monomethyl ether acetate (PGMEA), 1-methoxy-2-propanol or ethyl-3-ethoxy propionate. Therefore, in this study, we made an attempt to synthesize tetra phenoxy-substituted halogen-rich MPcs and studied their aggregation behavior, thermal stability, transmittance property and solubility in PGMEA.

2. Experimental

2.1. Chemicals and instruments

Tetrachlorophthalonitrile, PGMEA and pentanol were purchased from TCI chemicals. 1,8-Diazabicycloundec-7-ene (DBU), $CoCl_2$, $Ni(OCOCH_3)_2$, $Cu(OCOCH_3)_2$ and $Zn(OCOCH_3)_2$ were purchased from Aldrich. All other reagents and solvents were of analytical grade, were obtained from Samchun chemicals and were used as received. All reactions were performed under nitrogen atmosphere, and the reaction progress was monitored using thin layer chromatography (TLC). Column chromatography was performed with 230–400 mesh silica gel purchased from Merck. Transparent glass plates were supplied by the Duran group. Binder was provided by LG chemicals.

Electronic absorption spectra were recorded on an Agilent 8453 spectrophotometer. FT-IR spectra were recorded with an FTS-175C spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference at ambient temperature. The NMR spectra were mainly recorded on a BRUKER AVANCE III 300 Magnet: Ascend TM series, 14.1 T, ^1H resonance frequency 300 MHz and AVANCE III 600 Magnet: Ascend TM series, 14.1 T, ^1H resonance frequency 600 MHz, Top Spin 3.1 (software) spectrometers. Elemental analyses were performed using the Thermo Scientific FLASH 2000 series. The melting point was determined using a Barnstead Electrothermal 9200 apparatus. Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI-TOF) mass spectra were collected on a Bruker Autoflex III with Sinapinic acid as the matrix. Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere at a heating rate of 10 °C/min using a Mettler-Toledo Thermogravimetric Analyzer.

2.2. Preparation of MPc-based films

The solution for the MPc-based film was composed of acrylic binder (4.03 g), PGMEA (0.95 g) and MPc (0.02 g). The thin film was prepared by spin coating the composed material (1.5 ml) on a transparent glass slide using spin coater JS301. The coating speed was initially 50 rpm for 10 s, increased to 350 rpm and kept constant for 100 s. All spin coated MPc based films were 1.8 μm in thickness.

2.3. Synthesis of 4-(3-diethylamino)phenoxy-3,5,6-trichlorobenzene-1,2-dinitrile (*3*)

Compound **3** was synthesized according to the reported procedure [27]. To the solution of tetrachlorophthalonitrile (**1**) (2 g, 7.5 mmol) in anhydrous DMF (15 ml), 3-(diethylamino)phenol (**2**) (1.24 g, 7.5 mmol) was added. The reaction was allowed to stir for 15 min, and finely powdered anhydrous Na_2CO_3 (1.59 g, 15 mmol) was added in portions to the reaction mixture over 1 h with efficient stirring. Then, the mixture was stirred at 30 °C for 3 h. After 3 h, the reaction was cooled to room temperature, poured into ice-cold water, extracted with ethyl acetate, washed with 1 M NaOH and washed with a brine solution. The organic layer was dried using Na_2SO_4, and the solvents were evaporated to obtain the crude product. The crude product was purified by column chromatography using hexane-ethyl acetate (90:10) as eluent. Yield (1.9 g 65%), ^1H NMR ($CDCl_3$, 300 MHz) δ, 6.99 (t, $J = 8.4$ Hz, 1H), 6.38 (dd, $J = 8.4$ & 2.1 Hz, 1H), 6.22 (t, $J = 2.1$ Hz, 1H), 5.68 (dd, $J = 7.8$ & 1.5 Hz, 1H), 3.26 (q, $J = 6.9$ Hz, 4H) 1.10 (t, $J = 2.1$ Hz, 6H) (Fig. S1), ^{13}C NMR ($CDCl_3$, 75 MHz) 155.9, 152.8, 148.6, 136.2, 135.3, 132.1, 129.2, 115.7, 113.6, 110.8, 106.7, 99.1, 98.03, 43.4, 11.4 (Fig. S2). FT-IR (KBr pellet) (γ, cm^{-1}) 2980 (Ar–C–H) 2920–2880 (Aliphatic-C-H), 2235 (C≡N), 1280 (C–O–C) (Fig. S3). LC-MS: m/z 396 [M+2] (Fig. S4).

2.4. General procedures for MPcs *4*–*7*

Scheme 1 shows the general pathway for the synthesis of MPcs **4**–**7**. To a mixture of compound **3** (0.3 g, 0.76 mmol) and the corresponding anhydrous metal salts (0.19 mmol) ($CoCl_2$, $Ni(OCOCH_3)_2$, $Cu(OCOCH_3)_2$ and $Zn(OCOCH_3)_2$) in n-pentanol (5 ml), catalytic amount of DBU was added. The reaction mixture was refluxed at 140 °C for 20 h under nitrogen atmosphere. After 20 h, the reaction was cooled to room temperature, and methanol was added. The green solid product was precipitated, collected by filtration, washed with methanol and dried under vacuum. The crude product was purified by column chromatography using chloroform-methanol as eluent.

2.4.1. {2,9,16,23-Tetrakis-[3-(diethylamino)phenoxy]-1,3,4,8,10,11,15,17,18,22,24,25-dodecachloro-phthalocyaninato} cobalt(II) (*4*)

MPc **4** was synthesized by following the general procedure for MPcs. The crude green solid product was purified by column chromatography using chloroform-methanol (99:1) as eluent. Yield: 0.110 g (35%). Melting point >200 °C Anal. Calcd for $C_{72}H_{56}Cl_{12}CoN_{12}O_4$: C, 52.81; H, 3.45; N, 10.26%. Found: C, 52.90; H, 3.48; N, 10.31. FT-IR (KBr pellet) (γ, cm^{-1}) 2980 (Ar–CH), 2920–2870 (aliphatic-CH), 1600 (C=C), 1240 (Ar–O–Ar) (Fig. S5). MALDI-TOF-MS m/z: 1638 $[M + H]^+$ (Fig. S6).

2.4.2. {2,9,16,23-Tetrakis-[3-(diethylamino)phenoxy]-1,3,4,8,10,11,15,17,18,22,24,25-dodecachloro-phthalocyaninato} nickel(II) (*5*)

MPc **5** was synthesized by following the general procedure for MPcs. The crude green solid product was purified by column