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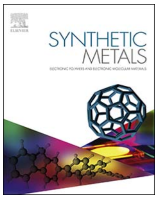

Novel homoleptic, dimeric zinc(II) phthalocyanines as gate dielectric for OFET device

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ABSTRACT

A novel multicomponent system consisting of benzene-1,4-diyldimethanimine bridged dimeric zinc-phthalocyanine groups was synthesized. Firstly, a novel unsymmetrically nitro and 2,4-di-*tert*-butylphenoxy groups substituted zinc (II) phthalocyanine was synthesized and then nitro group was reduced to amino functional group. All newly synthesized compounds were characterized by UV–Vis, FTIR, ^{1}H-NMR, MALDI-TOF MS and elemental analysis spectral data. The potential of these compounds as gate dielectric were investigated by fabricating bottom gate top contact OFET using poly 3-hexylthiophene-2,5-diyl as active layer. Field effect mobility values of 3.2×10^{-4} cm^2/V s was obtained when using ITO-coated glass as gate electrode. It was found that the density of leakage current was about 2 nA/cm^2 at 5 V. The capacitance density of 11.8 nF/cm^2 was achieved at a frequency of 5 Hz with slightly smaller values at higher frequency.

1. Introduction

Phthalocyanines are planar aromatic macrocyclic compounds with four iminoisoindolin units and conjugated 18 π-electrons in the inner core. The design of phthalocyanines substituted by the functional groups in peripheral position of the ring intimately follows the requirements of their intended applications. Therefore, research efforts have been focused on these compounds intensively in recent times, owing to their feasibility in many areas such as photodynamic therapy (PDT) [1,2], semiconductors [3], Langmuir–Blodgett films [4], nonlinear optics [5], sensing devices in the gas phase and in liquids [6,7], electrocatalysis [8,9], electrochromism [10] and liquid crystals [11]. The unique electron transfer properties of phthalocyanines facilitate the fast paced growth of the feasibility particularly in some fields like electrochromism, electrocatalysis and energy production technologies such as fuel cells and optoelectronic devices [12].

Multimeric or dimeric phthalocyanines, being multifunctional materials and having more than one phthalocyanine units on the same molecule, have been less studied [13]. The types of dimers are classified by the effect of the type of linkage between the macrocyclic units. Dimeric structures have many types such as conjugated homo and hetero dimers, linear dimers, lanthanoid and actinoid sandwich dimers and self-assembled dimeric form [14]. Polynuclear multi-electron transfer catalyst applications [15,16] commonly use such types of dimers because of their electrocatalytic properties [17].

Although monomeric phthalocyanines are widely studied, the number of dimeric phthalocyanines present in the literature much lower than of monomeric phthalocyanines. Therefore it would be attractive to study dimeric phthalocyanines and see the difference of their properties according to monomeric phthalocyanine structures.

Because of their wide applications possibilities in organic electronic devices such as flexible displays [18], electronic paper [19] and sensors [20,21], organic field-effect transistors (OFETs) have attracted great attention in the last decade. The parameters such as operating voltage and field effect mobility, which are used to characterize an OFET, controlled by the reliability of gate insulator and the density of charge traps at the dielectric–semiconductor interface. Polymeric materials such as polyvinylalcohol [22], polyvinylphenol [23] and poly(4-vinyl phenol) [24] are more interesting as gate dielectric because of their simple chemical synthesis and alteration and capabilities for a solution process. However, their use in OFETs is limited because of their low dielectric constant and high leakage current. Therefore, development of a suitable gate dielectric with high capacitance and low leakage current is essential to achieve desired OFET performance.

In this work, after their widespread use as active layer in OFETs, a new Pc compound is proposed as a dielectric layer in OFETs. For this purpose, a novel homoleptic dimeric phthalocyanine with six 2,4-di-*tert*-butylphenoxy groups were synthesized and its dielectric perfor-

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mance in an OFET as dielectric layer was investigated.

2. Experimental

2.1. Instruments and chemicals

All chemicals and solvents which were purchased in high purity and all solvents were dried on molecular sieves (4Å). 2,4-di-*tert*-butylphenol (**2**) was used as supplied commercially. 4-Nitrophthalonitrile (**1**), 4-(2,4-di-*tert*-butylphenoxy)phthalonitrile (**3**) and 4-(4-nitrophenoxy) phthalonitrile (**4**) were synthesized according to the literature [25–27]. The synthesis steps were monitored by thin layer chromatography. Infrared spectra were obtained by using a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer. A Varian Unity Inova 500 MHz spectrophotometer was used for ^{1}H NMR spectra and an Agilent 8453 UV/Vis spectrophotometer was used for Electronic spectra in the UV–Vis region. Mass spectra of the synthesized substances were obtained by using a Bruker microflex LT MALDI-TOF MS. Melting points of the substances were determined using an Electrothermal Gallenkamp device. Elemental analyses were assigned with a Thermo Flash EA 1112.

2.2. Synthesis and characterization

2.2.1. [2,9,16-Tri-(2,4-di-tert-butylphenoxy)-23-(4-[4-nitrophenoxy])-phthalocyaninatozinc(II)] (5)

1,2-dicyano-4-(4-nitrophenoxy)benzene (**4**) (0.532 g, 0.002 mol), 4-(2,4-di-*tert*-butylphenoxy)phthalonitrile (**3**) (1 g, 3 mmol), Zn $(CH_3COO)_2$ (0.1097 g, 5 mmol) and a few drops of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) in dry DMF (1.5 mL) were mixed under nitrogen for 72 h at 160 °C. The mixture was cooled to room temperature and then methanol was added to this mixture. The crude product was filtered and the green precipitate was washed with methanol and ethanol. The product was dried under vacuum and then column chromatography with hexane/$CHCl_3$ = 1:6 (v/v) as the eluent gave the desired product which was soluble in THF, acetone, dichloromethane, chloroform, DMF and DMSO.

Yield: 0.363 g (18%); m.p. > 200 °C. FTIR ν_{max}/cm^{-1}: 3071 (CH arom.), 2955, 2906, 2867 (CH aliph.), 1588, 1340 (–NO_2), 1521, 1469, (arom. C=C), 1228 (Ar–O–Ar), 1164, 1085, 1044, 944, 864, 823, 743; ^{1}H NMR ($CDCl_3$): δ, ppm: 0.90 (br, 27 H, t-BuCH_3), 1.32 (br, 27 H, t-BuCH_3), 7.01–8.56 (m, 25 H, Ar–H); Anal. Calc. for $C_{80}H_{79}N_9O_6Zn$ (1327.949 g mol): C, 72.36; H, 6.00; N, 9.49; O, 7.23; found: C, 72.01; H, 5.62; N, 10.08; O, 7.36; UV–Vis (THF): λ_{max}/nm (10^{-5} log ε, L mol^{-1} cm^{-1}): 676 (5.10), 610 (4.37), 352 (4.71); MS MALDITOF): *m/z* (%100) 1327 $[M]^+$.

2.2.2. [2,9,16-Tri-(2,4-di-tert-butylphenoxy)-23-(4-[4-aminophenoxy])-phthalocyaninatozinc(II)] (6)

Compound (**5**) (0.6 g, 0.451 mmol), hydrazine hydrate (55 mL, in excess), and in catalytic quantity of 10% Pd/C (0.1 g) in dry dioxane (70 mL) was mixed under nitrogen atmosphere for 72 h. After the mixture was cooled to room temperature, the substance was quickly filtered. The filtrate was evaporated under vacuum and then washed with ethanol and methanol. The crude dark green phthalocyanine was further purified by column chromatography with $CHCl_3$/THF = 1:100 (v/v). Finally, the desired phthalocyanine was soluble in THF, acetone, chloroform, DMF and DMSO.

Yield: 0.678 g (69.7%); m.p. > 200 °C. Anal. Calc. for $C_{80}H_{81}N_9O_4Zn$ (1297.966 g/mol): C, 74.03; H, 6.29; O, 4.93; Found: C, 73.98; H, 6.07; O, 3.89; FTIR y_{max}/cm^{-1}: 3321, 3190,1610 (NH_2), 3070 (CH arom.) 2952, 2910, 2866 (CH aliph.), 1504, 1467, 1391, 1334, 1223 (Ar–O–Ar), 1084, 1041, 943, 820; ^{1}H NMR (THF): δ, ppm: 0.90 (br, 27 H, t-BuCH_3), 1.32 (br, 27 H, t-BuCH_3), 6.42–7.91 (m, 25 H, Ar–H), 5.42 (2H, s, –NH_2); UV–Vis (THF): λ_{max}/nm (10^{-5} log ε, L mol^{-1} cm^{-1}): 680 (4.11), 612 (4.39), 351 (4.71); MS (MALDI-TOF): m/z (%100) 1298 $[M + H]^+$.

2.2.3. (E,E)-(1,4-phenylene)bis[N-(4-[2,9,16-tri-(2,4-di-tert-butylphenoxy) phthalocyaninato zinc(II)-23-(4-oxyphenyl)methanimine] (8)

The compound (**6**) (0.04 g, 0.0308 mmol) and benzene-1,4-dicarbaldehyde (**7**) (0.00206 g, 0.0154 mmol), in dry THF (25 mL) was refluxed under nitrogen atmosphere for 24 h. After the mixture was cooled to room temperature, the substance was quickly filtered and the residue was removed. The solvent was evaporated under vacuum and then washed with ethanol and methanol. The crude dark product was further purified by column chromatography with $CHCl_3$/THF = 1:10 (v/v) as the eluent.

Yield: 0.0219 g (53.1%); m.p. > 200 °C. Anal. Calc. for $C_{168}H_{164}N_{18}O_8Zn_2$ (2694,03 g/mol): C, 74.90; H, 6.14; O, 4.75; Found: C, 74.87; H, 6.06; O, 4.73; FTIR y_{max}/cm^{-1}: 3050 (CH arom.) 2954, 2867 (CH aliph.), 1506, 1469, 1392, 1335, 1259 (Ar–O–Ar), 1605 (–N=CH),1085, 1042, 944, 820; ^{1}H NMR($CDCl_3$) δ, ppm: ^{1}H NMR (THF): δ, ppm: 1.20 (s, 54 H, t-BuCH_3), 1.29 (s, 54 H, t-BuCH_3), 7.20–8.43 (m, 54 H, Ar-H), UV–Vis (THF): λ_{max}/nm (10^{-5} log ε, L mol^{-1} cm^{-1}): 678(5.24), 612 (4.55), 351 (4.84); MS (MALDI-TOF): m/z (%100) 2694 $[M]^+$.

2.3. Fabrication and characterization of OFET devices

The OFETs were fabricated as bottom gate and top drain–source contact configuration and indium tin oxide (ITO) coated glasses were used as the substrate and gate electrode. Prior to Pc deposition, the substrates were cleaned by ultrasonic treatment in acetone, isopropyl alcohol, and de-ionized water. On these substrates, homoleptic dimeric phthalocyanine thin film, which acted as gate dielectrics, were coated by spinning of chloroform solution of the compounds at 2500 rpm. After drying the Pc film in a vacuum oven at 80 °C for 15 min to evaporate remaining solvent in the film, a solution of poly 3-hexylthiophene-2,5diyl (P_3HT) in toluene, with a concentration of 2×10^{-3} M, was spun on top of the Pc film rotating at 2500 rpm. The thickness measured with ellipsometry was 30 nm for dielectric layer, and was 140 nm for P_3HT layer. Gold source–drain electrodes with a thickness of 120 nm were then deposited onto the semiconducting layer through a shadow mask to fabricate bottom gate top contact OFET with a channel length (L) of 80 μm and a width (W) of 4 mm. The transfer and output characteristics of the device was measured in ambient atmosphere using a Keithley 617 programmable electrometer and a Keithley 2400 source-meter.

3. Results and discussions

3.1. Synthesis and characterization

A new multicomponent system consisting of benzene-1,4-diyldimethanimine bridged dimeric zinc-phthalocyanine groups was synthesized by a three step procedure. 4-Nitrophthalonitrile (**1**) synthesized according to the literature [25] is a common precursor to obtain different substituted phthalocyanines. The compound **3** was obtained by (**1**) and 2,4-di-*tert*-butylphenol (**2**) by using K_2CO_3 as a base at room temperature in anhydrous DMF under nitrogen atmosphere [27]. The cyclotetramerization of a mixture of **4** and **3** with zinc (II) acetate in the presence of DBU as a strong base results in the formation of a novel unsymmetrically nitro and 2,4-di-*tert*-butylphenoxy groups substituted zinc (II) phthalocyanine (**5**). Substituted nitro groups on the peripheral region of phthalocyanine provide many probabilities to acquire reactive binding areas such as reduction to an amine. For this purpose, [2,9,16-tri-(2,4-di-*tert*-butylphenoxy)-23-(4-[4-aminophenoxy])-phthalocyaninatozinc(II)] (**6**) was synthesized by using hydrazine hydrate as reductant to reduce the nitro group to the amino group [26]. Finally,