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New anthracene-based-phtalocyanine semi-conducting materials: Synthesis and optoelectronic properties

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ABSTRACT

A new anthracene-based semi-conducting phtalocyanines **AnPc** and **AnPc-Tr** were synthesized in solvent-free conditions. The supramolecular structure of these compounds was confirmed by NMR and FT-IR spectroscopies. Their optical properties were investigated by UV–vis and photoluminescence spectroscopies. The optical gaps were estimated from the absorption-onsets films, and the obtained values were of 1.50 eV and 1.47 eV for **AnPc-Tr** and **AnPc** respectively. In solid state, a weaker π–π-interactions of conjugated systems were obtained in the case of **AnPc-Tr** in comparison with **AnPc**. This behavior was explained by steric hindrance of triazol groups, which decrease the planarity of macromolecular structure. The HOMO and LUMO levels were estimated using cyclic voltammetry analysis; two phtalocyanine derivatives show a comparable ionization potential. The phtalacyanine containing triazole groups (**AnPc-Tr**) reveals a higher electron affinity in comparison with **AnPc**. Single-layer diode devices were fabricated and showed relatively low turn-on voltages.

1. Introduction

Metallo-phtalocyanines (MPcs) have a conjugated two-dimensional 18 π-electron system which allows the incorporation of more than 70 different metal or non-metal ions into their inner core they have had this specificity since their first synthesis at the beginning of the last century [1]. The most important artificial structural analogous of porphyrins, has many properties arising from their electronic delocalization and make these compounds applicable to different fields of materials science; such as opto-electronic devices [2], liquid crystals [3], as electrochromic substances [4], gas sensors [5], blood sterilization, sunlight activated herbicides and insecticides [6,7], cancer therapy (photodynamic therapy) such as the second-generation photosensitizer which is now at trial stage [8]. Despite the frequent and considerable use of individual phtalocyanine (Pc) as chromophores, multichromophoric systems where Pc are covalently linked to other electro or photoactive units such as organic moieties that have fluorescent nature and which are of great interest [9]. These systems can also serve as models for the study of energy and electron-transfer processes in artificial photosynthetic systems.

Pcs derivatives that absorb at various wavelengths of visible light and fluorescence with high efficiency and are good candidates for organic photoelectronic devices such as photosensitizing solar cells [10] and organic light emitting diodes [11]. The purpose of the Substitution of Pcs was to improve material properties and to facilitate the implementation and application. Phtalocyanines exhibit excellent chemical and photochemical properties, but have poor fluorescent properties [12]. The interaction of a fluorescence probe with a phtalocyanine core may change the fluorescent characteristics of the aromatic structure. For example, it may be the binding process where fluorescent probe bind chemically or physically to the phtalocyanine molecules, thereby causing a shift in their fluorescence spectra or a change in the fluorescence intensity [13,14]. In this paper we report the synthesis and characterization of two Zn(II) phtalocyanine derivatives substituted by either four anthracene **AnPc** or four triazol anthracene **AnPc-Tr**. This choice was made for the good opto-electronic properties of anthracene. This is the first aromatic material employed in organic light emitting diode (OLEDs). The first experiments were carried out by Pope in the early 1960s [15]. Soon after, several reports on single-crystal anthracene-based OLEDs were published and good quantum yields were obtained (up to 5%). Nevertheless, such devices are thick therefore they require very high operating voltage

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(over 100 V) and also semi-conductor layer in organic field effect transistor (OFET) [16]. The introduction of the triazol group aims to improve the optical properties, triazol derivatives have attracted considerable interest in OLEDs because of their electron transporting as well as hole blocking and/or exciton confining properties, to improve the quantum efficiency and lower the operating voltage of OLEDs [17].

2. Experimental

2.1. Materials and measurements

Phtalic anhydride (99%, Sigma–Aldrich), 9-(chloromethyl)anthracene (98%, Acros), sodium azide (99.5%, Sigma), propargyl alcohol (99%, Aldrich), sodium ascorbate (98%, Sigma), thionyl chloride (99%, Sigma) copper(II) sulfate (99%, Aldrich), were used as received. The commercially available solvents were used without purification.^{1}H NMR and ^{13}C NMR spectral data were obtained on Bruker AV 300 spectrometer. FT-IR spectra were acquired on a PerkinElmer BX FT-IR system spectrometer by dispersing samples in KBr pellets. UV–vis absorption spectra were recorded on a Cary 2300 spectrophotometer. DSC was performed on a Setaram instrumentation-regulation DSC 131 system with a heating rate of 10 °C min^{-1}.

Photoluminescence (PL) spectra were obtained on a Jobin–Yvon spectrometer HR460 coupled to a nitrogen cooled Si charged-coupled device (CCD) detector. Samples were excited with a 450 W Xenon lamp at 370 nm. For solid state measurements, the films were spin-coating onto quartz substrate from 50 μL of DMF solution (2.10^{-2} M) and using tr min^{-1} speed. The film thicknesses were measured by a Dektak profilmometer and were about 70 nm. Cyclic voltametry (CV) was performed on a EG&G model 273 potentiostat/galvanostat (Princeton Applied Research) in a three-electrode cell and using material films that were drop-cast onto an indium tin oxide (ITO) a working electrode. The measurement were carried out at a scanning rate of 50 mV s^{-1} against a satured calomel reference electrode (SCE) and using 0.1 M tetrabutylammonium perchlorate ($(n\text{-Bu})_4ClO_4$) in acetonitrile as supporting electrolyte. The electrochemical cell was externally calibrated by a ferrocene standard. The measurements were performed at 25 °C and the cell was deoxygenated with argon before each reductive scan.

2.2. Synthesis of 4-nitrophtalimide (1)

The mixture of nitric acid (0.27 mol) and sulfuric acid (1.62 mol) was stirred in an ice bath maintained for 30 min to room temperature [1]. The phtalimide (1) was added dropwise to acidic solution and heated at 35 °C while stirring until a colorless solution was achieved. After stirring for 4 h, the white solid was precipitated from ice water, filtered and washed with water. The resultant Crude was dried under ambient conditions. 83% yield; ^{1}H NMR (300 MHz, DMSO-d_6; δ: ppm): 8.02 (d, J = 5.7 Hz, 1H, H—Ar); 8.35 (s, 1H, H—Ar); 8.55 (d, J = 6.9 Hz, 1H, H—Ar); 11.75 (s, 1H, N—H). ^{13}C NMR (75 MHz, DMSO-d_6,δ): 118.17; 124.93; 129.87; 134.43; 137.66; 151.71; 167.61; 167.92.

2.3. Synthesis of 4-nitrophtalamide (2)

Compound 1 was stirred in 32% ammonia solution (70 mL) for 24 h. The resulting deep yellow product was filtered and washed with cold water until disappearance of excess of ammonia [1]. The title compound was dried at 110 °C. 90% yield.; ^{1}H NMR (300 MHz, DMSO-d_6; δ: ppm): 7.63 (s, 2H); 7.71 (d, J = 8.1, 1H); 8.02 (s, 1H); 8.08 (s, 1H); 8.29 (dd, J J = 2.4 Hz, J = 8.7 Hz, 1H); 8.32 (d, J = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 122.34, 124.38; 129.12; 137.19; 142.65; 147.03; 167.67; 168.67.

2.4. Synthesis of 4-nitrophthalonitrile (3)

The thionyl chloride (286 mol) was slowly added to 50 mL of *N*, *N*-dimethylformamide at a temperature lower than 5 °C, was stirred in an argon atmosphere. 15 g of 4-nitrophthalamide was added and the reaction was maintained for 18 h. The crude product was precipitated from a mixture of water–ice [1]. Yield 89%; ^{1}H NMR (300 MHz, DMSO-d_6; δ: ppm): 8.44 (d, J = 8.7, 1H, H—Ar); 8.68 (dd, J = 2.1 Hz, J = 8.4 Hz, 1H, H—Ar); 9.04 (d, J = 2.1, 1H, H—Ar). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 114.55; 114.86; 116.60; 120.22; 128.53; 128.81; 135.27; 149.70. FTIR: 3090 (C—H aromatic); 2245 (CN); 1534 (asymmetric N—O band); 1351 (symmetric N—O band); 852 (C—N).

2.5. Synthesis of 9-anthrylmethyl acetate (4)

Sodium acetate (1.98 mmol) and 9-(chloromethyl)anthracene (1.32 mmol) was stirred in ethanol (20 mL) at 50 °C for 6 h. The mixture was precipitated in water; the obtained product was an orange powder. Yield 95%; ^{1}H NMR (300 MHz, DMSO-d_6; δ: ppm) 2.00 (s, 3H, CH_3—C); 6.11 (s, 2H, CH_2—O); 7.58 (m; 4H; H—Ar); 8.10 (d, 2H, ^3J = 12.0 Hz, H—Ar); 8.36 (d, 2H ^3J = 9.3 Hz, Ar-H); 8.7 (s, 1H, H—Ar). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 20; 60; 125.26; 125.92; 126.44; 126.76; 128.81; 128.92; 130.11; 130.86; 170.46. FTIR (cm^{-1}): 3032 (w, aromatic C—H stretching); 1745 (s, esters stretching); 1442(s, C=O stretching); 1379 (s, C=C stretching); 707 (s, aromatic C—H out-of-plane bending).

2.6. Synthesis of 9-anthrylmethanol (5)

9-Anthrylmethyl acetate (1.79 mmol) was dissolved in anhydrous DMF (20 mL), sodium hydroxide (2.69 mmol) was added. After stirring at 50 °C for 8 h, the crude reaction was precipitated in water; the obtained product was an yellow powder. Yield 90%; ^{1}H NMR (300 MHz, DMSO-d_6; δ: ppm): 5.31 (s, 1H, OH); 5.60 (s, 2H, CH_2—O); 7.62 (m, 4H, H—Ar); 8.13 (d, 2H, H—Ar); 8.36 (d, 2H, H—Ar); 8.70 (s, 1H, H—Ar). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 55.30; 124.79; 125.02; 125.76; 127.02; 128.67; 129.76; 131.05; 132.90. FTIR (cm^{-1}): 3442 (CH_2—OH, stretching); 3003 (w, aromatic C—H stretching); 1490 (s, C=C stretching); 738 (s, aromatic C—H out-of-plane bending).

2.7. Synthesis of anthracene-based phtalonitrile (6)

4-Nitrophtalonitrile (3) and 9-anthrylmethanol (5) (1.442 mmol) was dissolved in DMSO (20 mL) under nitrogen, then anhydrous K_2CO_3 (7.78 mmol) was added over 2 h. The mixture was stirred for 24 h at room temperature. Finally water (100 mL) was added, and the aqueous phase was extracted with chloroform. ^{1}H NMR (300 MHz, DMSO-d_6; δ: ppm): 6.30 (s, 2H, CH2—O); 7.51 (m, 6H, Ar—H); 8.12 (m, 3H, Ar—H); 8.61 (d, 2H, J = 9.0, Ar—H); 8.80 (s, 1H, Ar—H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 63.55; 106.14; 115.30; 116.23; 120.54; 120.81; 123.99; 125.32; 125.67; 126.91; 128.98; 129.22; 130.63; 130.89; 135.69; 162.12. FTIR (cm^{-1}): 3050 (w, aromatic C—H stretching); 2218 (C—N, stretching); 1490 (s, C=C stretching); 738 (s, aromatic C—H out-of-plane bending).

2.8. Synthesis of 4-(proyn-3-yloxy)phthalonitrile (8)

4-Nitrophtalonitrile (3) (2.89 mmol) was dissolved in anhydrous DMF (20 mL) under nitrogen. The propargyl alcohol (PrAl) (7) (8.67 mmol) was added to the mixture. Stirred for 10 min