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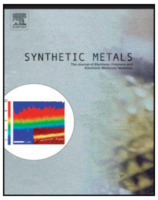

Carbazole-substituted metallo-phthalocyanines: Synthesis, electrochemical, and spectroelectrochemical properties☆

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ABSTRACT

The syntheses of tetrasubstituted metallo-phthalocyanines (cobalt, zinc, and manganese) bearing four 9H-carbazole-9-ethoxy units have been reported. All of the synthesised compounds have been characterised by using FT-IR, UV–vis, ^{1}H NMR, and MALDI-TOF/MS spectroscopic data. The aggregation behaviours of the newly synthesised compounds were investigated in different concentrations. Electrochemical and spectroelectrochemical characterisation of Cl-MnPc was performed in DMF. Two metal-based reductions followed a Pc ring-based reduction. An irreversible Pc ring-based oxidation could only be detected with square wave voltammetry. *In situ* spectroelectrochemical and electrocolorimetric measurements were performed in order to determine the colours and spectra of the electrogenerated species of the complex.

1. Introduction

Phthalocyanines (Pcs) are an important class of aromatic macrocycles with high chemical and thermal stability that possess unique physical and chemical properties [1]. The central part of the molecule consists of four nitrogens directly involving complexation. The core is capable of coordinating almost all metal ions and this in turn enables the macrocycle to have a broad spectrum of properties [2]. Phthalocyanines derivatives gives opportunities to develop their applications in various fields such as chemical sensors, liquid crystals, second generation photosensitisers for photodynamic therapy, optical limiting devices, and non- linear optics [3–8].

Carbazoles are important aromatic heterocycles. There are two six-membered rings on either side of a five-membered nitrogen-containing ring [9]. Carbazoles are present in many natural and synthetic products with different pharmacological activities, such as antitumour, antihistaminic, psychotropic, antibiotic, anti-inflammatory, and antioxidative activities [10,11]. In addition, some of their derivatives have excellent optical and electrical properties. Accordingly, the synthesis of carbazole derivatives is still an interesting topic [12,13].

Carbazoles have become the topic of numerous studies concerning the charge carrier transport materials and light emitting diodes (LED) [14]. The heterocycle has an electro-active nitrogen atom as the center of redox activity. When the nitrogen is oxidized, they will have a powerful interaction between the nitrogen and the benzene rings and thus, they exhibit electrochemical and spectral properties, as expected from the structure. It is therefore they are used as photoactive and electroactive materials. Synthesizing and characterizing carbazoles are important in fabricating materials [15,16]. According to our knowledge, a few literatures are known about carbazole substituted phthalocyanines [17,18]. In the present article, the synthesis, characterisation, and structural investigation of Co(II), Zn(II), and Mn(III) phthalocyanines containing 9H-carbazole-9-ethoxy groups are described. Further, the wavelength of the absorption of the Q band and the aggregative properties of the compounds **4**–**6** were investigated. Furthermore, electrochemical behaviours of Cl-MnPc were also determined to decide possible usage of the complexes in various electrochemical technologies, such as electrocatalysis, electrosensing, and electrochromism.

2. Experimental

2.1. Materials and equipments

All chemicals and reagents were purchased from Merck Chemicals and Sigma-Aldrich Chemicals, and used without any further purification. ^{1}H NMR spectra were recorded on Agilent

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VNMRS 500 MHz FT-NMR spectrometer; chemical shifts (δ, ppm) were determined with TMS as the internal reference. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (universal attenuated total reflectance sampling accessory) spectrometer; electronic spectra were recorded on a Scinco LabProPlus UV/Vis spectrophotometer. Mass spectra were performed on Bruker Microflex MALDI-TOF/MS spectrometer. 4-Nitrophthalonitrile (**1**) was prepared according to the reported procedure [19].

2.2. Electrochemical in situ *spectroelectrochemical and* in situ *electrocolorimetric measurements*

The cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed with a Gamry Reference 600 potentiostat/galvanostat controlled by an external personal computer, and we utilised a three-electrode configuration at 25° C. A Pt disc with a surface area of 0.071 cm^2 was used as a working electrode. As the counter electrode, Pt wire was used. Saturated calomel electrode (SCE) was the reference electrode of choice and we separated it from the solution bulk with a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dimetlyformamide (DMF) was preferred as the supporting electrolyte at 0.10 mol dm^{-3} concentration.

UV–vis electrnic spectra and chromaticity diagrams were recorded by an Ocean Optics QE65000 diode array spectrophotometer. *In-situ* spectroelectrochemical measurements were carried out by using a three-electrode configuration inside a quartz thin-layer spectroelectrochemical cell at 25° C. The working electrode was a semi-transparent Pt mesh electrode. A Pt wire counter electrode which was separated by a glass bridge and a saturated calomel reference electrode which was separated from the bulk of the solution by a double bridge were utilised. *In-situ* electro-colorimetric measurements, under potentiostatic control, were recorded using an Ocean Optics QE65000 diode array spectrophotometer at colour measurement emission mode by setting up a similar three-electrode configuration with the thin-layer quartz spectroelectrochemical cell. We have used, for this purpose, the standard illuminant A having two degree observer at a constant temperature in a light booth, which was designed to exclude external light. The CIE standard illuminant A is intended to represent typical, domestic, incandescent light source. Its relative spectral power distribution is similar to a Planckian radiator at a temperature of *ca.* 2856 K. Due to the nature of the conic distribution in the eyes, the values of tristimuli depend on the observer's viewing field. To eliminate this variable, the CIE has defined the standard (colorimetric) observer. Originally this value was taken to be the chromatic response of the average human viewing ares through a 2°. Thus the CIE 1931 Standard Observer is also referred to as the "CIE 1931 2° Standard Observer". Prior to each set of measurements, background colour coordinates (x, y, and z values) were taken at open-circuit using the electrolyte solution not having the phthalocyanines under study. During the measurements, readings were, under kinetic control, taken as a function of time, however only the colour coordinates at the initial and final states of each redox process were reported.

2.3. Synthesis

*2.3.1. 4-[9H-Carbazole-9-ethoxy]phthalonitrile (**3**)*

4-Nitro-phthalonitrile (**1**) (0.46 g, 2.66 mmol) and 9H-carbazole-9-ethanol (0.62 g, 2.94 mmol) were added successively with stirring to dry DMF (12.00 mL). After they were dissolved, anhydrous K_2CO_3 (0.80 g, 5.80 mmol) was added portionwise over 2 h and the mixture was stirred vigorously at 50 °C for 4 days. Then, the crude product was poured into water (100.00 mL) and the precipitate formed was filtered off, washed with water, and crystallised from ethanol to give the yellow product. Yield: 0.78 g (87%), m.p. 169 °C. ^1H NMR (500 MHz, DMSO-d_6), (δ: ppm): 8.12–8.11 (d, 2H, Ar-H), 7.90–7.88 (d, 1H, Ar-H), 7.66–7.65 (d, 2H, Ar-H), 7.57–7.56 (d, 1H, Ar-H), 7.47–7.44 (t, 2H, Ar-H), 7.23–7.18 (m, 3H, Ar-H), 4.83–4.81 (t, 2H, CH_2), 4.56–4.54 (t, 3H, CH_2). ^{13}C NMR (500 MHz, DMSO-d_6), (δ: ppm): 42.13 (CH_2), 68.17 ($O{-}CH_2$), 106.52 (aromatic C), 109.98 (aromatic C), 110.02 (aromatic C), 116.02 (aromatic C), 116.55 (C=N), 116.60 (C=N), 119.48 (aromatic C), 120.21 (aromatic C), 120.45 (aromatic C), 120.60 (aromatic C), 120.75 (aromatic C), 120.80 (aromatic C), 122.63 (aromatic C), 122.71 (aromatic C), 126.00 (aromatic C), 126.17 (aromatic C), 135.98 (aromatic C), 140.48 (aromatic C), 140,56 (aromatic C), 161.74 (aromatic C). FT-IR ν_{max}/cm^{-1}: 3049 (H–Ar), 2944 (alkyl C—H), 2229 (C=N), 1249 (C—O—C).

*2.3.2. General procedures for phthalocyanine derivatives (**4**–**6**)*

4–[9H-Carbazole-9-ethoxy]phthalonitrile (**3**) (0.11 g, 0.33 mmol) was dissolved in 1-hexanol (2.00 mL). Anhydrous metal salts (0.09 mmol) [$CoCl_2$, 11.61 mg; $Zn(CH_3COO)_2$, 16.47 mg; $MnCl_2$, 11.25 mg] and a catalytic amount of DBU (1,8-diazabicyclo [5.4.0]undec-7-ene) was added to the reaction medium. All reactions were carried out in a sealed glass tube (10 mm × 75 mm) under nitrogen atmosphere at 160 °C *ca.* 24 h. After cooling to the room temperature, the suspension was precipitated with methanol/water, filtered, washed with methanol, and acetone. The crude products were purified column chromatography on silica gel using THF solvent.

2.4. 2,9(10),16(17),23(24)-tetrakis-[9H-Carbazole-9-ethoxy]-phthalocyaninato cobalt (II) (4)

The blue product was purified by column chromatography on basic aluminium oxide using THF as eluent. Yield: 35.24 mg (32.04%). FT-IR ν_{max}/cm^{-1}: 3051 (C—H, aromatic); 2930 (C—H aliphatic), 1273–1229 (Ar–O–Ar). UV–vis (THF, $c = 6 \times 10^{-6}$ mol dm^{-3}), λ_{max}, nm (log ε): 329 (4.82), 660 (4.66). MS (MALDI-TOF), (*m*/*z*): 1409.36 $[M+H]^+$. $C_{88}H_{60}CoN_{12}O_4$: calcd. C 75.04, H 4.29, N 11.93%; found: C 75.44, H 4.30, N 11.55.

2.5. 2,9(10),16(17),23(24)-tetrakis-[9H-Carbazole-9-ethoxy]-phthalocyaninato zinc (II) (5)

The green product was purified by column chromatography on silica gel using THF as the eluent. Yield: 59.09 mg (53.72%). FT- IR ν_{max}/cm^{-1}: 3046 (C—H, aromatic), 2931 (C—H aliphatic), 1274–1236 (Ar–O–Ar). UV–vis (THF, $c = 6 \times 10^{-6}$ mol dm^{-3}), λ_{max}, nm (log ε): 346 (4.65), 613 (4.22), 676 (4.84). ^1H NMR (500 MHz, DMSO-d_6), (δ: ppm): 8.19–8.12 (m, Ar–H, 12H), 7.92–7.87 (m, Ar–H, 8H), 7.69–7.46 (m, Ar–H, 12H), 7.26–7.16 (m, Ar–H, 12H), 5.01 (br, CH_2, 8H), 4.81 (br, CH_2, 8H). $C_{88}H_{60}N_{12}O_4Zn$: calcd. C 74.70, H 4.27, N 11.88%; found: C 74.89, H 4.73, N 11.14.

2.6. 2,9(10),16(17),23(24)-tetrakis-[9H-Carbazole-9-ethoxy]-phthalocyaninato-(chloro)-manganese(III) (6)

The purification was performed similarly to **4**. Yield: 24.02 mg (21.84%). FT-IR ν_{max}/cm^{-1}: 3045(C—H, aromatic), 2926 (C—H aliphatic), 1273–1229 (Ar–O–Ar). UV–vis (THF, $c = 6 \times 10^{-6}$ mol dm^{-3}), λ_{max}, nm (log ε): 335 (4.75), 376 (4.68), 724 (4.95). MS (MALDI-TOF), (*m*/*z*): 1442.55 $[M+3H]^+$, 1407.93 $[M\text{-}Cl+3H]^+$. $C_{88}H_{60}ClMnN_{12}O_4$: calcd. C 73.40, H 4.20, N 11.67%; found: C 73.11, H 4.45, N 11.65.