



Comparable optical properties and dispersion parameters of monomeric axial ruthenium phthalocyanine thin films

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ABSTRACT

The ruthenium phthalocyanine complex $[(n\text{-hexyl})_8\text{PcRu}]$ (**2**) and their derivatives $[(n\text{-hexyl})_8\text{PcRu}(t\text{-buNC})_2]$ (**3**) and $[(n\text{-hexyl})_8\text{PcRu}(\text{Mepyr})_2]$ (**4**) have been synthesized and characterized. The optical properties of their films have been studied by spectrophotometer measurements of transmittance and reflectance at normal incidence of light in the spectral range of 200–2500 nm. Absorption spectra of the films showed B and C absorption bands in the UV region followed by a Q-band in the visible region. The absorption parameters such as molar extinction coefficient, oscillator strength and electric dipole strength have been reported. The type of electronic transition is determined from an analysis of the absorption coefficient and found to be indirect allowed transition with onset energy gap and optical energy gap. The single oscillator model has been applied to calculate the dispersion parameters. The oscillator energy, the dispersion energy, the high frequency dielectric constant, the lattice dielectric constant and the ratio of free charge carriers concentration to their effective mass were evaluated. The dielectric properties of the films were also determined, showing that peripheral and axial ligand substituents on the complexes have a significant effect on their surface coverage.

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1. Introduction

Generally phthalocyanines (Pcs) are a class of organic semiconductor with alternate single–double bond structure [1]. The phthalocyanine compounds have two types of aggregations which affect on electronic and optical properties of these compounds. One of them is face-to-face H-aggregation (transition dipoles are perpendicular to the line connecting their centers) and another one is side-to-side J-aggregation (transition dipoles are parallel to the line connecting their centers) [2]. Generally, J-aggregates of Pc molecules occurred by utilizing the coordination of the side substituent from one Pc molecule to the central metal ion in a neighbor molecule [3–5]. Phthalocyanines are objects of great interest for chemists, physicists and industrial scientists because of their potential role in emerging technologies, including gas sensor [6,7], solar cell [8], catalyst [9] biomedicine, electronic and optoelectronic devices [10]. One of the main targets in the chemistry of the phthalocyanines and their metallic complexes is the development of new materials that open new opportunities in advanced functional molecular materials such as photodynamic therapy (PDT) of cancer as second generation photosensitizers [2]. Many applications of phthalocyanine

compounds are based on their performance in thin films. These compounds, when deposited as thin films, interact with some oxidizing and reducing gases and volatile organic compounds by absorption processes onto the sensing layer [11]. Ruthenium(II)phthalocyanines have received relatively limited study but are of interest for a number of reasons. Non-ligated derivatives are hard to access [12] and most attention has focused on the merits of either single or double axial ligation. However, only a handful of examples of dimeric PcRu complexes have been reported.

In continuation of our studies on the synthesis of asymmetric and symmetric Pcs with axial ligands and investigation of their optical properties [13–21] we describe here the synthesis of new soluble axial derivatives of ruthenium phthalocyanine complexes RuPcs (**3**) and (**4**) that bear a functionalized *t*-butylisocyanide and pyridine axial ligands, respectively, to compare their optical and dielectric properties with previous work. This class of complex will offer interesting electronic and optical properties that may be utilized in a variety of applications.

2. Experimental techniques

2.1. Physical characterizations

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm^{-1} using

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KBr pellets. ^1H NMR spectra were recorded using a BVT 3000 Bruker Spectro spin instrument operating at 300.13 MHz. Spectra are referenced internally to residual solvent (CHCl_3). UV–vis spectra were recorded using an Agilent 8453 UV–vis spectrophotometer with chloroform used as solvent. FDMS mass spectra were recorded using a Varian MAT 711A spectrometer and reported as mass/charge (m/z). Elementary analyses were performed on a Carlo Erba Elemental Analyzer 1106.

2.2. Materials

All reagents and solvents were of commercial reagent grade and used without further purification. The following were purchased commercially and used as received; *t*-butylisocyanide and 4-methylpyridine (Aldrich).

Precursor 1,2-dicyano-4,5-bis(*n*-hexyl)benzene (**1**) and 2,3,9,10,16,17,23,24-octa(*n*-hexyl)phthalocyaninoruthenium(II) (**2**) were synthesized as reported in our previous work [22].

2.3. Synthesis

2.3.1. Bis(*t*-butylisocyanide){octa(*n*-hexyl)phthalocyaninato}ruthenium(II), [(*n*-hexyl)₈PcRu(*t*-buNC)₂] (**3**)

[(*n*-hexyl)₈PcRu] (**2**; 0.65 g, 0.5 mmol) was suspended in excess of *t*-butylisocyanide (0.42 g, 5 mmol) and the suspended solution was heated at 60 °C for 2 days under nitrogen atmosphere with stirring. The reaction mixture was cooled to room temperature. The excess of *t*-butylisocyanide was evaporated under vacuum. The crude product was washed several times with Methanol and then purified by silica column chromatography eluting with a mixture of *n*-hexane/ CHCl_3 (1/1). After evaporation of the solvent, it was dried for 15 h at 70 °C in vacuum, to yield 0.54 g (73%) of **3** as violet powder (Scheme 1).

IR (KBr, cm^{-1}): 3048mArH; 2122 (CN); 1928m(Ru–H); 1655m(C–N; C–C); 1479 d(C–CH in the plane); 1434mPh; 1092 d(C–CH in the plane); 745 d(C–C out of the plane); 694 d(C–C in the plane). ^1H NMR (CDCl_3): –0.49(s, 18H, $18 \times (\text{CH}_3)_3\text{NC}$), 0.9–1.04 (t, 24H, $8 \times \text{CH}_3$), 1.3–1.8 (m, 80H, $8 \times (\text{CH}_2)_5$), 8.0 (s, 8H, Ar–H). UV–vis (CHCl_3), λ_{max} (nm): 640, 580, 360 sh, 320 MS (FD): $m/z=1471.31$ (M^+), 1388.18 ($\text{M}^+-(t\text{-buNC})$). Elemental analysis: $\text{C}_{90}\text{H}_{148}\text{N}_{10}$ Ru, found C 72.97, H 9.87, N 9.11; Calcd. C 73.47, H 10.13, N 9.51.

2.3.2. Bis(4-methylpyridine){octa(*n*-hexyl)phthalocyaninato}ruthenium(II), [(*n*-hexyl)₈PcRu(4-MePy)₂] (**4**)

[(*n*-hexyl)₈PcRu] (**2**; 0.65 g, 0.5 mmol) was suspended in excess of 4-methylpyridine (0.46 g, 5 mmol) and stirred under nitrogen at 80 °C for 2 days. The reaction mixture was cooled to room temperature. The excess of 4-methylpyridine was evaporated under vacuum. The crude product was washed several times with Methanol and then purified by column chromatography on silica gel using a mixture of *n*-hexane/ CHCl_3 (1/1) as eluent. The solvent was removed and dried for 15 h at 80 °C in vacuum, to yield 0.48 g (65%) of **4** as blue violet powder (Scheme 1).

IR (KBr, cm^{-1}): 3050 mArH; 1920m(Ru–H); 1650m(C–N; C–C); 1480 d(C–CH in the plane); 1436mPh; 1082 d(C–CH in the plane); 750 d(C–C out of the plane); 690 d(C–C in the plane). ^1H NMR (CDCl_3): 0.9 (s, 6H, $2 \times (\text{CH}_3)\text{Pyr}$), 1.04–1.2 (t, 24H, $8 \times \text{CH}_3$), 1.5–1.7 (m, 80H, $8 \times (\text{CH}_2)_5$), 6.7 (q, 4H, $2 \times \text{HPyr}^b$), 7.6 (t, 4H, $2 \times \text{HPyr}^a$), 8.54 (s, 8H, Ar–H). UV–vis (CHCl_3), λ_{max} (nm): 645, 583, 468, 361 sh, 325. MS (FD): $m/z=1491.30$ (M^+), 1398.17 ($\text{M}^+-(4-$

Mepyr)). Elemental analysis: $\text{C}_{92}\text{H}_{144}\text{N}_{10}$ Ru, found C 73.91, H 9.07, N 8.88; calcd. C 74.09, H 9.73, N 9.39.

2.4. Thin film preparation

Thin films of ruthenium phthalocyanine complexes with different Ligands of thickness 100 nm were prepared by the conventional thermal evaporation technique, using a high vacuum coating unit (Edward Co., Model E 306 A, England). The films were deposited onto well-cleaned optically flat fused quartz substrates for optical measurements. The material was sublimated from a quartz crucible source heated by a tungsten coil in a vacuum of about 5×10^{-4} Pa. The rate of deposition was controlled to be 2.5 nm/s using a quartz crystal thickness monitor (Edwards, Model FTM4). Film thicknesses were determined accurately after deposition by using multiple-beam Fizeau fringes in reflection (Tolansky method) [23]. During the deposition the substrates temperature was kept at near room temperature. The transmittance $T(\lambda)$ and reflectance $R(\lambda)$ spectra of ruthenium phthalocyanine complexes films were measured at normal incidence of the light at room temperature in the spectral range 200–2500 nm using a computer-aided double beam spectrophotometer (JASCO model V-570 UV–vis–NIR). A blank quartz substrate identical to the one used for the thin film deposition was used as a reference for the transmittance scan.

3. Results and discussion

3.1. Synthesis and characterization of RuPcs (**2–4**)

The synthesis of the new RuPcs **3** and **4** complexes is shown in Scheme 1. The new complexes were synthesized by substitution group, which is included to facilitate purification of the complex using silica gel column chromatography. Complex **3** was obtained by heating **2** in excess of *t*-butylisocyanide, but complex **4** was obtained by heating **2** in excess of 4-methylpyridine. Solubilizing peripheral *n*-hexyl groups required purification with column chromatography.

These complexes were chosen for investigation because the Pc ligand strongly binds the metal ensuring that the probe metal atom remains coordinated during thin film formation.

The purified RuPcs **2–4** were identified by their NMR and FD-MS spectra. They exhibit well-resolved spectra with sharp peaks in both aromatic and aliphatic regions implying that the aggregation behavior is totally absent.

The IR spectra of complexes **3** and **4** have similar IR spectra to each other, with little influence from the axial ligand. They also exhibit additional bands in their IR spectra arising from the axial ligands that are not present in the ruthenium phthalocyanine spectra.

The ^1H NMR spectra of RuPcs **2–4** complexes are typical of axially substituted RuPcs. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton gave significant absorbance characteristic of the proposed structure. The aromatic protons appeared as a range of broad singlets over 8.00–8.54 ppm and the conformation of the alkyl groups in the obtained RuPcs **2–4** has been clearly shown in one environment for the methyl hydrogens of the hexyl groups between 0.9 and 1.2 ppm. From their ^1H NMR spectra, we can clearly show that all RuPcs **2–4** are well separated and isolated and represent pure compounds in accordance with their proposed molecular formula.

The complexes **2–4** have electronic spectra characteristic of RuPc complexes. They display intense Soret bands with maxima at 320–325 nm with an accompanying low-energy shoulder, and

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