Optical Materials 84 (2018) 8–15

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

New ruthenium(II) bipyridine complex bearing 2-aminophenylbenzimidazole: Synthesis, spectral characterization and optical properties

Shadia A. Elsayed[a], Eman A. Gaml[b,*], M.A. Nasher[b,c]

[a] Department of Chemistry, Faculty of Science, Damietta University, New Damietta, 34517, Egypt
[b] Department of Physics, Faculty of Science, Damietta University, New Damietta, 34517, Egypt
[c] Department of Physics, Faculty of Science, Sadah University, Sadah, Yemen

ARTICLE INFO

Keywords:
Ru(II)bipyridine
Spectra
XRD
Optical properties
Thin films

ABSTRACT

The new bipyridine-based ruthenium(II) complex $[Ru(bpy)_2(Hapbim)]^{2+}$ (bpy being 2,2′-bipyridine, and Hapbim is 2-aminophenylbenzimidazole) was synthesized and characterized. On the basis of elemental analysis, spectroscopic techniques (FTIR, ^{1}H NMR, UV-Visible), magnetic, conductivity and thermal analysis measurements, it was found that the Hapbim ligand coordinates to Ru(II) kernel in a neutral bidentate fashion through cyclic azomethine N of benzimidazole moiety along with the terminal nitrogen of the amino group forming six-membered chelate ring. Thin films of the Ru(II)-complex were prepared using thermal evaporation technique. The thin film structure was characterized using FTIR and X-Ray diffraction techniques. FTIR analysis revealed that the complex is chemically stable under both thermal evaporation and thermal annealing. The optical properties were studied by spectrophotometric measurements. The optical constants of the complex were calculated and it is found to have 1.5 eV band gap. Also, the effect of thermal annealing on the optical properties of the complex is studied. Annealing of the complex thin films increased the values of the dispersion parameters and decreased the value of the band gap.

1. Introduction

Transition metal complexes of nitrogen donor chelating agents are well known for their various applications in many research fields including biology [1], catalysis, solar power conversion and its storage [2–4]. In particular, ruthenium complexes bearing polypridyl ligands are of a considerable interest due to their photo-physical/chemical, electrochemical properties and high photochemical stability [5]. These complexes play important roles in several research areas including light emitting diodes [6], electroluminescent devices, dye sensitized solar cells [7,8], and solar energy conversion [9].

Ruthenium(II) containing 2,2′-bipyridine (bpy) have interesting properties including strong absorption of light in visible region due to metal-to-ligands charge transfer (MLCT), also their excited states have relatively long lifetime because of the forbidden transition from triplet excited state to singlet ground state [10–12]. The replacement of bpy by heterocyclic compounds containing N-donors has gained noticeable attention in recent time, due to the changes in their photochemical and photophysical properties occurred by incorporating these units [13]. The optical properties of the ruthenium complexes demonstrate significant device performance when prepared as thin films [14,15]. In addition to ruthenium(II) complexes, thin films of cobalt(II) and Mn(II) complexes containing benzimidazole moiety were prepared and structurally characterized, it was proven that annealing of thin films of these metal complexes improved their surface homogeneity as well as enhancement of their optical transmittance [16,17]. Manjunatha et al. [18] have reported the preparation of thin films from $[Ru\text{-salophen}]^{2+}$ complex (salophen = N, N' -disalicylidene-1,2-ethylendiimine) using a spin coating technique. The obtained data revealed that the complex exhibited a relatively large non-linear optical properties (NLO) along with optical switching behavior which enables it to be a promising material for fabricating optoelectric devices.

In this work, we report the synthesis of new ruthenium(II) bipyridine complex of 2(2′-aminophenyl)-1H-benzimidazole (2-aminophenylbenzimidazole) $[Ru(bpy)_2(Hapbim)]^{2+}$. Its structure was elucidated by means of spectroscopy (FTIR, ^{1}H NMR, UV-visible), thermal, magnetic, and molar conductivity measurements. Thin films of this complex were prepared and characterized along with investigating the effect of annealing on its optical properties. The molecular structures of the ligand and complex are shown in Figs. 1 and 2, respectively.

* Corresponding author.
E-mail address: emangamlph@gmail.com (E.A. Gaml).

https://doi.org/10.1016/j.optmat.2018.06.052
Received 24 April 2018; Received in revised form 20 June 2018; Accepted 21 June 2018
0925-3467/ © 2018 Elsevier B.V. All rights reserved.

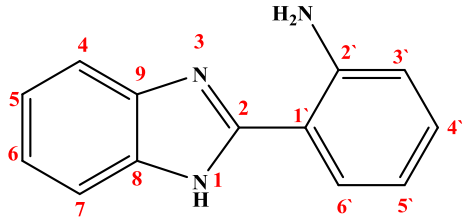

Fig. 1. Structure of structure of 2(2′-aminophenyl)-1H-benzimidazole with atom numbering scheme.

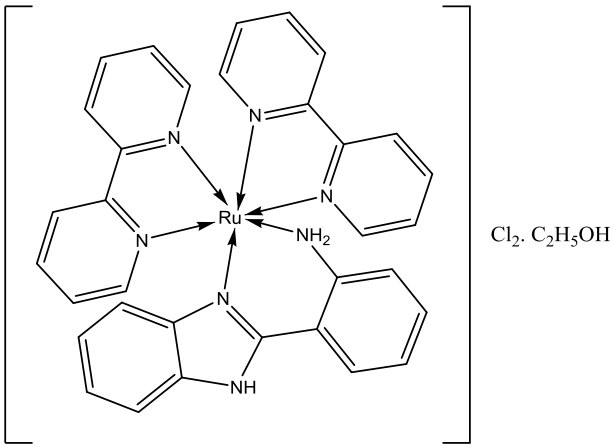

Fig. 2. Structure of $[Ru(bpy)_2(Hapbim)]Cl_2.C_2H_5OH$ complex.

2. Experimental

2.1. Materials and methods

2-aminophenylbenzimidazole and 2,2′-bipyridine were purchased from Alfa Aesar. *Cis*-$[Ru(bpy)_2Cl_2].2H_2O$ was prepared as reported elsewhere [19]. All solvents and reagents were used as received.

2.2. Instrumentation

Infrared spectroscopy was performed on JASCO 4100 FTIR spectrometer (4000 - 400 cm^{-1}) on KBr disc. ^1H NMR spectra were recorded in DMSO-d_6 on Bruker 400 MHz Electronic spectra (200–900 nm) were measured in ethanol using JASCO V- 630 spectrometer. Elemental analyses (C, H, N) were carried out at microanalytical unit at Cairo university. Magnetic susceptibility value of the complex was obtained using Johnson Matthey magnetic susceptibility balance. Molar conductivity of the complex (in CH_2Cl_2) was measured on YSI Model 32 Conductivity Bridge at room temperature. Thermal analysis data were collected in the temperature range 20–800 °C under nitrogen atmosphere 15.00 ml/min using Shimadzu TGA-50 instrument at a heating rate of 20 °C/min. Thin films of the powder phase of Ru-complex were prepared by thermal evaporation technique using Edwards (E306 A) coating unit. The powder of the complex was sublimated from quartz crucible into optically flat quartz substrates. The pressure during evaporation process was 10^{-5} Torr and the evaporation rate was maintained at 0.5 nm/s. The film thickness was measured using quartz crystal thickness monitor (Model TM-350 MAXTEK, Inc. USA) attached to the coating system. Thin films of the Ru(II)-complex were annealed at 423 K for 30 min. The X-Ray diffraction, XRD, measurements for the as synthetized powder, as deposited, and annealed thin films were carried out using Philips X-ray diffraction system, model X'Pert MPD. The operating voltage and current for the X-ray tube were 50 kV and 40 mA, respectively. The spectral data of transmittance and reflectance at nearly normal incidence were collected using spectrophotometric measurements by using double beam spectrophotometer JASCO model (V-570-UV-Vis.-NIR) in the wavelength range 200–2500 nm.

2.3. Optical constants calculation

To calculate the values of the refractive index (n), absorption coefficient (α) and the absorption index (k), we substitute the calculated values of the transmittance, T and reflection R in equation (1–3) [20]:

$$n = \left(\frac{1+R}{1-R}\right) + \left(\frac{4R}{(1-R)^2} - k^2\right)^{1/2} \quad (1)$$

$$\alpha = \frac{1}{d} Ln\left(\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2}\right) \quad (2)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

2.4. Synthesis

To an ethanolic solution of 2-aminophenylbenzimidazole (0.5 mmol, 0.105 g, 25 mL), *cis*-$[Ru(bpy)_2Cl_2].2H_2O$ (0.5 mmol, 0.26 g) was added. The reaction mixture was refluxed for 12 h during which the purple color of the solution turned dark red. The solution was then concentrated to one-third of its volume. The reddish brown precipitate was formed by adding an excess amount of diethyl ether. The product was collected by filtration through a sintered glass gooch, washed with ether, then dried in *vacuo*. Yield 0.23 g (67%), mp > 200 °C. Diamagnetic (μ_{eff} = 0 B M), molar conductance (10^{-3} M in CH_2Cl_2, Λ_M) = 180 Ω^{-1} cm^2 mol^{-1}. Elemental analysis (%) for $C_{35}H_{33}Cl_2N_7ORu$ (Mw = 739.67), Calcd (Found): C, 56.83 (56.78); H, 4.50 (4.10); N, 13.26 (13.0). FTIR (KBr, cm^{-1}): ν(NH) 3330, $\nu(NH_2)$ 3130, ν(C=N), 1597, ν(C=C) 1495–1520, ν(CH), 2998–3030, ν(Ru-N) 422. ^1H NMR (400 mHz, DMSO-d_6, δ ppm): 14.70 (1H, s, N(1)H), 7.43 (N(2′)H_2, s, 2H), 6.89 (1H, d, H(3′), J = 8.10 Hz); 7.89 (1H, d, (H(6′)), J = 7.6 Hz); 8.23 (1H, d, H(7), J = 6.6 Hz); 7.84 (1H, d, H(4), J = 6.5 Hz); 7.30–7.73(4H, m, H(4′, 5′, 5,6)); 8.8–9.05 (4H, d, H(3,3′), J = 7.6, 8.0, bpy); 8.01–8.1 (4H, m, H(4,4′), bpy); 7.61–7.66 (4H, m, H(5,5′), bpy); 8.70–8.78 (4H, d, (H6,6′), J = 8.0, 8.0 Hz, bpy); 4.38 (1H, s, $CH_3CH_2O\underline{H}$), 3.44 (2H, q, ($CH_3C\underline{H}_2OH$, J = 6.8 Hz), 1.06 (3H, t, $C\underline{H}_3CH_2OH$, J = 7.2 Hz). UV-Vis (EtOH, 1 × 10^{-5} M): λ_{max} (nm) (ε, L.mol^{-1}. cm^{-1}): 294 (78000), 356 (14700) and 499 (8500).

3. Results and discussion

3.1. Synthesis

The complex $[Ru(bpy)_2(Hapbim)]Cl_2.C_2H_5OH$ was prepared by the reaction of *cis*-$[Ru(bpy)_2Cl_2].2H_2O$ with 2-aminophenyl benzimidazole (Hapbim) in ethanol in 1:1 M ratio under reflux condition. The complex was powder-like, readily soluble in water and common organic solvents such as methanol, ethanol, CH_2Cl_2, DMF and DMSO. The molar conductance value of the complex was 180 Ω^{-1} cm^2 mol^{-1} to indicate that the complex is ionic in nature with two chlorides as counter ions (2:1).

3.2. FTIR spectra

The FTIR spectrum of the of 2-aminophenyl benzimidazole ligand (Fig. 3 a) shows two medium bands at 3383 and 3140 cm^{-1} assigned to the stretching vibrations of ν(NH) of NH_2 and ν(NH) of benzimidazole, respectively [21–23]. The spectrum of the complex (Fig. 3 b), reveals the shift of those bands to 3030–3383 cm^{-1} to lower frequency suggesting the participation of NH_2 nitrogen in the coordination to Ru(II) center. The sharp band observed at 1608 cm^{-1} assigned to ν(C=N) in the ligands is shifted in the complex to a lower frequency by

Download English Version:

https://daneshyari.com/en/article/7905834

Download Persian Version:

https://daneshyari.com/article/7905834

Daneshyari.com