Synthesis, photophysical and preliminary investigation of the dye-sensitized solar cells properties of functionalized anthracenyl-based bipyridyl and phenanthrolyl Ru(II) complexes

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Abstract. Four new amphiphilic ligands: 4-(2,3-dimethylacrylic acid)-2,2'-bipyridine (L_1), 4-(9-anthracenyl-10-(2,3-dimethylacrylic acid)-2,2'-bipyridine (L_2), 5-(2,3-dimethylacrylic acid)-1,10-phenanthroline (L_3) and 5-(9-anthracenyl-10-(2,3-dimethylacrylic acid)-1,10-phenanthroline (L_4), with their corresponding homonuclear ruthenium(II) complexes formulated as *cis*-[Ru- $(L_1)_3$ (PF₆)₂] (**C1**), *cis*-[Ru- $(L_2)_3$ (PF₆)₂] (**C2**), *cis*-[Ru- $(L_3)_3$ (PF₆)₂] (**C3**) and *cis*-[Ru- $(L_4)_3$ (PF₆)₂] (**C4**), have been synthesized and characterized by elemental analysis, ¹H- and ¹³C- NMR, FT-IR, UV-Vis and photoluminescence spectroscopy. The complexes exhibit broad and intense metal-to-ligand charge transfer (MLCT) transition bands in the visible region (400–700 nm), and red light emitting properties at room temperature. By comparison however, complexes **C1** and **C2** bipyridine moiety gave lower molar absorptivity coefficient at relatively similar wavelength characteristics (410–520 nm) when compared to **C3** and **C4** with phenanthroline based molecules. Cyclic voltammograms of the complexes revealed complex **C4** with most reduction potential which might be due to increase in the conjugation of the anthracene functionalized units. Preliminary investigation of the solar cell efficiency of the complexes on TiO₂ nanocrystalline films gave the best result with efficiency of 0.103% for **C1** under illumination at 1000 W/m² AM 1.5. Electrochemical impedance spectroscopy (EIS) technique however, revealed the charge transfer resistances (R_{ct}) of the electrons on the TiO₂ semiconductor.

Keywords. Ruthenium(II), polypyridyl ligands, spectroscopy, electrochemistry, DSSCs

1. Introduction

The quest for new materials that efficiently harvest solar light continues to be an important goal. Recently, considerable efforts have been focused on new photosensitizers, including ruthenium complexes^{1–10} and organic dyes,^{11–14} in dye-sensitized solar cells (DSSCs) since *cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II) [Ru(dcbpy)₂(NCS)₂] anchored on porous nanocrystalline TiO₂ electrode has exhibited 10% light-to-electric power conversion efficiency. It has been shown that one of the best way to enhance both the absorption coefficient and red-shift of the metal-to ligand charge transfer (MLCT) band in a ruthenium-based photosensitizer was to extend the π -conjugation length of the colorant's ancillary¹⁵ or

anchoring¹⁶ ligands. Other classes of ligands such as carboxylated terpyridine and phenanthroline showed enhanced UV-Vis absorption over a broad range due to their large conjugated backbone structure. These ligands can be utilized as efficient light harvesting sensitizers as well.¹⁷

The quest for new and alternative approaches for easy building and organizing various photoactive partners around photoactive metals is a developing field of research.¹⁸ Some authors reported the synthesis of heteroleptic ruthenium complexes by extending the conjugation length of the ancillary ligand.¹⁹ Such heteroleptic ruthenium complexes have a strong MLCT band and dye solar cells devices based on them display very good photovoltaic performance. In spite of this, the main drawback of these sensitizers is the lack of absorption in the red region of the visible spectrum and also relatively low molar extinction coefficient.²⁰ Many researchers have tried to overcome these shortcomings

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without significant success.^{21–24} The molecular engineering of ruthenium complexes for TiO₂-based solar cells presents a challenging task as several stringent requirements have to be fulfilled by the sensitizer.²⁵ 1,10-Phenanthroline and 2,2'-bipyridine has been used extensively as ligands form metal complexes for various applications such as fluorescence probes,^{26–29} electrocatalyst,³⁰ for dyes sensitized solar cells.³¹

The emphasis of the present work is the synthesis of four new ruthenium(II) bipyridyl and phenanthrolyl complexes incorporating anthracenyl units on the complexes thus showing the effect of increasing conjugation length of complexes through ligand substitution. We present here the synthetic methodology, photophysical characterization, spectroscopic, electrochemistry and preliminary solar cell properties of the complexes.

2. Experimental

2.1 Materials and general physicochemical measurements

All commercial reagents used were analytically pure and used without further purification. The starting material, 4'-Bromo-2,2'-bipyridine was synthesized as described in the literature.³² The ligands, L₁ = 4-(2,3-dimethylacrylic acid)-2,2'-bipyridine, L₂ = 4-(9-anthracenyl-10-(2,3-dimethylacrylic acid)-2,2'-bipyridine, L₃ = 5-(2,3-dimethylacrylic acid)-1,10-phenanthroline and L₄ = 5-(9-anthracenyl-10-(2,3-dimethylacrylic acid)-1,10-phenanthroline, with their corresponding homonuclear ruthenium(II) complexes formulated as *cis*-[Ru-(L₁)₃(PF₆)₂] (**C1**), *cis*-[Ru-(L₂)₃(PF₆)₂] (**C2**), *cis*-[Ru-(L₃)₃(PF₆)₂] (**C3**) and *cis*-[Ru-(L₄)₃(PF₆)₂] (**C4**), were synthesized with modifications to the reported procedure (scheme 1).^{33,34} All thin-layer chromatography (TLC) analyses were done with aluminium sheets pre-coated with normal phase silica gel 60 F254 (Merck, 0.20 mm thickness) unless otherwise stated. Gel filtration was performed using Sephadex LH-20 previously swollen in specified solvents prior to loading of extract onto the column

(3.5 cm × 8.5 cm). Melting points were determined using a Gallenkamp electrothermal melting point apparatus. Microanalyses were carried out with a Fisons elemental analyzer and infrared spectra were obtained as KBr discs on a Perkin Elmer System 2000 FT-IR and Bruker Tensor 27 spectrophotometer. UV-Vis absorption and fluorescence spectra were recorded in a 1 cm path length quartz cell on a Perkin Elmer Lambda 35 spectrophotometer and Perkin Elmer Lambda 45 spectrofluorimeter, respectively. ¹H- and ¹³C-Nuclear Magnetic Resonance (NMR) spectra were run on a Bruker EMX 400 MHz spectrometer for ¹H and 100 MHz for ¹³C. The chemical shift values were reported in parts per million (ppm) relative to (TMS) as internal standard. Chemical shifts were also reported with respect to DMSO d₆ at δ_C 40.98 and DMSO d₆ at δ_H 2.50 or CDCl₃ at δ_C 77.30 and δ_H 7.24 for synthesized ligands and complexes. All electrochemical experiments were performed using Autolab potentiostat PGSTAT 302 (EcoChemie, Utrecht, The Netherlands) driven by the general purpose Electrochemical System Data Processing Software (GPES, software version 4.9). A conventional three-electrode system was used. The working electrode was a bare glassy carbon electrode (GCE), Ag|AgCl wire and platinum wire was used as the pseudo reference and auxiliary electrodes, respectively. The potential response of the Ag|AgCl pseudo-reference electrode was less than the Ag|AgCl (3 M KCl) by 0.015 ± 0.003 V. Prior to use, the electrode surface was polished with alumina on a Buehler felt pad and rinsed with excess millipore water. All electrochemical experiments were performed in freshly distilled dry DMF containing TBABF₄ as supporting electrolyte.

2.2 Dye-sensitized solar cell fabrication and photo-response measurement

The preparation and measurement of I-V curves of sandwiched solar cells are as follows. The dye solutions were prepared in the concentration range of 2–3 × 10^{−4} M in dimethylformamide and a commercially made TiO₂ nanocrystalline from Solaronix was

Scheme 1. General synthetic procedure for **C1–C4** complexes. L_x or L_y = functionalized bipyridine or phenanthroline ligands.

dipped into the dye solution for 14–16 h at room temperature. The dye-coated electrodes were rinsed with ethanol and used as such for photovoltaic measurements. The dye deposited film is used as a working electrode. A sandwich cell was prepared with a second conducting glass coated with chemically deposited platinum from 0.05 M hexachloroplatinic acid. The platinum coated counter electrode and the dye coated TiO₂ film of surlyn polymer frame (Dupont) were tightly held using a pressure hot filler to seal the two electrodes. A thin-layer of electrolyte consisting of 0.6 M BMII; 0.05 M I₂; 0.1 M LiI; 0.5 M tert-butyl pyridine in 1:1 acetonitrile and valeronitrile was introduced into inter electrode space from the counter electrode side through pre-drilled holes. The drilled holes were sealed with cellophane tape. Photo-electrochemical data were measured using a 450 W Xenon light source that was focused to give 1000 W/m² (the equivalent of one sun at air mass 1.5) at the surface of the test cell. The applied potential and measured cell current were measured using a Keithley model 2400 digital sources meter. The current–voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. The process was fully automated using Wavemetrics software.

Further, impedance analysis was carried out with the objective to investigate the overall internal resistance of the cell which in turn influences the cell performance. Nyquist plot in between Z_{real} and Z_{imag} impedance was recorded with the Autolab FRA equipment using a 10 mV rms sinusoidal modulation.

2.3 Synthesis of ligands L₁–L₄ and their corresponding Ru(II) bis-hexafluorophosphate complexes

2.3a Synthesis of 4-(2,3-dimethylacrylic acid)-2,2'-bipyridine (L₁): 4-Bromo-2,2'-bpy (1.05 g, 3.38 mmol) and 2,3-dimethylacrylic acid (DMAA) (0.34 g, 3.38 mmol) were dissolved in MeOH (40 mL) in a 250 mL flask. Triethylamine (Et₃N) (1.0 mL) and palladium-carbide (0.050 g) were added and the mixture was reflux for 8 h at a temperature between 110 and 120°C. The reaction was allowed to cool to room temperature and the solvent removed under reduced pressure. The residue was dissolved in degassed water and then extracted with chloroform. The chloroform extract was concentrated *in vacuo* to obtain a brilliant colourless liquid which solidified after 48 h at room temperature. The resultant residue was recrystallized in Et₂O (30 mL). Colour: white crystalline solid; melting

point: ND; IR (KBr): 3054, 2927, 2676, 1965, 1690, 1648, 1581, 1559, 1456, 1419, 1346, 1251, 1141, 1089, 1040, 992, 893, 757, 653, 631, 619, 555. ¹H NMR (400 MHz, DMSO-d₆): δ 8.66 (d, J = 4.0 Hz), 8.41 (d, J = 8.0 Hz), 7.86 (dd, J = 7.6, 8.0 Hz), 7.36 (dd, J = 5.2, 7.2 Hz), 1.73 (s, CH₃), 1.66 (d, CH₃). ¹³C NMR (400 MHz, DMSO-d₆): δ 169.76, 156.21, 149.98, 137.86, 136.88, 129.74, 124.81, 121.32, 14.81, 12.71. Elemental Analysis: Found: C 70.71, H 5.55, N 11.31; required C₁₅H₁₄N₂O₂: Calculated: C 70.85, H 5.55, N 11.02. Percentage yield: 0.90 g, 67%.

2.3b Synthesis of 4-(9-anthracenyl-10-(2,3-dimethylacrylic acid)-2,2'-bipyridine (L₂): 4-Bromo-2,2'-bpy (1.00 g, 4.82 mmol) and 9-bromo-10-(2,3-dimethylacrylic acid)-anthracene (1.72 g, 4.82 mmol) were dissolved in benzene-dichloromethane (50 mL, v/v, 1:1), followed by the addition of Et₃N (1 mL), KOH and palladium-carbide (0.05 g). The reaction was carried out under reflux for 12 h at temperature 110–120°C. Purification and isolation of the product followed as reported for L₁ above. Colour: Yellow crystalline solid; Melting point: 167–169°C; IR (KBr): 3427, 3056, 2926, 1952, 1802, 1690, 1622, 1582, 1558, 1524, 1456, 1437, 1420, 1349, 1304, 1256, 1162, 1149, 1089, 1040, 1028, 995, 926, 747, 676, 654, 619, 605, 578. ¹H NMR (400 MHz, DMSO-d₆): δ 9.20 (2d, J = 1.6, 4.4 Hz), 8.57 (dd, J = 3.2, 6.8 Hz), 8.26 (d, J = 2.0 Hz), 8.24 (d, J = 1.6 Hz), 7.62 (dd, J = 3.2, 6.8 Hz), 2.17 (s, CH₃), 1.67 (s, CH₃). ¹³C NMR (400 MHz, DMSO-d₆): δ 156.76, 150.31, 146.27, 144.21, 135.94, 131.03, 128.52, 128.25, 127.44, 126.49, 124.21, 123.51, 123.04, 30.90 and 21.92. Elemental Analysis: Found: C 80.71, H 5.55, N 6.31; required C₂₉H₂₂N₂O₂: Calculated: C 80.91, H 5.15, N 6.51. Percentage yield: 1.93 g, 71%.

2.3c Synthesis of 5-(2,3-DMAA)-1,10-phenanthroline (L₃): The method of synthesis followed was as described for L₁ (section 2.3a). 5-Bromo-1,10-phenanthroline (1.00 g, 3.86 mmol) and 2,3-dimethylacrylic acid (0.39 g, 3.86 mmol) were dissolved in MeOH (40 mL) in a 250 mL flask. Et₃N (1.0 mL) and palladium-carbide (0.050 g) were added and the mixture was refluxed for 14 h between 110 and 120°C. The product of reaction was recrystallized in Et₂O. Colour: White-pink crystalline solid, melting point: ND, IR (KBr): 3419, 3032, 2929, 1694, 1652, 1619, 1589, 1561, 1506, 1420, 1385, 1343, 1256, 1219, 1140, 1093, 1080, 1037, 1015, 843, 766, 734, 769, 625, 530; ¹H NMR (400 MHz, CDCl₃): δ 11.32 (br, OH), 8.97 (t, 2H, H-2, 9), 7.92 (t, 2H, H-3, 8), 7.91 (s, 1H,

H-6), 7.44 (d, 1H, H-4), 6.82 (d, 1H, H-7), 1.67 (s, CH₃), 1.58 (d, CH₃); ¹³C NMR (400 MHz, CDCl₃): δ 150.39, 150.30, 146.30, 146.21, 138.79, 136.13, 128.81, 128.72, 126.68, 126.59, 123.27, 123.19, 14.74, and 12.14; Elemental Analysis: Found: C 73.65, H 5.11, N 10.19; required C₁₇H₁₄N₂O₂: Calculated: C 73.37, H 5.07, N 10.07. Percentage yield: 0.74 g, 53%.

2.3d Synthesis of 5-(9-anthracenyl-10-(2,3-dimethylacrylic acid)-1,10-phenanthroline (L4): The method of synthesis followed was as described for L₂ (section 2.3a). 5-Bromo-1,10-phenanthroline (1.0 g, 3.86 mmol) and 9-bromo-10-(2,3-dimethylacrylic acid)-anthracene (1.37 g, 3.86 mmol) were dissolved in benzene-dichloromethane (70 mL, v/v, 1:1), followed by the addition of Et₃N (1 mL), KOH and palladium-carbide (0.05 g). The reaction was carried out under reflux for 12 h at temperature 110–120°C. Isolation and purification of the residue was followed as reported in section 2.3b. Colour: yellow crystalline solid; melting point: 167–169°C; IR (KBr): 3427, 3055, 2979, 2924, 2552, 1966, 1871, 1802, 1579, 1558, 1453, 1417, 1304, 1255, 1140, 1089, 1040, 994, 926, 756, 654, 619, 579; ¹H NMR (CDCl₃): δ 9.18 (d, *J* = 3.2 Hz), 8.23 (d, *J* = 7.2 Hz), 7.77 (s), 7.62 (dd, *J* = 4.4, 8.0 Hz), 6.97 (d, *J* = 7.2 Hz), 1.81 (t, CH₃), 1.23 (t, CH₃); ¹³C NMR (CDCl₃): 150.28, 146.19, 139.25, 135.97, 128.61, 126.49, 123.06, 14.42, 11.74. Elemental Analysis: Found: C 81.75, H 4.62, N 6.33; required C₃₁H₂₂N₂O₂: Calculated: C 81.92, H 4.88, N 6.16; Percentage yield: 1.40 g, 59%.

2.3e Synthesis of tris-(4-(2,3-dimethylacrylic acid)-2,2'-bipyridyl-ruthenium(II) bis-hexafluorophosphate complex (C1): In a 250 mL flask, [RuCl₂(DMSO)₄] (0.05 g, 1.03 mmol) was dissolved in *N,N*-dimethyl-formamide followed by the addition of ligand L₁ (0.08 g, 3.09 mmol). The mixture was refluxed at 120°C for 5 h in the dark. The solution was allowed to cool to room temperature and filtered to remove unreacted starting material. The filtrate was concentrated to dryness and 40 mL of 0.05 M NaOH solution was added to give dirty brown precipitate which was filtered off. The pH of the resulting solution was adjusted to 3 with 0.5 M HNO₃. The solution was left to stand in the fridge (−2°C) for 12 h before being filtered and concentrated *in vacuo*. Aqueous solution of NH₄PF₆ was added to precipitate the residue from the bulk, and then filtered. The crude residue product was adsorbed onto Sephadex LH-20 adsorbent in a glass column and eluted using solvent system D (chloroform-methanol, 50%, 250 mL).³⁵ Colour: Dark brown solid; melting

point: 201–204°C; IR (KBr) ν_{max}/cm^{−1}: 3430, 2926, 2855, 1622, 1607, 1497, 1464, 1446, 1424, 1385, 1314, 1270, 1245, 1162, 1125, 1070, 838, 763, 731, 610, 557, 472, 421; UV-Vis (λ_{max}/nm, ε = M^{−1} cm^{−1}, DMF): 343 (2059), 447 (3218), 914 (880) and 1015 (1200); Emission wavelength: (λ_{exc.} = 470 nm, λ_{em} = 747 nm). ¹H NMR (DMSO-d₆): δ 8.62 (d, *J* = 5.6 Hz, 1H), 8.06 (s, 1H), 7.69 (s, 1H), 7.43 (s, 1H). ¹³C NMR (DMSO-d₆): δ 157.23, 151.82, 128.52, 125.03. Elemental Analysis: Found: C 46.63, H 3.60, N 7.54; required RuC₄₅H₄₂N₆O₆P₂F₁₂: Calculated: C 46.84, H 3.67, N 7.28. Percentage yield: 0.083 g, 64%.

2.3f Synthesis of tris-4-(9-anthracenyl-(2,3-dimethylacrylic acid)-2,2'-bipyridyl-ruthenium(II)-bis-hexafluorophosphate complex (C2): The complex was prepared in a similar manner as described for C1 above. Ligand (L₂) (0.22 g, 0.51 mmol) and [RuCl₂(DMSO)₄] (0.08 g, 0.17 mmol) were added as a mixture and refluxed in DMF (60 mL). The product was obtained after precipitation from excess aqueous NH₄PF₆. Colour: orange solid; melting point: 226–227°C; IR (KBr): 3430, 3076, 2928, 2865, 1902, 1678, 1622, 1591, 1580, 1437, 1332, 1321, 1304, 1285, 1256, 1206, 1170, 1098, 1028, 969, 937, 926, 809, 747, 694, 622, 604, 579, 387; UV-Vis (λ_{max}/nm, ε = M^{−1} cm^{−1}, DMF): 358 (4342), 379 (4960), 401 (5557), 447 (5770), 907 (1410) and 1011 (1970); Emission wavelength: (λ_{exc.} = 640 nm, λ_{em} = 710 nm). Selected ¹H NMR data (CDCl₃): δ 8.83 (d, *J* = 7.6 Hz), 8.56 (m), 8.17 (s), 7.74 (s), 7.53 (s); Electrochemical Data: Ru²⁺/Ru³⁺ = 0.64 V; E_{anodic} = 0.42 V, E_{cathodic} = −0.99 V. Elemental Analysis: Found: C 62.45, H 3.55, N 4.63; required RuC₈₇H₆₆N₆O₆P₂F₁₂: Calculated: C 62.11, H 3.95, N 4.99. Percentage yield: 0.135 g, 45%.

2.3g Synthesis of tris-5-(2,3-dimethylacrylic acid)-1,10-phenanthroline Ru(II) bis-hexafluorophosphate complex (C3): The complex was prepared in a similar manner as described for C1 above. Ligand L₃ (0.16 g, 0.58 mmol), [RuCl₂(DMSO)₄] (0.09 g, 0.19 mmol) were dissolved and refluxed in DMF (60 mL). A red oily product was obtained after column chromatography (Et₂O-MeOH, 50%), and was precipitated by adding excess of aqueous NH₄PF₆. Colour: Orange solid; Melting point: 236–239°C; IR (KBr) ν_{max}/cm^{−1}: 3551, 3479, 3414, 3238, 2928, 2852, 1637, 1617, 1428, 1412, 1342, 1256, 1206, 1147, 1095, 1018, 927, 839, 775, 747, 722, 620, 557, 529, 474, 407; UV-Vis (λ_{max}/nm, ε = M^{−1} cm^{−1}, DMF): 421 (12 477), 443 (13 030); Emission wavelength: (λ_{exc.} = 470 nm, λ_{em} = 715 nm); Selected ¹H NMR data (CDCl₃): δ 8.75 (d, *J* = 8.4 Hz),

8.36 (s), 8.06 (d, $J = 5.2$ Hz), 7.74 (dd, $J = 5.2$, 8.4 Hz), 6.71 (d, $J = 6.8$ Hz), 2.06 (s, CH₃), 1.71 (m, CH₃); Electrochemical Data: Ru²⁺/Ru³⁺ = 0.84 V, $E_{1/2} = 0.15$ V, 0.47 V. Elemental Analysis: Found: C 50.01, H 3.55, N 6.48; required RuC₅₁H₄₂N₆O₆P₂F₁₂: Calculated: C 49.97, H 3.45, N 6.86. Percentage yield: 0.13 g, 53%.

2.3h Synthesis of tris-5-(9-(anthracenyl)-(2,3-dimethylacrylic acid)-1,10-phenanthroline ruthenium(II) bis-hexafluorophosphate complex (C4): The complex was prepared in a similar manner as described for **C1** above. Ligand L₄ (0.10 g, 0.22 mmol) and [RuCl₂(DMSO)₄] (0.04 g, 0.07 mmol) were dissolved in DMF/MeOH (60 mL, 1:1, v/v) and refluxed. The product was precipitated by adding excess aqueous NH₄PF₆. Colour: Dark orange solid; Melting point: >300°C; IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3550, 3474, 3414, 2926, 1638, 1617, 1464, 1447, 1309, 1256, 1162, 1028, 926, 838, 761, 747, 731, 620, 578, 557, 475; UV-Vis ($\lambda_{\max}/\text{nm}$, $\epsilon = \text{M}^{-1} \text{cm}^{-1}$ DMF): 343 (9230), 362 (12330), 383 (17096), 405 (18240), 452 (11556); Emission wavelength: ($\lambda_{\text{exc}} = 470$ nm, $\lambda_{\text{em}} = 676$ nm). Selected ¹H NMR data (CDCl₃): δ 8.83 (d, $J = 8.0$ Hz), 8.56 (dd, $J = 3.2$, 6.8 Hz), 8.17 (t), 7.82 (dt, $J = 3.2$, 6.8 Hz), 7.73 (d, $J = 5.6$ Hz), 7.53 (dd, $J = 6.0$, 6.4 Hz); ¹³C NMR (CDCl₃): δ 157.42, 152.07, 138.79, 131.26, 128.75, 125.34, 13.94; Electrochemical Data: $E_{\text{anodic}} = 0.43$ V, Ru²⁺/Ru³⁺ = 0.71 V; $E_{1/2} = -0.58$ V. Elemental Analysis: Found: C 64.01, H 4.11, N 4.23; required RuC₉₃H₆₆N₆O₆P₂F₁₂: Calculated: C 63.66, H 3.79, N 4.79. Percentage yield: 0.08 g, 60%.

3. Results and discussion

3.1 Synthesis of ligands and complexes

Functionalized anthracene, 2,2'-bipyridine and 1,10-phenanthroline derivatives were synthesized according to established procedure.³² The initial aromatic substitution of one of the bromide ion on 9,10-dibromoanthracene with 2,3-dimethylacrylic acid was successful due to the fact that we were able to find a satisfactory solvent system combination (50%, dichloromethane-benzene), to overcome the poor solubility property of 9,10-dibromoanthracene in common organic solvents.³⁵ The synthesis of the metal precursor [RuCl₂(DMSO)₄] and all the complexes **C1–C4** (figure 1), was carried out by following the general route.^{33,34} The first step was the coordination of the DMSO ligand with RuCl₃·H₂O followed by the sequential substitution of the DMSO with synthesized ligands

(scheme 1). All complexes were purified in column chromatography. However, attempts were not made to isolate the various side product fractions from column chromatography. The major products purity was ascertained using thin-layer chromatography (TLC) in appropriate solvent systems which were then followed by precipitation in aqueous solution of ammonium hexafluorophosphate.

3.2 Infrared studies of complexes

The FT-IR spectra of the starting materials, the ligands and the complexes showed certain characteristic absorption bands that were compared and assigned on careful comparison. Due to structural similarities among the various ligands, a strong vibrational band between 3427 and 3419 cm⁻¹ was found. This gave an indication of the presence of an O-H group possibly from the carboxylic acid moiety in the ligands. The vibrational frequency bands between 3076 and 3027 cm⁻¹ may be due to the presence of an α , β -unsaturated carboxylic acid and/or aromatic C-H stretching characteristics of the molecules. The band at 2928 cm⁻¹ shows the presence of C-H stretching of methyl groups. The bands at 1694, 1690, and 1622 cm⁻¹ are due to carbonyl stretching and the aromatic C=C stretching band was found in the region of 1621 cm⁻¹. Bands in the region 1581–1502 cm⁻¹ were assigned to the C-N stretching of the polypyridyl groups. The strong bands at 1456–1417 cm⁻¹ were assigned to C-H deformation of the methyl groups and the presence of ethereal groups (C-O) in the molecules was confirmed with the bands at 1256, 1216 cm⁻¹. At the fingerprint region, the strong peak band at 926 cm⁻¹ was conspicuously absent in those ligands containing no anthracenyl functionalities. This band is indicative of the C-C bond linkage between the anthracene and the bipyridine or phenanthroline ligand.

In the FT-IR spectra of the complexes, it was observed that nearly all the complexes showed an upward shift in absorption frequency for the O-H stretching vibration at 3550 cm⁻¹. No major change in frequency was observed in the region of 3237–2850 cm⁻¹. Furthermore, peaks in the region 770 and 730 cm⁻¹ demonstrate the existence of four adjacent hydrogen atoms common to the anthracenyl ligands and their corresponding complexes. All vibrational peaks in the region are found relatively weak and broad in the complexes, which may be ascribed to the loss of crystallinity and the broad distribution of the anthracene chain length.³⁶ The weak absorption frequencies between 466 and 444 cm⁻¹, respectively, show

Figure 1. Proposed structures for the complexes.

the coordination of nitrogen atoms of the ancillary ligands to ruthenium central metal atom.³⁷

3.3 Electronic absorption and emission studies of **C1–C4** complexes

The UV-Vis spectra of complexes **C1–C4** are shown in figure 2 below. The UV-region, 200–300 nm, contained the $\pi \rightarrow \pi^*$ intra ligand absorption for the bipyridyl and phenanthrolyl ligands. This region is not shown here in the spectra. The near-visible region between 350 and 405 nm was occupied by the vibronic absorption peaks for the substituted anthracene. The vibronic peaks were

of higher intensity in **C4** for a substituted phenanthroline ligand than its counterpart **C2**, containing the bipyridyl ligand. The peaks were not found in both **C1** and **C3** complexes. At the visible region, 410–520 nm, all the complexes show the metal-to-ligand charge transfer transitions (MLCT) characteristics of a Ru(II) complexes. For the bipyridyl ruthenium(II) complexes (**C1** and **C2**), virtually, the wavelength differ by only 1 nm (445 and 446 nm), respectively, but higher molar extinction coefficient is recorded for **C2**. The opposite could be said for the phenanthroline complexes as found in **C3** and **C4**. By comparison, complex **C4** absorption maximum wavelength at 452 nm which is blue-shifted ($ca = 5$ nm) in **C3**.

The emission spectra of the complexes **C1**, **C2**, **C3** and **C4** are shown in figure 3. It is observed that all the complexes show good photoluminescence properties. However, the information from the spectra shows that towards the near infrared region, emission of the complexes is governed by the molecular weight. **C1** with the smallest molecular weight (863.94 a.u) gave the highest emission wavelength at 748 nm which is blue-shifted ($ca = 39, 33$ and 72) for **C2**, **C3** and **C4**, respectively.

Figure 2. UV-Vis absorption spectra of complexes **C1–C4** in DMF.

3.4 NMR spectral studies of ligands and complexes

The proton NMR spectrum of **L1** contains six peaks at 8.66 (d, 1H), 8.41 (d, 1H), 7.86 (dd, 1H), 7.36 (1H), 1.73 (s, 3H), 1.66 (d, 3H) ppm. The bipyridine

Figure 3. Emission spectra of complexes **C1–C4** in DMF.

peak positions are very similar to the starting bromobipyridine material. The principal difference is due to the inclusion of the methyl resonance at the upfield region of the spectrum. The ^{13}C NMR spectrum gave the anticipated peaks at 169.76, 156.21, 149.98, 137.86, 136.88, 129.74, 124.81, 121.32, 14.81 and 12.71. The bipyridine peaks due to chemical equivalency were observed in the range of 156–128 ppm. The peak at 169.76 ppm was assigned to the carbonyl carbon; the two peaks at 124.81 and 121.32 were assigned to the alkenyl carbons, while the methyl groups were found at 14.81 and 12.71 ppm. The proton NMR spectrum of **L₂** shows five signals at the aromatic region at δ 9.20 (d), 8.57 (dd), 8.26 (d), 8.24 (d), 7.62 (dd) were assigned to the bipyridine and anthracene moieties. The two singlet peaks at the aliphatic region were assigned to the methyl groups at δ 2.17 and 1.67 ppm. The ^{13}C spectrum of **L₂** was similar to that of **L₁** except those additional peaks at 131.03, 128.25, 127.44 and 126.49 ppm that were assigned to the anthracenyl carbons signals. The proton NMR spectrum of **L₃** is very similar to that obtained for **L₁**, but for ^{13}C NMR that contained two additional carbon peaks of the phenanthroline ligands. In **L₄**, two doublets, one doublet of doublet and a single peak were observed at the aromatic region (δ 9.18–6.97 ppm). These were assigned to H–2, 9; H–4, 7, and H–3, 8, respectively and the singlet peak assigned to H–6. However, it was difficult to distinguish those peaks for anthracenyl protons in the spectrum for which a downfield shift ($ca = 0.21$ ppm) was observed when compared to **L₃**.

Complex **C1** was purified using Sephadex LH-20 column chromatography and was obtained as a dark-brown solid. The proton NMR spectrum of the complex shows only one doublet peak at δ 8.62 ppm and three singlet peaks at 8.06, 7.69 and 7.43 ppm at the

aromatic region. When compared to the proton NMR spectrum data of the coordinating ligand **L₁**, all proton peaks experience upfield shifts in the chemical shift values, this is attributed to the effect of the lone pair-lone pair electron donor property of the nitrogen atoms of the bipyridyl rings to the ruthenium metal centre. However, unlike in **L₁**, the aliphatic region of the spectrum is devoid of the presence of the methyl protons chemical shift to signify the presence of the substituent group of the 2,3-dimethylacrylic acid. This result was further corroborated with the absence of the carbonyl and/or methyl peaks in the ^{13}C NMR spectrum. We tend to adduce the loss of these peaks to the fragmentation of 2,3-dimethylacrylic acid possibly during intense heating and/or column chromatography in Sephadex LH-20. Due to the poor solubility of **C2** in various organic solvents, an unsatisfactory proton NMR spectrum was obtained and it was difficult to assign individual peaks based on the available data. The proton NMR spectrum of **C3** showed expected peaks for a 5-substituted phenanthroline ligand. In the aromatic region of the spectrum, one doublet of doublet, three doublet peaks and a single peak were observed. The peaks at δ 8.75, 8.06 and 6.71 ppm were assigned to H–2, 9; H–4 and H–7 protons. The doublet of doublet peak at δ 7.74 ppm was assigned to protons H–3, 8. The singlet peaks at δ 2.06 and a multiplet peak at δ 1.71 were assigned to the methyl protons. The proton NMR spectrum of **C4** shows six peaks at δ 8.83 (d, $J = 8.0$ Hz), 8.56 (dd, $J = 3.2, 6.8$ Hz), 8.17 (t), 7.82 (dt, $J = 3.2, 6.8$ Hz), 7.73 (d, $J = 5.6$ Hz) and 7.53 (dd, $J = 6.0, 6.4$ Hz). The phenanthroline peak positions are very similar to that of **C3**. The only difference is due to the anthracenyl peaks. The resonances were assigned to the protons on the phenanthroline ligand and those of the anthracene

Figure 4. Cyclic voltammogram of **C2** at 1×10^{-3} M in freshly distilled DMF containing 0.1 M TBABF₄ as supporting electrolyte. Step potential = 5 mV, amplitude = 50 mV vs. Ag|AgCl.

Figure 5. Cyclic voltammogram of **C3** at 1×10^{-3} M in freshly distilled DMF containing 0.1 M TBABF₄ as supporting electrolyte. Step potential = 5 mV, amplitude = 50 mV vs. Ag|AgCl.

Figure 6. Cyclic voltammogram of **C4** at 1×10^{-3} M in freshly distilled DMF containing 0.1 M TBABF₄ as supporting electrolyte. Step potential = 5 mV, amplitude = 50 mV vs. Ag|AgCl.

unit. The ¹³C NMR spectrum shows seven peaks at δ 157.42, 152.07, 138.79, 131.26, 128.75, 125.34 and 13.94 ppm. The carbonyl peak was assigned to the peak at 157.42 ppm, the peaks at 152.07, 138.79 and 131.26 are due to the phenanthroline peaks and the two intense peaks at 128.75 and 125.34 are the anthracene peaks. The methyl group was assigned to the peak at 13.94 ppm.

3.5 Cyclic voltammetry studies of complexes

In the potential range +1.5 to -1.5 at a scan rate 50 mV s^{-1} , the cyclic voltammogram of **C2**, **C3** and **C4** (figures 4, 5 and 6), were examined using Ag|AgCl electrode in DMF solvent with 0.1 M tetra butyl ammonium hexafluorophosphate as supporting electrolyte. The voltammograms display the Ru(III)/Ru(II) couple at positive potentials and the ligand-based reduction couples at negative potentials. The potentials are summarized in table 1. A well-defined reversible peak was observed for **C2** at 0.64 V. This potential was assigned to the Ru(III)/Ru(II) couple. Other ligand-based oxidation potential for **C2** was found at 0.42 V. In the negative potential, **C2** shows reduction potential at -0.62

and -0.99 V. For the derivatized phenanthroline complexes **C3** and **C4**, three reversible oxidation processes at 0.15, 0.47 and 0.84 V were observed for **C3** while **C4** shows only one oxidation and/or reduction peak at 0.43 and -0.58 V, respectively. However, the reduction wave was not well-defined in **C3**. Based on the strong negative potential in **C2** compared to **C3**, the influence of conjugation is shown, thus giving the support to the increase in number of anthracene molecular unit in the complex and a corresponding increase in its electron donating ability. The cyclic voltammogram of **C1** could not be established based on its poor solubility in solvents.

3.6 Dye-sensitized solar cells studies

Application of these complexes in the dye-sensitized solar cells (DSSCs) shows interesting properties, and useful insight into the sensitization of wide-band gap semiconductors by anthracenyl-based molecules was gained. I/V curves for the evaluated complexes **C1**–**C4** are displayed for the shunt and series resistance (R_{sh} and R_s). The short circuit currents (J_{sc}),

Table 1. Summary of the electronic absorption and evaluation of DSSCs characteristics of **C1**–**C4**.

Dye	$\lambda_{abs}^a/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	J_{sc} (mA/cm ²)	$V_{oc} \times 10^{-3}$ (V)	P_{max}	Fill factor (FF)	(η) %
C1	447 (3218)	35.2×10^{-3}	-60	9.09×10^{-3}	-4.9×10^3	0.103
C2	447 (5770)	ND	ND	ND	ND	ND
C3	443 (13030)	193.0×10^{-3}	-240	6.48×10^{-3}	-139.8×10^3	0.074
C4	452 (11556)	9.1×10^{-3}	-20	121.2×10^{-6}	-13.3×10^3	0.001

ND, not determined.

open circuit potentials (V_{oc}), fill factors (FF) and the conversion efficiencies (η) are listed in table 1. The solar conversion efficiency was calculated using the equation: ($\eta = J_{sc} \times V_{oc} \times FF / P_{input}$), where, $P_{input} = 0.088$ W. Based on the data generated from I/V curves, the DSSCs efficiencies of the molecules show very low overall performance. It was difficult to obtain good films of the TiO_2 nanocrystalline semiconductor, and thus a low device resistance, low open circuit voltage, V_{oc} , and low short circuit current, I_{sc} values

were obtained. The highest conversion efficiency was recorded for **C3** (<0.103%) closely followed by **C1** (0.074%). The difference between the performances of the complexes may be attributed to various factors among which include the surface concentrations. The poor absorption of **C2** and **C4** on the semiconductor led to conversion efficiency as low as 0.001% for **C4**. This may be interpreted to result from the bulky anthracenyl groups in the molecules. The bulky sensitizers require more space on the TiO_2 surface and penetrate less

Figure 7. Comparison of Nyquist plots (left) and Bode plots (right) of complexes **C1**–**C4** for DSSCs at a constant illumination of 1000 W/m^2 .

easily in the small cavities of the nanocrystalline TiO_2 than the sterically less hindered molecules. The effects can be compared with the corresponding ratios of J_{sc} values, which range from 4% to 21% in the complexes. Here, it is clear that J_{sc} depends on the dye surface concentration. Though, it has been reported that ratios are significantly higher than what would be expected if the surface concentration were the only determining factor.^{38,39} V_{oc} was observed to decrease with decrease in surface concentration, in our cells, the low dye coverage has led to lower current output values as could be found in the I/V curves. Indeed, the fitting of the cells I/V characteristics revealed a low R_{sh} , indicative of a high recombination rate at the photoanode surface and high R_s , indicative of the ohmic losses at the counter electrode and the contacts. Although, the tested compounds have appreciable absorption wavelengths in the visible region of absorption for metal-to-ligand charge transfer (MLCT) transitions, the energy difference between the LUMO levels and the TiO_2 conduction band could affect the electron injection from the excited dyes. This could be a very significant factor in the overall performance of the DSSCs. Electrolyte leakage was observed during the preparation of the cells, this may have contributed to the low efficiency of the complexes. It is well-known that electrode must be able to transport the charge carrier between photoanode and counter electrode. After the complex injects electrons into the conduction band of TiO_2 , the oxidized dye must be reduced to its ground state rapidly. The leakage of the electrolyte from the cells may have blocked the smooth transport of the electrons from the complexes to the semiconductor band gap.

3.7 Electrochemical impedance spectroscopy (EIS) studies

The impedance analysis of the cell was carried out with an objective to investigate internal resistance of the cell attributable to charge transfer process. The conversion efficiency of the cell can be improved based on the understanding of the charge transfer process and internal resistance of the cell. The components of the DSSC that contributes to impedance are porous TiO_2 electrode, counter electrode, and electrolyte.^{40–42} In this work, the analysis was done using both the Nyquist plots and Bode plots (figure 7) which is associated with the different adsorption of complexes on TiO_2 semiconductor and was measured at open-circuit voltage. The ohmic serial resistance (R_s) corresponds to the electrolyte and the FTO resistance and the resistances R_{ct2} relate to charge-transfer resistance occurring at the dye-sensitized TiO_2 film/solution interface.⁴³

4. Conclusion

The design, synthesis, spectroscopic and electrochemical characterization of a number of new functionalized polypyridine ligands and their corresponding Ru(II) homonuclear complexes are reported. We further examined the sensitizing properties of the complexes in the dye-sensitized solar cells (DSSCs). Though, it has been established through various studies the importance of visible and or near-infrared absorption, as well as high molar extinction coefficient as parameters important for the enhancement of the solar efficiency of the dye-sensitized solar cells. The main idea in this work has focused on the extension of the $\pi \rightarrow \pi$ conjugation bonds of both the ligands and their corresponding complexes with a view to enhancing the molar absorptivity coefficient.

The complexes reported showed good photophysical and photoluminescence at the visible and near-infrared region of the electromagnetic spectrum. The electroredox properties of complexes showed that they might be useful in the design of chemosensors, photoemitters and other photoelectrochemical processes. Further work is however, necessary to fine-tune the surface morphology of the complexes as well as those for semiconductors to bring about strong adsorption at the interface which would enhance the photon conversion efficiency of the compounds.

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