APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 125–129 **Materials, Nanoscience and Catalysis** **AOC**

Synthesis and photophysical properties of novel amphiphilic ruthenium (II) complexes containing 4,4′-dialkylaminomethyl-2,2′-bipyridyl ligands

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Received 29 August 2005; Revised 15 September 2005; Accepted 27 October 2005

The synthesis of a number of new 2,2′-bipyridine ligands functionalized with bulky amino side groups is reported. Three homoleptic polypyridyl ruthenium (II) complexes, $[Ru(L)_3]^{2+}$ $2(PF_6^-)$, where L is 4,4′-dioctylaminomethyl-2,2′-bipyridine (Ru4a), 4,4′-didodecylaminomethyl-2,2′-bipyridine (Ru4b) and 4,4′-dioctadodecylaminomethyl-2,2′-bipyridine (Ru4c), have been synthesized. These compounds were characterized and their photophysical properties examined. The electronic spectra of three complexes show pyridyl $\pi \rightarrow \pi^*$ transitions in the UV region and metal-to-ligand charge transfer bands in the visible region. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: dialkylaminomethyl; substituted bipyridyl ligands; amphiphilic; ruthenium (II) complexes

INTRODUCTION

There is great interest in ruthenium (II) complexes with 2,2′-bipyridine ligands and their derivatives because of their light-induced electron and energy transfer properties.[1–5] Systematic variations of substituents have served as important tools for the understanding of physical properties of metal complexes.[6] The photochemical function can be modulated through the ligand design.[7] Functionalization and linkage of bipyridine ligands were used to create supramolecular systems.[8,9] The 4,4′-disubstitution pattern is desirable, because substitution at these positions does not lead to steric complications during complexation. This approach has been complicated first by the fact that, traditionally, 4,4′-halomethylbipyridine **2** has been difficult to access cleanly and in high yield. However, the use of 4,4′-disubstituted bipyridines as metal-chelating agents so far has been restricted, probably because the syntheses reported for these compounds are rather laborious and the yields moderate to low.[10,11] To the best of our knowledge only a few reports exist detailing the synthesis of 4,4′-dialkylaminomethyl-2,2′-bipyridines.[12] However, these old workings knew little development and not reported the properties of ligands for these molecules. The goal of this work was to develop organometallic complexes of ruthenium (II)-containing ligands with new amino sites for applications in photobiology and in supramolecular domain (interfacial catalysis).

This paper describes the details of synthesis, characterization and different spectral properties of a series of metal-free 4,4′-dioctylaminomethyl-2,2-bipyridines **3a**, 4,4′-didodecylaminomethyl-2,2′-bipyridines **3b** and 4,4′-dioctadecylaminomethyl-2,2′-bipyridines **3c** and the final corresponding ruthenium(II) complexes. The influence of alkylaminomethyl substitution on the spectroscopy of 2,2′-bipyridine and its metal complexes will be discussed.

EXPERIMENTAL

General considerations

All chemicals were obtained from Aldrich or Acros and were used as received unless otherwise indicated. Diethyl ether, THF, toluene and hexane were freshly distilled from sodium.

^1H (300 MHz), and ^{13}C (75.4 MHz) NMR spectra were recorded on a Bruker AC 300PNMR spectrometer. Chemical shifts are reported as δ values in ppm relative to

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Me_4Si as internal standard. Electrospray mass spectrometry (ESMS) was performed on Micromass LCT-TOF mass spectrometer. The elemental analysis was performed using RSIC. Ultraviolet-visible absorption spectra were recorded on a Hewlett Packard 8452 diode array spectrophotometer.

Luminescence measurements were conducted on a Photon Technology International fluorescence spectrophotometer. Samples were excited at 452 nm. Emission was observed between 500 and 800 nm and emission intensities were measured at 618 nm and corrected for the instrument's response. Quantum yields were calculated by comparison with $\text{Ru(bipy)}_3{}^{2+}$ ($\Phi_{std} = 0.033$) in aerated solution at room temperature using the following equation:[13]

$$\Phi = \Phi_{std}(A_{std}/A)(I/I_{std})$$

where Φ and Φ_{std} are the quantum yields of ruthenium complexes and the standard samples; A and A_{std} are the absorbances at the excitation wavelength; and I and I_{std} are the integrated emission intensities.

Synthesis of the ligands

Synthesis of 4,4′-bis[(trimethylsilyl)methyl]-2,2′-bipyridine (1)

The compound **1** was synthesized from 4,4′-dimethyl-2,2′-bipyridine by a modified procedure described in the literature.[14] We used a hexane solution of lithium diisopropylamide (2 M in hexanes, 11 ml) in THF (32 ml), to which was added slowly a solution of 4,4′-dimethyl-2,2′-bipyridine (1.842 g, 10 mmol) in THF (50 ml) at −78 °C. The brown mixture was stirred at −78 °C for 20 min, was warmed to −10 °C for 25 min, and then cooled to −78 °C before addition of trimethylsilyl chloride (TMSCl; 3.3 ml, 26 mmol). Crude **1** was purified by recrystallization from a minimal amount of hexane at −4 °C. Washing with copius quantities of very cold CH_3CN left TMS product **1** as a white crystalline solid: 3.165 g (96%); ^{1}H NMR ($CDCl_3$) δ: 0.04 (s, 18 H), 2.21 (s, 4H), 6.94 (d, 2H), 8.05 (br s, 2H), 8.46 (d, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 2.2, 27.1, 120.4, 123.0, 148.3, 150.8, 155.5.

Synthesis of 4,4′-bis(chloromethyl)-2,2′-bipyridine (2)

The compound **2** was synthesized from the corresponding 4,4′-(trimethylsilylmethyl) derivative by a modified procedure of the CsF method described in the literature.[14,15] To dry acetonitrile solution (10 ml), 3.28 g (10 mmol) of 4,4′-bis[(trimethylsilyl)methyl]-2,2′-bipyridine **1** and 9.46 g (40 mmol) Cl_3CCCl_3 were added with 6 g (40 mmol) anhydrous CsF at 25 °C under nitrogen atmosphere. Acetonitrile (100 ml) was added and the heterogeneous reaction mixture was stirred at 60 °C for 4 h. After complete conversion, the mixture was cooled to 25 °C and poured into a separating funnel containing EtOAc and water (100 ml each). The product was extracted with EtOAc (3 × 100 ml); the combined organic fraction was shaken with brine (100 ml) and dried over Na_2SO_4. Filtration and concentration on a rotary evaporator afforded the product, **2** as an off-white crystalline solid: 2.40 g (95%). ^{1}H NMR ($CDCl_3$) δ: 4.63 (s, 4H), 7.38 (7.38, dd, 2H), 8.43 (s, 2H), 8.70 (d, 2H). ^{13}C NMR ($CDCl_3$) δ: 43.39, 120.1, 122.8, 146.3, 146.7, 149.4, 155.8. Anal. calcd for $C_{12}H_{10}Cl_2N_2$: C, 56.94; H, 3.98; N, 11.07; found: C, 58.80; H, 4.01; N, 11.02.

Synthesis of ligands 3a, 3b and 3c

The ligands 4,4′-dialkylaminomethyl-2,2′-bipyridine **3a**, **3b** and **3c** were prepared by refluxing dialkylamine with 4,4′-bis(chloromethyl)-2,2′-bipyridine in CH_3CN in the presence of K_2CO_3, and purified on a silica column using an ethyl acetate–hexane (1 : 1) solvent mixture.

4,4′-dioctylaminomethyl-2,2′-bipyridine (3a)

Yellow-red oil: (70%); ^{1}H NMR ($CDCl_3$) δ: 0.83 (t, 12H, CH_3), 1.33 (m, 8H, $-CH_2-$), 1.29 [m, 32H, $-(CH_2)_4-$], 1.39 (m, 8H, $-CH_2-$), 2.36 (t, 8H, $-CH_2-N-$), 3.62 (s, 4H, $N-CH_2-$), 7.07 (dd, 2H, 5-H and 5′-H), 8.18 (s, 2H, 3-H and 3′-H), 8.50 (d, 2H, 6-H and 6′-H); ^{13}C NMR ($CDCl_3$) δ: 155.12, 150.17, 148.05, 122.70, 120.19, 57.04, 53.19, 30.84, 28.51, 28.30, 26.40, 26.09, 21.64, 13.08 ppm; ESIMS (m/z) calcd: 662.6226; found: 663.5516; anal. calcd for $C_{44}H_{78}N_4$: C 79.71, H 11.86, N 8.45. Found: C, 78.76; H, 11.67; N, 7.90.

4,4′-didodecylaminomethyl-2,2′-bipyridine (3b)

White crystalline solid (65%); ^{1}H NMR ($CDCl_3$) δ: 0.83 (t, 12H, CH_3), 1.33 (m, 8H, $-CH_2-$), 1.29 [m, 64H, $-(CH_2)_4-$], 1.39 (m, 8H, $-CH_2-$), 2.36 (t, 8H, $-CH_2-N-$), 3.62 (s, 4H, $N-CH_2-$), 7.07 (dd, 2H, 5-H and 5′-H), 8.18 (s, 2H, 3-H and 3′-H), 8.50 (d, 2H, 6-H and 6′-H); ^{13}C NMR ($CDCl_3$) δ: 155.12, 150.17, 148.05, 122.70, 120.19, 57.04, 53.19, 30.84, 28.51, 28.50, 28.30, 28.30, 26.40, 26.30, 26.09, 26.09, 21.64, 13.10 ppm; ESIMS (m/z) calcd: 886.8730; found: 887.8735. Anal. calcd for $C_{60}H_{110}N_4$: C 81.20, H 12.49, N 6.31. Found: C, 80.24; H, 12.30; N, 5.87.

4,4′-dioctadodecylaminomethyl-2,2′-bipyridine (3c)

White crystalline solid (85%); ^{1}H NMR ($CDCl_3$) δ: 0.83 (t, 12H, CH_3), 1.33 (m, 8H, $-CH_2-$), 1.29 [m, 112H, $-(CH_2)_4-$], 1.39 (m, 8H, $-CH_2-$), 2.36 (t, 8H, $-CH_2-N-$), 3.62 (s, 4H, $N-CH_2-$), 7.07 (dd, 2H, 5-H and 5′-H), 8.18 (s, 2H, 3-H and 3′-H), 8.50 (d, 2H, 6-H and 6′-H); ^{13}C NMR ($CDCl_3$): δ: 155.12, 150.17, 148.05, 122.70, 120.19, 57.04, 53.19, 30.84, 28.51, 28.30, 28.30, 28.30, 28.09, 28.09, 28.09, 26.45, 26.45, 26.40, 26.40, 26.40, 26.35, 26.35, 21.64, 13.10 ppm; ESIMS (m/z) calcd: 1223.2487; found: 1224.1569; anal. calcd for $C_{84}H_{158}N_4$: C 82.41, H 13.01, N 4.58; found: C, 81.43; H, 12.80; N, 4.27.

Synthesis of the ruthenium (II) complexes

The synthetic procedure for the preparation of Tris-homoleptic complexes **4a–c** followed published procedures[16,17] with slight modifications.

Tris(4,4′-dioctylaminomethyl-2,2′-bipyridine) ruthenium (II) hexafluorophosphate $[Ru(3a)_3]^{2+}$ $2(PF6)^-$ (Ru4a)

A mixture of 4,4′-dioctylaminomethyl-2,2′-bipyridine (**3a**) (0.150 g, 0.226 mmol) and ruthenium (III) chloride hydrate

(0.156 g, 0.075 mmol) was refluxed in 50 ml ethanol for 6 h. While still hot, the solution was filtered. The red-orange mixture was rotary-evaporated, washed with ether to remove excess ligand, and dissolved in 10 ml hot methanol, and the new mixture was filtered. The methanol solution was further purified by chromatography on a cation exchange chromatography column (Sephadex, 40–120 mesh) with methanol as the eluent. The orange band was collected, and the solvent was rotary-evaporated. A solution of 2 g of NH_4PF_6 dissolved in water–methanol (10:3) was added, resulting in the precipitation of the complex, which was filtered, rinsed with water and subsequently dried. It gave one pot on a silica gel TCL plate using 5:4:1 acetonitrile–water–saturated KNO_3 (aq.) as the developing reagent. Yield: 0.128 g (85%). ^1H NMR ($CDCl_3$) δ: 0.83 (t, 12H, CH_3), 1.33 (m, 8H, $-CH_2-$), 1.29 [m, 32H, $-(CH_2)_4-$], 1.39 (m 8H, $-CH_2-$), 2.36 (t, 8H, $-CH_2-N-$), 3.91 (s, 8H, $N-CH_2-$), 6.99 (dd, 2H, 5-H and 5′-H), 8.56 (s, 2H, 3-H and 3′-H), 7.55 (d, 2H, H-6 and H-6′). IR (KBr, cm^{-1}): PF_6^-, 837. ESIMS (m/z) (CH_3CN) 2090 ([M-PF_6^-]); anal. calcd for $C_{132}H_{234}F_{12}N_{12}P_2Ru$: C, 79.70; H, 9.91; N, 7.06. Found: C, 78.75; H, 9.24; N, 9.12.

Tris(4,4′-didodecylaminomethyl-2,2′-bipyridine) ruthenium (II) hexafluorophosphate $Ru(3b)_3]^{2+}$ $2(PF6)^-$ (Ru4b)

Preparation of this complex was analogous to that of Ru4a. Yield: 83%. White crystalline solid (65%); ^1H NMR ($CDCl_3$) δ: 0.83 (t, 12H, CH_3), 1.33 (m, 8H, $-CH_2-$), 1.29 [m, 64H, $-(CH_2)_4-$], 1.39 (t, 8H, $-CH_2-$), 2.36 (t, 8H, $-CH_2-N-$), 3.91 (s, 8H, $N-CH_2-$), 6.99 (dd, 2H, 5-H and 5′-H), 8.56 (s, 2H, 3-H and 3′-H), 7.55 (d, 2H, H-6 and H-6′). IR (KBr, cm^{-1}): PF_6^-, 837. ESIMS (m/z) (CH_3CN) 2763 ([M-PF_6^-]); anal. calcd for $C_{180}H_{330}F_{12}N_{12}P_2Ru$: C, 70.80; H, 10.89; N, 5.50; found: C, 69.96; H, 10.15; N, 5.43.

Tris(4,4-dioctadodecylaminomethyl-2,2′-bipyridine) ruthenium (II) hexafluorophosphate $Ru(3c)_3]^{2+}$ $(PF6)^{2-}$ (Ru4c)

Preparation of this complex was analogous to that of Ru4a. Yield: 78%. White crystalline solid (85%); ^1H NMR ($CDCl_3$) δ: 0.83 (t, 12H, CH_3), 1.33 (m, 8H, $-CH_2-$), 1.29 [m, 112H, $-(CH_2)_4-$], 1.39 (m, 8H, $-CH_2-$), 2.36 (t, 8H, $-CH_2-N-$), 3.91 (s, 8H, $N-CH_2-$), 6.99 (dd, 2H, 5-H and 5′-H), 8.56 (s, 2H, 3-H and 3′-H), 7.55 (d, 2H, H-6 and H-6′). IR (KBr, cm^{-1}): PF_6^-, 837. ESIMS (m/z) (CH_3CN) 3773 ([M-PF_6^-]); anal. calcd for $C_{252}H_{474}F_{12}N_{12}P_2Ru$: C, 74.48; H, 11.76; N, 4.14; found: C, 73.60; H, 10.98; N, 4.08.

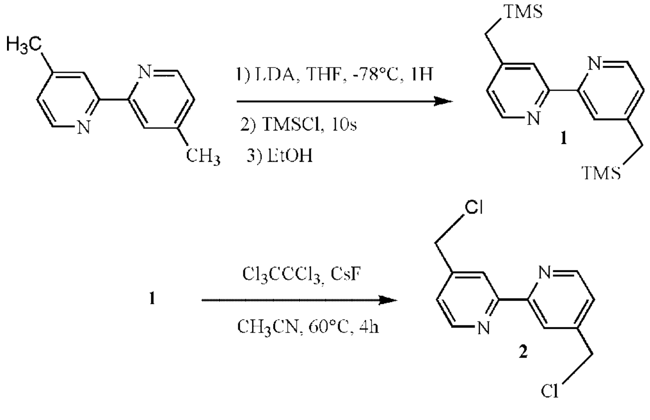
RESULTS AND DISCUSSION

Synthesis and properties of 4,4′-dialkylamino-methyl-2,2′-bipyridyls 3a, 3b and 3c

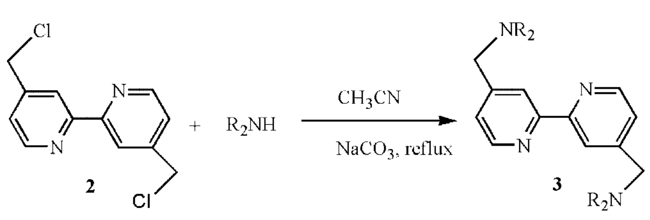
At first, the compound 4,4′-bis(bromomethyl)-2,2′-bipyridine were prepared by partial oxidation of the methyl groups of 4,4′-dimethyl-2,2′-bipyridine by *N*-bromosuccinimide (NBS). The yields were relatively low because of the lack of selectivity, which is an inherent property of radical reactions. A complication in the preparation and handling of the ligands arose from their thermal instability. This is presumably due to the formation of cationic, oligomeric pyridiniums that form by the nucleophilic displacement of bromide from the C–Br bond by the pyridine nitrogen atom.[18] The amphiphilic 4,4′-dialkylaminomethyl-2,2′-bipyridine ligands were prepared by a method which represents a significant simplification of earlier methods.[19–21] Another common pathway to 4,4′-bis(chloromethyl)-2,2′-bipyridine is silylation reaction of dimethyl-2,2′-bipyridine synthesis that proceeds via 4,4′-bis(trimethylsilyl)methyl-2,2′-bipyridine **1**.[22,23] Following isolation of **2**, chlorination was achieved by the addition of CsF and an electrophilic chloride source, Cl_3CCCl_3 to afford 4,4′-bis(chloromethyl)-2,2′bipyridine **2** (Scheme 1).

Reaction of 4,4′-bis(chloromethyl)2,2′-bipyridine **2** with dialkylamines afforded ligands **3** (Scheme 2). In a typical experiment dropwise addition of CH_3CN solution containing 1 equivalent of 4,4′-bis(chloromethyl)2,2′-bipyridine **2** to a solution of dialkylamines (2 equivalents in CH_3CN) at reflux in the presence of Na_2CO_3 yielded, after chromatography (see Experimental section), ligand **3** (75% yield). A low yield (<5%) of compound **3c** was obtained when Et_3N was used as base instead of Na_2CO_3.

Bipyridines **3a**, **3b** and **3c** show very good solubility in ether, toluene, dichloromethane and chloroform, but they hardly dissolve in solvents with higher polarity such as



Scheme 1.



3a, $R=CH_3(CH_2)_7$-; **3b**, $R=CH_3(CH_2)_{11}$-; **3c**, $R=CH_3(CH_2)_{17}$-

Scheme 2.

acetone, acetonitrile and alcohols. The new ligands exhibited the expected NMR spectroscopy properties (see Experimental section).

UV–vis spectra data of **3a**, **3b** and **3c** are summarized.in Table 1; the UV–vis spectral data are shown in Fig. 1. As shown in Fig. 1, the three compounds **3a**, **3b** and **3c** exhibit more intense and red shifted $\pi \rightarrow \pi^*$ absorption bands at around 286 nm. The major reason for the red shift of **3a**, **3b** and **3c** could be ascribed to lower LUMO energy level due to the electron-donating effect of alkylaminomethyl substituents.

*Synthesis of metal complexes with **3a**, **3b** and **3c** as ligands*

Three different types of ruthenium complexes with alkylaminomethyl-substituted bipyridyl ligands were synthesized; homoleptic complexes $[Ru(L)_3]^{2+}$ $(PF_6^-)_2$ (**4a**, L = **3a**; **4b**, L = **3b** and **4c**, L = **3c**). The general procedure for the synthesis of complexes was a 1 : 3 molar ratio mixture of the appropriate ruthenium (III) chloride precursor and the 4,4′-dialkylaminomethyl-2,2′-bipyridine ligand in absolute ethanol, refluxed under argon for about 6 h, during which time the violet solution became more red-orange, indicating formation of the complex.

Table 1. Electronic absorption[a] for free bipyridine ligands

	3a	3b	3c
λ_{max} (nm)	286 (12 000)	286 (14 000)	286 (30 000)
($\varepsilon = M^{-1}\ cm^{-1}$)	244 (11 000)	244 (13 000)	244 (27 000)

[a] In CH_2Cl_2.

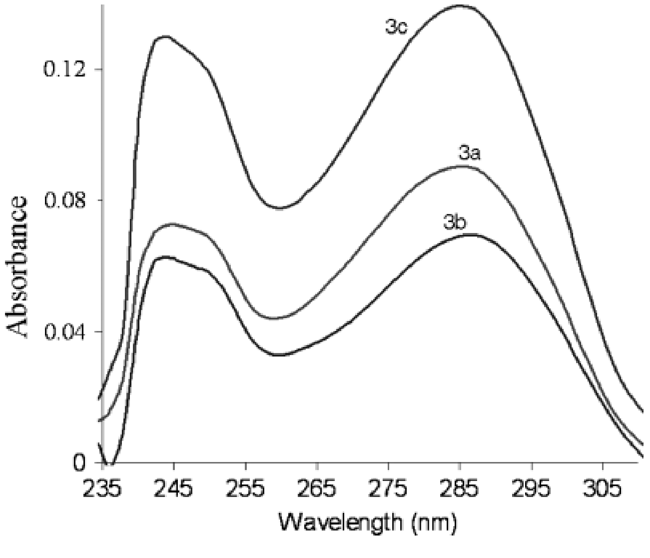


Figure 1. UV–vis spectra of free bipyridines **3a**, **3b** and **3c** in CH_2Cl_2.

Spectroscopic studies of the metal complexes

Dramatic changes in the ^1H NMR chemical shifts are sometimes observed when a ligand was coordinated to ruthenium. ^1H NMR spectra of the complexes Ru4a, Ru4b and Ru4c revealed clear separation of the three aromatic proton resonances. Hydrogen at 6 and 6′- positions of the 4,4′-dialkylaminomethyl-2,2′-bipyridines exhibited the expected shift from 8.50 to 7.55 ppm upon ruthenium coordination.

UV–vis spectra were shown in Fig. 2. The extinction coefficients were obtained from Beer's law studies and were determinated from at least four points. Absorptions were located across the UV–vis region commencing at approximately 550 nm. Three distinct peaks and two shoulders were observed. The peaks were located in the 420–460, 280–290 and 240 nm regions. Shoulders were found at about 500 and 320 nm. The assignments for absorption bands were made on the basis of the well documented optical transitions in $Ru(bipy)_3{}^{2+}$,[24–27] and its derivatives as $Ru(dmb)_3{}^{2+}$ [Tris(4,4′-dimethyl-2,2′-bipyridyl) ruthenium(II)].[28] The absorbances between 420 and 465 nm were assigned to metal-to-ligand charge transfer (MLCT) transitions $d(\pi)Ru \rightarrow \pi^*(bpy)$ band in the visible region (*ca* 423–464 nm). The second transitions at higher energy between 280 and 290 were assigned to ligand-centered charge transfer, which was consistent with other reported LC ($\pi \rightarrow \pi^*$) transitions for these types of complexes.[28] The MLCT transitions between 450 and 500 nm followed the energy trend: $[Ru(dmb)_3]^{2+}$ > Ru4a ≈ Ru4c > Ru4b. Electron-withdrawing substituents on bipyridine ligand shifted the frequency energy to higher values,[29] indicating that the alkylaminomethyl substituent was more electron-donating than the methyl group.

Photophysical data of emission maximum and emission quantum yields are listed in Table 2. The room temperature spectra in acetonitrile for four complexes are given in Fig. 3.

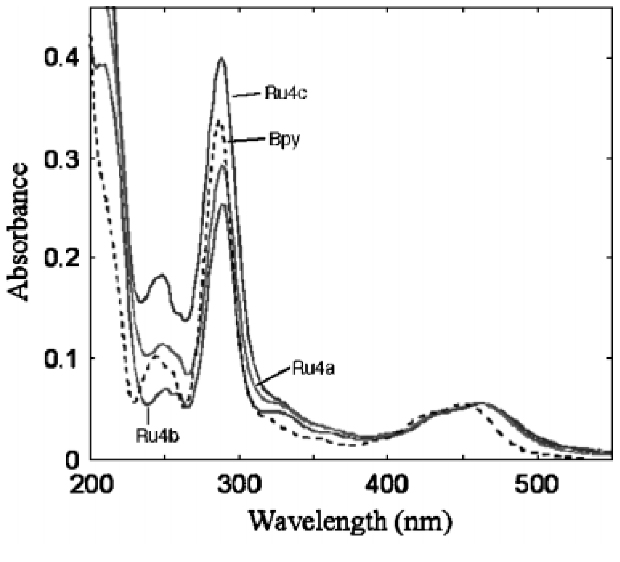


Figure 2. UV–vis spectra of homoleptic complexes in CH_3CN.

Table 2. Electronic absorption (UV–vis) and emission of complexes[a] Ru4a, Ru4b, Ru4c, Ru(dmb)$_3$ and Ru(bpy)$_3$ in CH$_3$CN at 23 °C

Complex	$\lambda_{\mathrm{abs\,max}}$ (nm), log ε[b]	$\lambda_{\mathrm{em\,max}}$ (nm)	Φ_{em} ($\times 10^{-3}$)
Ru4a	462	632	64
Ru4b	464	635	75
Ru4c	462	638	55
Ru(dmb)$_3$	458[c]	630[c]	73[c]
[Ru(bpy)$_3$]$^{2+}$	450(4.15)	628	61

[a] All Ru complexes were hexafluorophosphate salts.
[b] $\varepsilon = \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, error on log $\varepsilon = \pm 0.1$, $\lambda_{\mathrm{ex}} = 450$ nm.
[c] Values taken from van Wallendeal *et al.*[28]

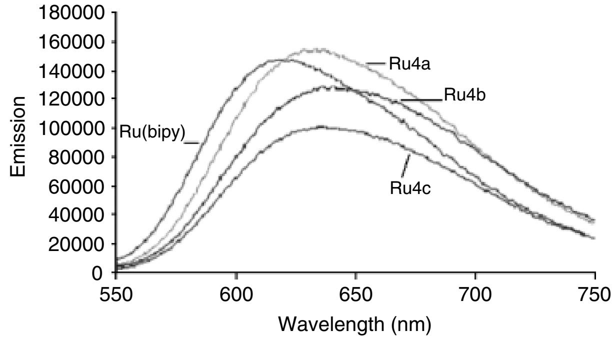


Figure 3. Emission spectrum of complexes of Ru(bpy)$_3$$^{2+}$, Ru4a, Ru4b and Ru4c in CH$_3$CN.

All the spectra show structureless, broad peaks. Emission maxima occurred at 632, 635 and 638 nm for Ru4a, Ru4b and Ru4c, respectively. Emission maximum followed the energy trend Ru(bpy)$_3$$^{2+}$ > Ru4a > Ru4b > Ru4c. This suggests a decrease in the ^{3}MLCT energy gap with substitution by longer alkylamono chains and is consistent with the observed trend in the absorption spectra of three compounds. The emission is likely to originate from an excited state of ^{3}MLCT [^{3}MLCT $d\pi(\mathrm{Ru}) \rightarrow \pi^*$diimine]. The emission energy of these complexes is slightly lower than that of Ru(bpy)$_3$$^{2+}$ ($\lambda_{\mathrm{em}} = ca$ 618 nm in CH$_3$CN).

The emission quantum yields at room temperature were measured in acetonitrile and the data are listed in Table 2. The emission quantum yields were calculated by comparison with the well-documented emission quantum yield for Ru(bpy)$_3$$^{2+}$.[13]

CONCLUSION

In summary, three new amphiphilic polypyridyl ruthenium complexes, Ru4a, Ru4b and Ru4c, were synthesized and systematically characterized by spectroscopy methods. The results represented indicate the extent to which the introduction of alkylaminomethyl groups in Ru[(bpy)$_3$]$^{2+}$ affects photophysical and photochemical properties. Owing to the electron- donating character of amino groups, increasing interest has been expressed in the use of 4,4′-dialkylaminomethyl-2,2′-bipyridines **3** as a ligand in transition metal bipyridyl complexes in both electrochemical and photochemical studies. Furthermore, it can be used as a building block in supramolecular assemblies.

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