Oligothiophene-2-yl-vinyl bridged mono- and binuclear ruthenium(II) tris-bipyridine complexes: Synthesis, photophysics, electrochemistry and electrogenerated chemiluminescence

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Abstract

A series of mono- and binuclear ruthenium(II) tris-bipyridine complexes tethered to oligothienylenevinylenes have been synthesized and characterized by ^{1}H NMR, ^{13}C NMR and TOF-MS spectrometry. Photophysics, electrochemistry and electrogenerated chemiluminescence (ECL) properties of these complexes are investigated. The electronic absorption spectra of the mononuclear ruthenium complexes show a significant red shift both at MLCT (metal-to-ligand charge transfer) and $\pi-\pi^*$ transitions of oligothienylenevinylenes with increase in the number of thiophenyl-2-yl-vinyl unit. For the binuclear complexes these two absorption bands are overlapped. All the metal complexes have very weak emission compared to that of the reference complex $Ru(bpy)_3^{2+}$. The first reduction potentials of all mononuclear ruthenium complexes are less negative than that of $Ru(bpy)_3^{2+}$, due to the moderate electron-withdrawing effect of oligothienylenevinylenes. For binuclear ruthenium complexes, only one Ru(II/III) oxidation peak ($E_{1/2} = 0.96$ V vs. Ag/Ag$^+$) was observed, suggesting a weak interaction between two metal centers. Three successive reduction processes of bipyridine ligands are similar among all ruthenium complexes except for **RuTRu**, which has a very sharp peak owing to the accumulation of neutral product on the electrode surface. All these ruthenium complexes exhibited different ECL property in CH_3CN solution without any additional reductant or oxidant. For three mononuclear ruthenium complexes, the ECL intensity strengthens with increase in the number of thiophene-2-yl-vinyl unit. However, the ECL efficiency dramatically decreased in the binuclear ruthenium complexes. The ECL efficiencies of all the reported complexes do not exceed that of $Ru(bpy)_3^{2+}$, where the ECL efficiency decreases in the order of **RuTRu** > **Ru3T** > **Ru2T** > **RuT** > **Ru2TRu** (**RuT**, bis-2,2′-bipyridyl-(4-methyl-4′-(2-thienylethenyl)-2,2′-bipyridine) ruthenium dihexafluorophosphate; **Ru2T**, bis-2,2′-bipyridyl-(4-methyl-4′-{(E)-2-[5-((E)-2-thienylethenyl)-thienylethenyl]}-2,2′-bipyridine) ruthenium dihexafluorophosphate; **Ru3T**, bis-2,2′-bipyridyl-(4-methyl-4′-{(E)-2-{(E)-2-[5-((E)-2-thienylethenyl)-thienylethenyl]}}-2,2′-bipyridine) ruthenium dihexafluorophosphate; **RuTRu**, bis-2,2′-bipyridyl-ruthenium-bis-[2-((E)-4′-methyl-2, 2′-bipyridinyl-4)-ethenyl]-thienyl-bis-2,2′-bipyridyl-ruthenium tetrahexafluorophosphate; **Ru2TRu**, bis-2,2′-bipyridyl-ruthenium-(E)-1,2-bis-{2-[2-((E)-4′-methyl-2,2′-bipyridinyl-4)-ethenyl]-thienyl}-ethenyl-bis-2,2′-bipyridyl-ruthenium tetrahexafluorophosphate).
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1. Introduction

Since the first report on the phenomenon of luminescence upon electrolysis by Duffort et al. [1], a large number of papers and patents have been published on new materials that exhibit electrogenerated chemiluminescence (ECL)

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properties. Many organic compounds [2,3] and transition metal complexes [4] have been observed to show ECL. Compared to the pure organic substances, the organometallic complexes seem to be more attractive. $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) is the first transition metal complex to show ECL property and continues to play an important role in many applications. The unique photophysical and photochemical properties [5] made it widely used in analytical field, particularly in medical diagnostic [6,7], environmental assays, and electroluminescence device [8]. As an analytical technology, ECL offers more advantages over other detection techniques like fluorescence due to lower detection limit, controlled chemiluminescence, and regeneration of reagent [9]. However, in some cases, higher sensitivity is required to increase the accuracy. Thus, the ECL efficiency of a label becomes a crucial issue.

Although there are many factors affecting the ECL efficiency [10–14], the inherent molecular structure seems much more important. A promising approach to raise the ECL efficiency is the use of multimetallic systems due to their multiple redox centers. Richter et al. studied a bimetallic ruthenium complex $[(bpy)_2Ru]_2(bphb)^{4+}$, which has an ECL efficiency by 2–3 times higher than that of $[Ru(bpy)_3]^{2+}$ [15]. Recently, homometallic complexes with two and three $[Ru(bpy)_3]^{2+}$ units connected by the amino acid lysine (Lys) and dipeptide (LysLys) exhibited an increase of 30% in ECL intensity [16]. The work was further extended to dendrimeric systems containing eight $[Ru(bpy)_3]^{2+}$, whose ECL intensity is 5 fold over the parent complex $[Ru(bpy)_3]^{2+}$ [17].

Except for the saturated amino acid connected homometallic complexes and the dendrimeric systems mentioned above, π-conjugated system will be another candidate as a bridge between the two $[Ru(bpy)_3]^{2+}$. A number of significant research endeavors have focused on the oligo- and/or poly(thiophenes) for the construction of linearly conjugated thiophene-containing architectures, including pure push–pull organic molecules [18] and π-conjugated materials containing transition metals [19]. Theoretical studies show that the oligo- and poly(thiophenes) typically display strong fluorescence from a $^1π–π^*$ singlet excited state. A $^3(π–π^*)$ state can be formed in moderate yields by direct optical excitation of these systems. In addition, oligothiophenes also show unique electronic and photonic properties, which have played a key role in organic thin film transistor [20], nonstructural heterojunction solar cells [21] and OLEDs [22]. Their potential use as possible ECL materials has already been established.

Thus, photochemical and photophysical behavior of oligothiophene-containing substances have become an important field of research. Although a few papers report on the structures of oligothiophene-bridged ruthenium complexes [23], the ECL properties have not been well explored. Very recently, we reported on the aryl diamide centered binuclear ruthenium complexes [24]. On the continuation of these studies, we have designed a new series of ligands, in which oligothienylenevinylenes are used to develop mono-
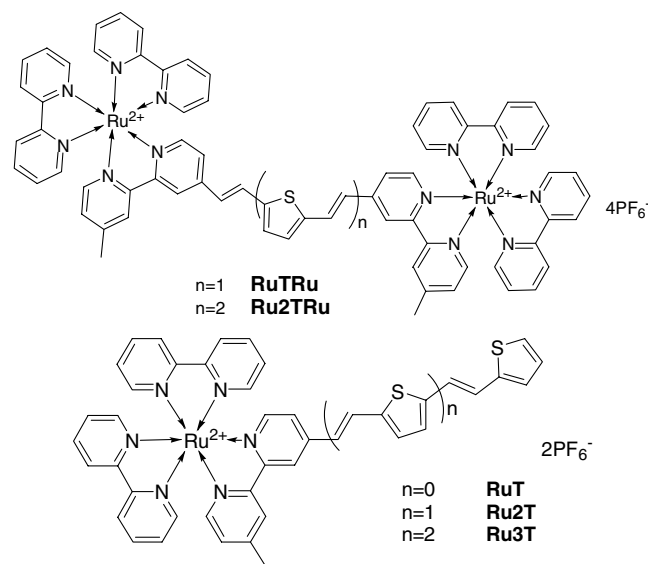

Fig. 1. The structures of mono- and binuclear ruthenium complexes.

and dinuclear tris(2,2′-bipyridine)ruthenium(II) derivatives. Herein we describe the convenient synthesis, structural characterization, spectroscopic, electrochemical and ECL properties of several mono- and binuclear complexes of this type (see the chemical structures in Fig. 1), with very promising results.

2. Result and discussion

2.1. Synthesis of ligands and metal complexes

In order to obtain mono- and binuclear ruthenium complexes, the preparation of the starting ligands is crucial. In this study, we adopt Wittig or Wittig–Hornor reaction for the preparation of four new ligands, since other reactions are not suitable for these target molecules. For example, the Heck reaction needs to use terminal aryl alkenes [25], which is not easily available. For the Wittig reaction or Wittig–Hornor reaction, both bipyridine substituted phosphonate and thiophene-2-yl-vinyl substituted carbaldehyde are easily available according to the literatures [26]. We first explored the synthesis of the simplest ligand having one thiophene unit 3 (**BPY-T**), although it was previously prepared by using a different synthetic route [27]. Thiophen-2-yl-methyl-phosphonic acid diethyl ester (**1**) reacts smoothly with 4′-methyl-2,2′-bipyridine-4-carbaldehyde (**2**) in the presence of NaH to give ligand 3 (**BPY-T**) in an acceptable yield. In sharp contrast, the reaction of thiophene formaldehyde with bipyridine substituted methyl phosphonate give extremely low yield. The ^1H NMR spectrum of this product is consistent with the data reported in the literature [27]. The analogue 6 (**BPY-2T**) was obtained by Wittig reaction. The starting materials are (*E*)-1-(2-formyl-5-thienyl)-2-(2-thienyl)ethene (**4**) and (4′-methyl-[2,2′]bipyridinyl-4-ylmethyl)-triphenyl phosphonium bromide (**5**). However, this product is very unstable

when purified by both silica gel column chromatography with Et$_3$N added as eluent and neutral aluminum oxide column chromatography. Thus, ligand **6** was directly used to prepare corresponding ruthenium complex. The ligand containing three thiophene units **8** (**BPY-3T**) was prepared by the phosphonium bromide **5**, where the reaction temperature is higher than that of **6** (**BPY-2T**) (Scheme 1).

As a symmetrical thiophene derivative having two bipyridine moieties, compound **10** (**BPY-T-BPY**) was first prepared by 2-fold Wittig–Hornor olefination of diphosphonate **9** with 4′-methyl-2,2′-bipyridine-4-carbaldehyde (**2**) in the presence of NaH. In contrast, the analogue **12** (**BPY-2T-BPY**) could not be prepared by using Wittig–Hornor reaction in the same manner as **10**; the reaction of oligothiophene-2-yl-vinyl phosphonate with 4′-methyl-2,2′-bipyridine-4-carbaldehyde did not give **12** in spite of our repeated attempts. Finally, this compound was obtained by the reaction of thiophene dialdehyde (**11**) with phosphonium bromide (**5**) (Scheme 2). More vigorous con-

ditions are required compared to that of **BPY-2T** and **BPY-3T**, which needed not only higher temperature but also longer reaction time owing to the poor solubility in CH$_3$OH of the dicarbaldehyde. Likewise, product **12** has extremely poor solubility in even the most polar aprotic solvents, making purification and characterization more difficult. Therefore, for ligands **6** (**BPY-2T**) and **10** (**BPY-T-BPY**), it is rather difficult to measure their ^{13}C NMR. Nevertheless, the structures of the four ligands were well confirmed by ^{1}H NMR. The ^{1}H NMR of ligand **10** displayed a set of doublets at δ 6.95 and 7.59 with a coupling constant of 16 Hz for the methylene protons between thiophene and bipyridine. The ^{1}H NMR spectrum of ligand **12** showed single peak for two protons on centered methylene due to similar chemical environment. The spectrum also exhibited a set of doublets at δ 6.90 and 7.54 with a coupling constant of 16 Hz, which can also be assigned to methylene protons between thiophene and bipyridine, indicating the amount of thienylenevinylene unit nearly
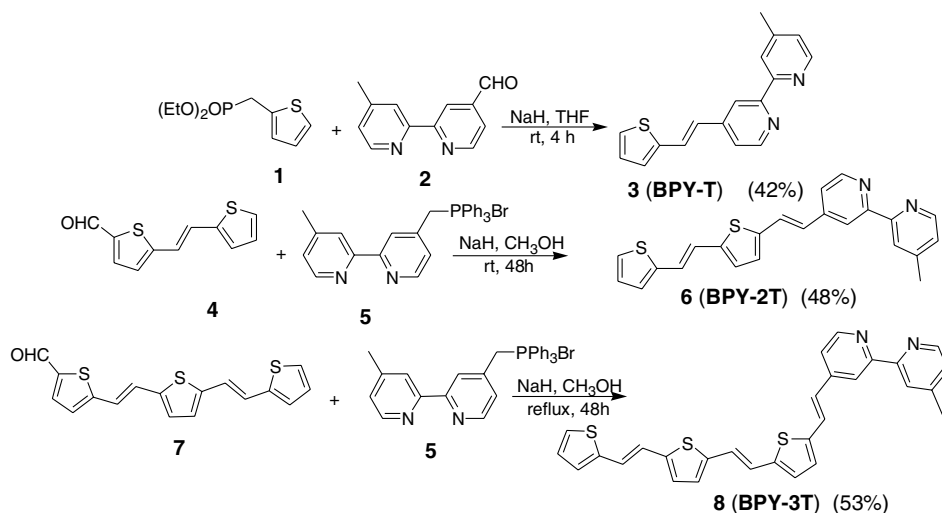
Scheme 1. The synthetic routes of ligands containing one bipyridine.
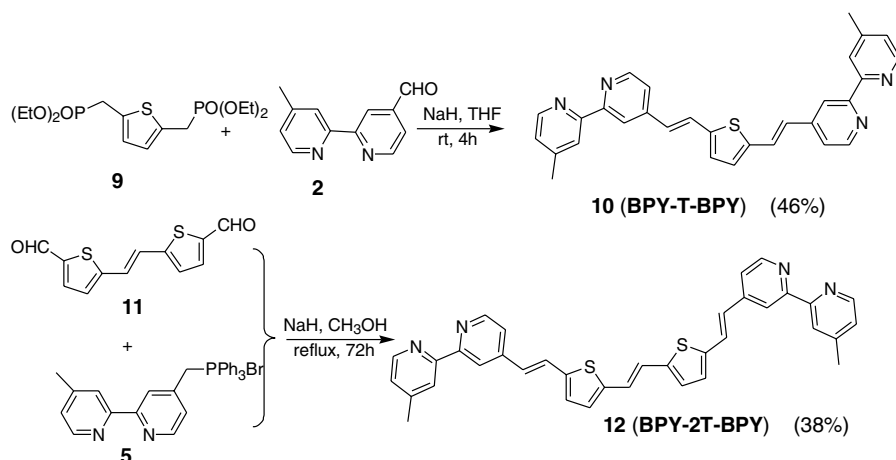
Scheme 2. The synthetic routes of ligands containing two bipyridines.
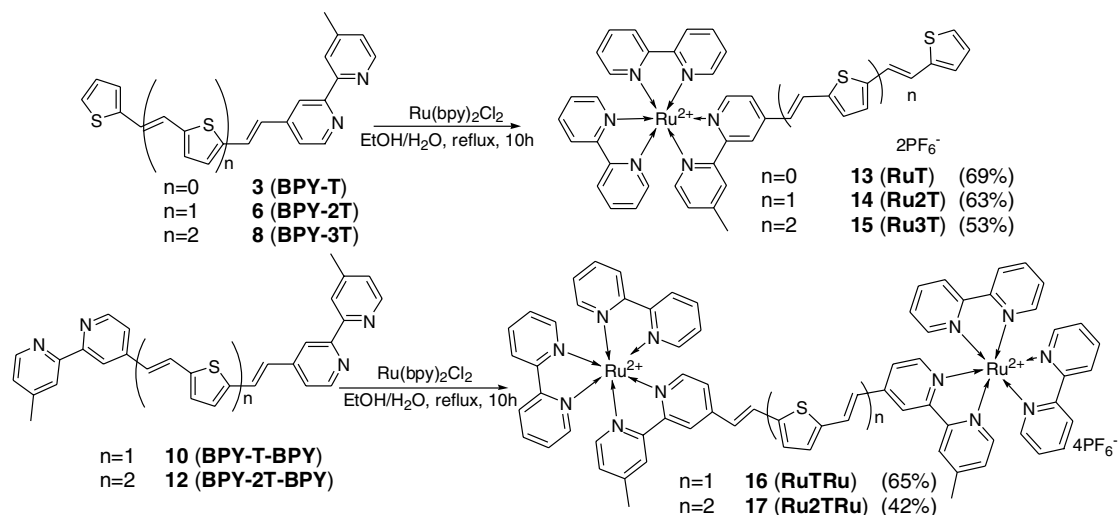
Scheme 3. The synthetic routes of ruthenium complexes.

has little effect on chemical shifts from methylene protons between thiophene and bipyridine. The ^{1}H NMR spectrum of known compound 3 (BPY-T) exhibited similar chemical shifts with a coupling constant of 16 Hz [27]. In the similar analysis, ligands 6 (BPY-2T), 8 (BPY-3T) presented all E-form of double bond when considering the double bond of the starting materials.

With the four ligands as building blocks in hand, the preparation of mono- and binuclear tris(2,2′-bipyridine)ruthenium(II) derivatives were readily assembled in one step. The coordination reaction was carried out by treatment of cis-Ru(bpy)$_2$Cl$_2$ · 2H$_2$O to the appropriate ligand in EtOH/H$_2$O (1:1), leading to the formation of complexes 13–17, with yield ranging from 40% to 60%

(Scheme 3). These products were purified by silica gel column chromatography and were characterized on the basis of ^{1}H NMR, ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry. Each proton was well assigned by ^{1}H–^{1}H COSY. In the ^{1}H NMR spectrum for all ruthenium complexes, the chemical shift for each proton in unsubstituted bipyridine ligand is nearly the same as that reported in the literature [28], which provides an evidence for the presence of Ru(bpy)$_3$ unit. Four chemical shifts behave in the following order: H$_{b3}$ (8.50) > H$_{b4}$ (8.06) > H$_{b6}$ (ca. 7.72) > H$_{b5}$ (7.4). The ^{1}H NMR signals in the substituted bipyridines and oligothiophene-2-yl-vinylenes are easily assigned according to the peak splitting patterns and their ^{1}H–^{1}H COSY spectra. Fig. 2 illustrates the data of
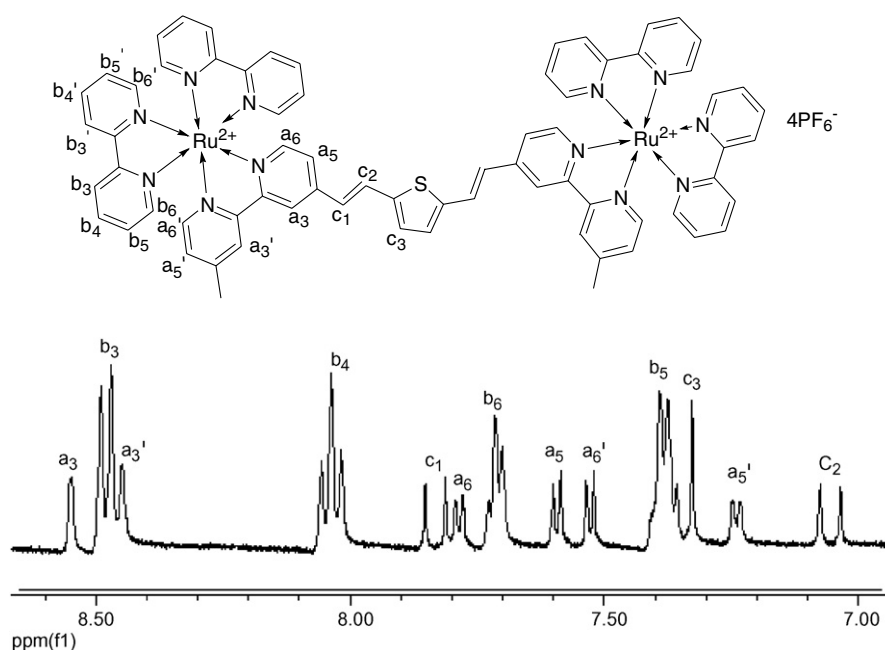
Fig. 2. The ^{1}H NMR spectrum of 16 (RuTRu) in CD$_3$CN.

the protons on **16** (**RuTRu**) as an example. Clear difference in the ^{1}H NMR spectra of these compounds was only evident in the low field region for different oligothenylenevinylene bridges.

2.2. Absorption and emission

We first explored the absorption spectra of the four thiophene-containing ligands (**BPY-2T**, **BPY-3T**, **BPY-T-BPY**, **BPY-2T-BPY**) in CH_2Cl_2 solution, which are illustrated in Fig. 3 and the spectroscopic data are summarized in Table 1. All four ligands exhibited two kinds of absorption bands. A narrow strong absorption at ca. 280 nm is due to the π–π^* transition of bipyridine, similar to the characteristic absorption of ancillary bipyridine in the $[Ru(bpy)_3]^{2+}$. For ligands **BPY-2T** and **BPY-3T**, the lower energy bands with maxima 390 nm and 458 nm, respectively, are assigned to oligothenylenevinylenes [29]. For ligands **BPY-T-BPY** and **BPY-2T-BPY**, these two bands are assigned to oligothenylenevinylenes substituted pyridine [30]. In the low-energy region, the absorption maximum is red-shifted by about 70 nm for **BPY-3T** compared to **BPY-2T**, and the similar result can be observed in **BPY-2T-BPY** with respect to **BPY-T-BPY**. This is supported by the fact that red shift occurs due to the increase in the length of conjugated system.

The excitation and emission spectra of the four ligands are examined in the same solvent at room temperature and are illustrated in Fig. 4. The emission maxima and quantum yields are listed in Table 1. Compounds **BPY-2T**
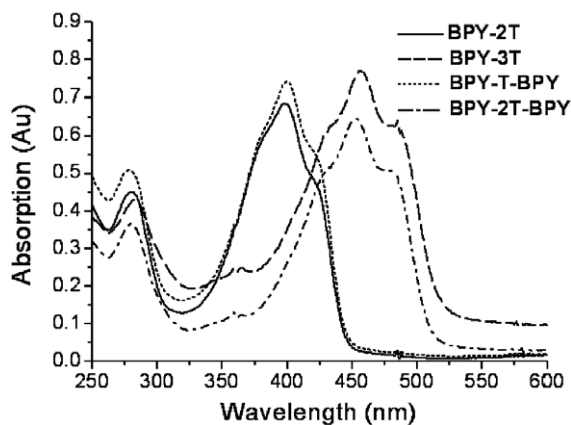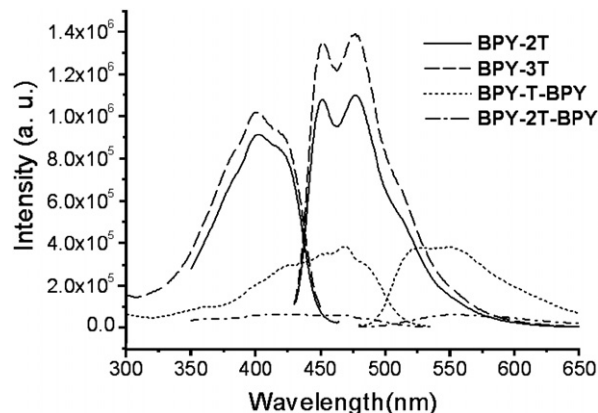

Fig. 4. Excitation and emission spectra of four ligands.

and **BPY-T-BPY** show the same two emission maxima at 450/485 nm, while **BPY-3T** shows emission at 550 nm and **BPY-2T-BPY** shows emission at 525/550 nm. Except for **BPY-3T**, other three compounds have vibrational fine structure. The emission maximum is red-shifted with increase in the number of thienylenevinylene unit, e.g. by 100 nm for **BPY-3T** with comparison to that of **BPY-2T**, 70 nm for **BPY-2T-BPY** to **BPY-T-BPY**. The similar emission maximum is also observed for **BPY-3T** and **BPY-2T-BPY**, although **BPY-3T** has very weak luminescence. The quantum yield is obtained in diluted CH_2Cl_2 solution referenced to quinine in H_2SO_4 (0.1 M) solution ($\Phi = 0.55$) [31]. The quantum yield behaves in the following order: **BPY-T-BPY** > **BPY-2T** > **BPY-2T-BPY** > **BPY-3T**, which decreases with increase in the number of thiophene-2-yl-vinyl unit.

The UV–Vis absorption spectra of a series of mono- and binuclear tris(2,2′-bipyridine)ruthenium(II) complexes in CH_3CN solution (10^{-5} M) are studied subsequently (Fig. 5, Table 2). The absorption spectra of all ruthenium complexes contain four kinds of absorption bands, which are assigned to one bipyridine, one bridged ligands of thiophene-2-yl-vinyl unit and two characteristic MLCT tran-

Fig. 3. UV–Vis absorption spectra of four ligands in CH_2Cl_2 (10^{-5} M) at rt.

Table 1
Photophysical properties of four ligands

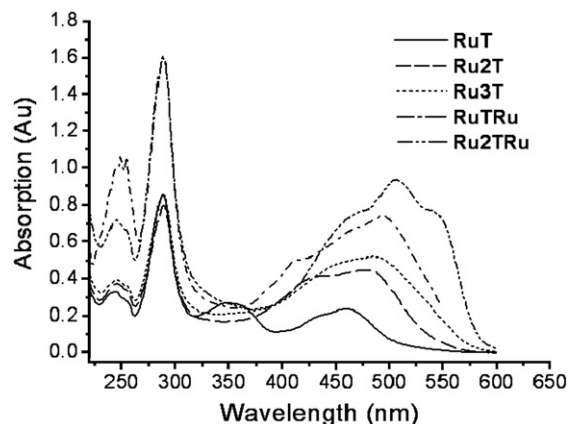| Complexes	Absorption			Emission	Φ
	λ_{max}/nm	ε/cm^{-1} mol^{-1} L		λ_{max}/nm	
BPY-2T	279	390/416	6.9×10^4	455/485	0.045
BPY-3T	283	458/485	7.8×10^4	550	0.005
BPY-T-BPY	278	390/419	7.6×10^4	455/485	0.042
BPY-2T-BPY	279	454/480	6.7×10^4	525/550	0.012

Fig. 5. UV–Vis absorption spectra of metal complexes (10^{-5} M) in CH_3CN.

Table 2
Photophysical properties of five ruthenium complexes

Complexes	Absorption λ_{max}/nm				Emission λ_{max}/nm	Φ	τ_{em} (µs)	k_r (10^4 s^{-1})	k_{nr} (10^6 s^{-1})
Ru(bpy)$_3^{2+}$	245	288		453	618	0.062	0.9	6.9	1.2
RuT	244	288	347	459	625	0.016	0.23	7.3	4.4
Ru2T	249	289	420	480		$<10^{-3}$	2.35	<0.04	0.42
Ru3T	248	289	487			$<10^{-3}$	1.47	<0.07	0.68
RuTRu	248	288	493		625	0.004	1.15/0.01	0.4	100
Ru2TRu	248	288	505		620	0.001	0.009	0.1	110

sitions, respectively. Firstly, all the complexes exhibit a strong narrow absorption band at about 288 nm, which is attributed to the π–π* transition of bipyridine ligands [32]. It is likely that this band contains contribution from both the bridging and ancillary bipyridine moieties. The similar maximum is observed in the reference complex [Ru(bpy)$_3$]$^{2+}$, indicating that the energy level of bipyridine is not very sensitive to the number of either the thiophene-2-yl-vinyl unit or the [Ru(bpy)$_3$]$^{2+}$ moiety. But the absorption intensity greatly differs and behaves in the following order: **Ru2TRu** ∼ **RuTRu** > **RuT** ∼ **Ru2T** ∼ **Ru3T**, suggesting that intensity is proportional to the number of [Ru(bpy)$_3$]$^{2+}$. Secondly, the weak and broad absorption bands at 347 nm for **RuT** and 420 nm for **Ru2T** are both assigned as a π–π* transition for the bridging ligand containing thiophene-2-yl-vinyl unit [33]. As for **Ru3T**, the absorption band corresponding to the π–π* transition of the bridging ligand is overlapped with the MLCT band domain in the range of 430–500 nm. The absorption maximum for the bridging ligand bound to the ruthenium ion is red-shifted with the increase in the number of thiophene-2-yl-vinyl in monometallic complexes. Finally, for **RuT** and **Ru2T**, in lowest energy region a broad band (459 nm for **RuT** and 480 nm for **Ru2T**) is a characteristic absorption band assignable to MLCT transition. The MLCT band also displays red shift with respect to that of the parent complex [Ru(bpy)$_3$]$^{2+}$, in proportion to the length of chain in mononuclear complexes. The π–π* transition of bridged ligands and MLCT bands for **RuTRu** and **Ru2TRu** are also overlapped at the region of 410–550 nm. The MLCT absorption band contains two types of transitions: π(Ru) → π* (ancillary bipyridine) and dπ(Ru) → π* (the capping bipyridine). In the UV region a narrow band at 248 nm is the absorption of MLCT. Note that the absorption intensity of MLCT of binuclear complexes is stronger than that of monometallic complexes. The reason lies that the intensity is proportional to the number of tris(2,2′-bipyridine)ruthenium(II) unit: as strong as 2-fold.

The excitation and emission spectra for the solutions of metal complexes in CH$_3$CN are shown in Fig. 6. The quantum yields of luminescence for all ruthenium complexes were also examined in the same solution with [Ru(bpy)$_3$]$^{2+}$ as reference ($\Phi = 0.062$) [34]. The detailed data are listed in Table 2. The emission spectrum shows a broad band with the emission maximum at ca. 625 nm. At room temperature emission intensity of ruthenium complexes in dilute CH$_3$CN solution decreased dramatically with increase in
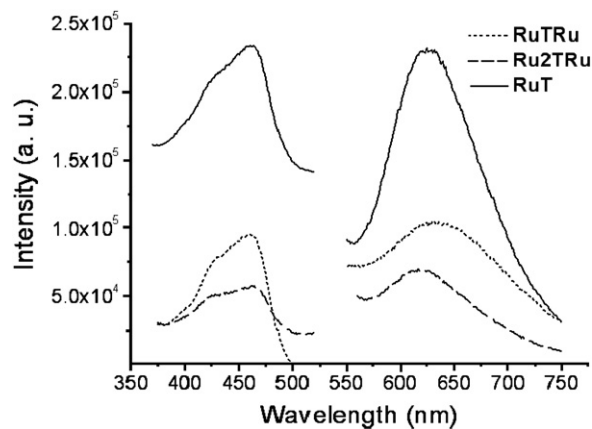

Fig. 6. Excitation and emission spectra of all ruthenium complexes (10^{-5} M) in CH$_3$CN.

the number of thiophene-2-yl-vinyl compared to that of [Ru(bpy)$_3$]$^{2+}$. Luminescence is obtained only for **RuT** and **RuTRu** and less in **Ru2T**, **Ru3T** and **Ru2TRu**. The emission for **RuT** can be attributed to MLCT transition according to general regulations of MLCT assignment [33] that the wavelength fall in between the 580 and 700 nm, with the τ_{em} value measured less than 1.0 µs, its k_r value calculated to be within $(0.5–1) \times 10^5$, and the broad band seems structureless. Complexes **Ru2T** and **Ru3T** have nearly no emission and longer lifetime (2.35 µs and 1.47 µs, respectively), which is likely due to the existence of energy level of intraligand ^{3}(π–π*) [30a]. Complex **RuTRu** has also a longer lifetime (1.15 µs). The possible reason is same as mentioned above. There exists the other kind of shorter lifetime (0.01 µs), likely due to oligothienylenevinylenes quenching. **RuTRu** and **Ru2TRu** have also very low quantum yield and the very weak emission intensities. It is very hard to attribute the origin of their emission. The quantum yield

Table 3
The electrochemical data of ruthenium complexes[a]

Complexes	$E_{1/2}$ (V)				
	Oxidation	Reduction			$\Delta E_{1/2}$
Ru(bpy)$_{2+3}$	0.95	−1.67		−1.88	−2.15	2.62
RuT	0.95	−1.60		−1.84	−2.06	2.55
Ru2T	0.97	−1.55		−1.88	−2.05	2.52
Ru3T	0.97	−1.44		−1.85	−2.04	2.41
RuTRu	0.96	−1.38		−1.75	−2.09	2.34
Ru2TRu	0.96	−1.42	−1.65	−1.85	−2.15	2.38

[a] Measured with Ag/AgNO$_3$ as reference electrode.

reduces in monometallic complexes with the increase in the number of thiophene-2-yl-vinyl. The similar result is observed in binuclear complexes. The possible reason is that oligothienylenevinylenes have a quenching effect on the emission of ruthenium complexes. It has been shown there exists linear correlations between absorption or emission energies of MLCT, respectively, and electrochemical properties ($\Delta E_{1/2}$, the difference between oxidation potential of metal-centered and the first reduction potential of coordinated ligand) [30a,35]. For our metal complexes, according to the data of Tables 2 and 3, red shifts in absorption energies (0.19 V) of binuclear complex **RuTRu** relative to the mononuclear complex **RuT** is comparable

to the difference in $\Delta E_{1/2}$ of 0.21 V. The similar result could be observed in complex **Ru2TRu** compared to **Ru2T**. The lowest energy absorption of our metal complexes being MLCT transition is well consistent with the correlation of electrochemical and spectroscopic properties. But for emission spectra of all metal complexes, this consistence is not evident.

2.3. Electrochemistry

The electrochemical properties of all ruthenium complexes were characterized by cyclic voltammetry (shown in Fig. 7) in CH_3CN solution (10^{-4} M). The relevant
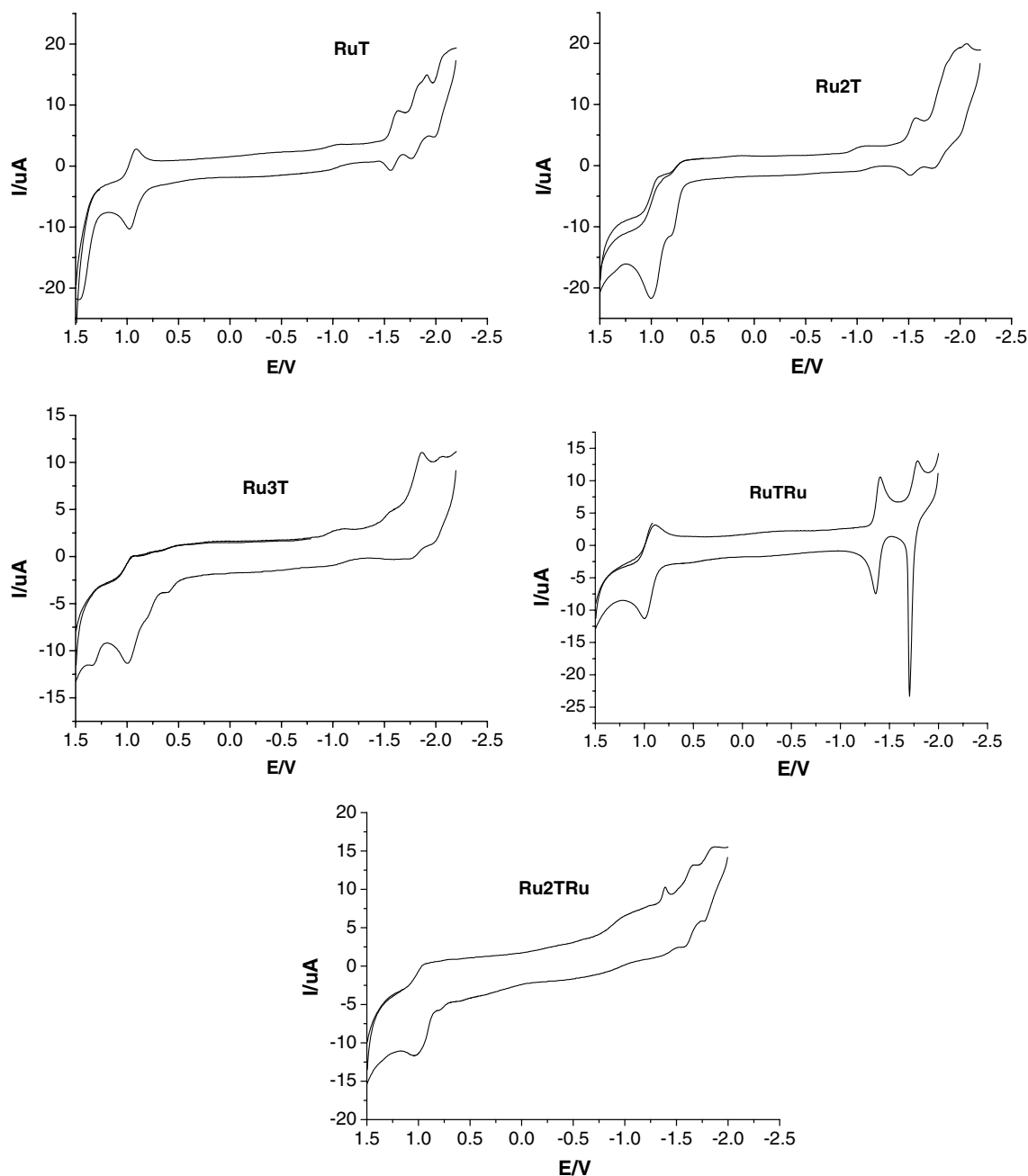

Fig. 7. Cyclic voltammogram of all ruthenium complexes (0.1 mM) in 0.05 M of *n*-Bu₄NPF₆/CH₃CN at a scan rate of 100 mV/s.

oxidation and reduction potentials are listed in Table 3. Cyclic voltammetry of all five ruthenium complexes in CH_3CN displays an oxidation process, which is assigned to Ru(II/III) couple. The oxidation peaks were observed with $E_{1/2}$ at 0.95 V for **RuT**, 0.97 V for **Ru2T** and **Ru3T**, 0.96 V for **RuTRu** and **Ru2TRu**. These oxidation potentials are very close to those obtained for the parent complex $[Ru(bpy)_3]^{2+}$ under identical conditions, indicating that the oligothienylenevinylene bridges have little effect on the oxidation of ruthenium complexes, no matter the number of the thiopheneylenevinylene unit and mono- or binuclear ruthenium complex it connected. The cyclic voltammograms of these binuclear ruthenium complexes (**RuTRu** and **Ru2TRu**) show only a single oxidation wave, which suggests little or weak interaction between the two metal centers.

In cathodic region, as a general trend, the values of the reduction potentials become more positive compared to those of the reference $[Ru(bpy)_3]^{2+}$. In the monometallic series, **RuT** shows a first reduction peak at $E_1 = -1.60$ V, **Ru2T** at -1.55 V and **Ru3T** at -1.44 V, reflecting the electron-withdrawing effect of the site chains. The second reduction potentials of **RuT** and **Ru3T** are more positive than that of $[Ru(bpy)_3]^{2+}$, whereas, **Ru2T′** is identical. Similar trend was observed for the series on the third reduction wave with -2.06 V for **RuT**, -2.05 V for **Ru2T**, and -2.04 V for **Ru3T**. Although more positive, the differences are not distinct by only 10 mV. The first reduction processes of **RuT**, **Ru2T** and **Ru3T** assigned to the reduction of the thiophene-2-yl-vinyl substituted bipyridine ligands, and the second and the third ones are attributed to the reduction of the ancillary bipyridine ligands. We also observed that the second and the third reduction potentials have almost no relation to the length of conjugated system. However, there is a significant difference for the first reduction potentials, which indicates the different electron environment of bipyridine linked by various thiophene-2-yl-vinyl.

For the binuclear series, **RuTRu** has three reduction peaks at $E_{1/2}$ − 1.38, −1.75, and −2.09 V, corresponding to the reductions of one thiophen-2-yl-vinyl substituted bipyridines and two ancillary bipyridines, respectively. These values are more positive than that of the reference $[Ru(bpy)_3]^{2+}$, indicating bipyridines are easy to reduce, in agreement with literature data reported by Raymond and coworkers [33]. It is interesting that a negative reduction wave exhibited a large sharp peak ($E_{1/2} = -1.75$ V), which is likely due to the precipitation of the reduced species on the electrode surface [32]. Complex **Ru2TRu** has four reduction potentials ($E_{1/2} = -1.42$ V, -1.65 V, -1.85 V, -2.15 V). The last two reduction potentials are nearly identical to those of the reference compound $[Ru(bpy)_3]^{2+}$. The first two less negative reduction potentials are assigned to the sequential reduction of the bridging ligand containing thiophen-2-yl-vinyl substituted two bipyridines. The possible reason is that the first electron is added to the bridging ligand and shortens bridging distance, which results in

different reduction potentials for the bridging ligand reduction processes [33].

2.4. Electrogenerated chemiluminescence

The generation of $[Ru(bpy)_3]^{2+}$-based ECL mainly involves two kinds of mechanisms. One is annihilation reaction and the other is coreaction that needs additional reductants (such as TrPA and $C_2O_4^{2-}$) or some oxidants (such as $S_2O_8^{2-}$). Since the discovery of coreaction reaction about the ECL of $[Ru(bpy)_3]^{2+}$, annihilation reaction has been used rarely in analytical chemistry compared to coreaction due to its lower ECL efficiency. A series of molecules designed in this paper will behave based on the mechanism involving annihilation reaction without any additional reductant (Fig. 8). Of the three monometallic ruthenium complexes, emission maxima was observed centering at 557 nm for **RuT**, 580 nm for **Ru2T**, and 587 nm for **Ru3T**, exhibiting a red shift with increase in the number of thiophene-2-yl-vinyl. The emission intensities of ECL strengthened with the increase in the length of conjugated oligothienylenevinylenes (i.e. **Ru3T** > **Ru2T** > **RuT**). For the bimetallic complexes, emission maxima center at 598 nm for **RuTRu** and 593 nm for **Ru2TRu** (Table 4). The ECL emission intensity differs greatly from each other. **RuTRu** has much stronger ECL intensity than that of **Ru2TRu**, which is possible due to the rotation of bridge of **Ru2TRu** and make ECL intensity decrease through energy transfer process. ECL intensity of all metal complexes is weak compared to that of the reference
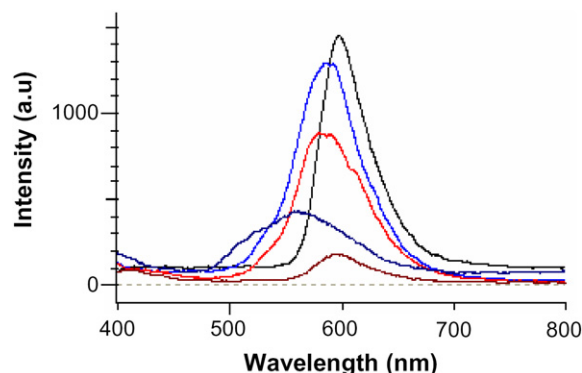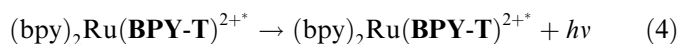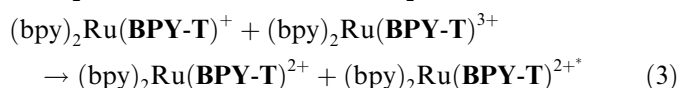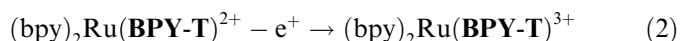

Fig. 8. ECL spectra of 10^{-4} M solution of all ruthenium complexes in MeCN containing 50 mM Bu_4NPF_6 as an electrolyte at room temperature with potential stepped up from −1.8 to +1.4 V pulse for 0.5 s.

Table 4
ECL data for five ruthenium complexes

Complexes	λ_{max}/nm	ECL Intensity/a.u.
$Ru(bpy)_{2+3}$	620	4030
RuT	557	443
Ru2T	580	888
Ru3T	587	1290
RuTRu	598	1453
Ru2TRu	593	183

$[Ru(bpy)_3]^{2+}$. The possible reason is that all metal complexes are more easy to obtain electron compared to $Ru(bpy)_3]^{2+}$ according to the first reduction potentials, which is more difficult to make metal ruthenium(II) change into ruthenium(I). Thus, annihilation reaction is not easy to occur and ECL intensity becomes very weak. The detailed reason is under investigation.

The annihilation reaction mechanism of ECL about $[Ru(bpy)_3]^{2+}$ involves electron-transfer reaction between an oxidized and a reduced species, both of which are produced by alternating pulse potential. In the present paper, the detailed reaction processes are outlined below, with **RuT** as an example:

$$(bpy)_2Ru(\textbf{BPY-T})^{2+} + e^+ \rightarrow (bpy)_2Ru(\textbf{BPY-T})^+ \qquad (1)$$

$$(bpy)_2Ru(\textbf{BPY-T})^{2+} - e^+ \rightarrow (bpy)_2Ru(\textbf{BPY-T})^{3+} \qquad (2)$$

$$(bpy)_2Ru(\textbf{BPY-T})^+ + (bpy)_2Ru(\textbf{BPY-T})^{3+}$$
$$\rightarrow (bpy)_2Ru(\textbf{BPY-T})^{2+} + (bpy)_2Ru(\textbf{BPY-T})^{2+*} \qquad (3)$$

$$(bpy)_2Ru(\textbf{BPY-T})^{2+*} \rightarrow (bpy)_2Ru(\textbf{BPY-T})^{2+*} + h\nu \qquad (4)$$
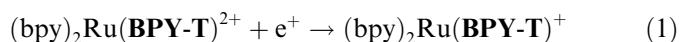
When a double-potential step is applied to an electrode, the reduced $(bpy)_2Ru(\textbf{BPY-T})^+$ specie can react with oxidized $(bpy)_2Ru(\textbf{BPY-T})^{3+}$ to generate an excited state $(bpy)_2Ru(\textbf{BPY-T})^{2+*}$, which will form the ground state with light emission. In order to obtain the possibility that annihilation reaction occur (shown Eq. (3)), we calculated the free energy (ΔG_{anni}) of this reaction glancingly. ΔE is available from the difference between the first oxidation potential and first reduction potential in the cyclic voltammogram ($\Delta E = \Delta E_{oxi} - \Delta E_{red}$). For example, for **RuT**, $\Delta E = 2.55$ V. The energy of emitting light (ΔH), as calculated by the emission maximum is about 2.25 V. According to the Eq. (5), the energy of annihilation reaction (ΔG_{anni}) is inferior to zero. Thus, excited state of Ru^{2+*} species may be populated directly by annihilation reaction [15,36]. The detailed reaction mechanism will be continued studying in our laboratory.

$$\Delta G_{anni} = -\Delta E + \Delta H \qquad (5)$$

3. Experiment

3.1. General

^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian spectrometer at 400 MHz. Chemical shifts are referenced to chloroform peak (7.26 ppm) or acetonitrile peak (1.95 ppm). UV–Vis absorption spectra were recorded on a model 8452A Hewlett–Packard diode array spectrophotometer referenced against a solvent blank. Photoluminescence spectra were measured on a PTI-C-700 fluorescence spectrometer. Electrochemistry was performed with a CH Instrument Model 660. All experiments were performed with the protection of Argon with Bu_4NPF_6 as supporting electrolyte, glassy-carbon as working electrode and Ag/AgNO_3 electrode as reference. ECL spectra were measured

by using Hitachi Fluorescence spectrophotometer F-4500 and recorded in CH_3CN solution with the sample concentration of 0.1 mM using Bu_4NPF_6 as supporting electrolyte, Pt-grid cylinder (CH Instruments) as Working electrode, Platinum wire (1.0 mm diameter) as counter electrode and Ag^+/Ag electrode as reference electrode.

All of the chemicals were purchased from commercial corporations and used without further purification except for THF and ether, which were distilled from sodium diphenyl ketone under argon. DMF was distilled from molecular sieves, KOH and P_2O_5, respectively, and CH_3OH was distilled from Mg. dichloromethane was distilled from CaH_2. Thiophen-2-yl-methyl-phosphonic acid diethyl ester (**1**) [37], [5-(diethoxy-phosphorylmethyl)-thiophen-2-yl]-phosphonic acid diethyl ester (**9**) [37], 5-(2-(thiophen-2-yl-vinyl)-thiophen-2-carbaldehyde (**4**) [38], *trans*-1,2-bis(5-formyl-2-thienyl)ethylene (**11**) [39], 4′-methyl-2,2′-bipyridine-4-carbaldehyde (**2**) [40], (4,4-dimethyl-2,2′-bipyridyl-4-yl)triphenyl phosphonium bromide (**5**) [41], *cis*-Ru(bpy)_2Cl_2 · 2H_2O (**42**), 4-methyl-4′-(2-(2-thiophen)ethenyl)-2,2′-bipyridine (**3**), and bis-2,2′-bipyridyl-4-methyl-4′-(2-thienylethenyl)-2,2′-bipyridine) ruthenium dihexafluorophosphate dehydrate (**13**) [27]5-{2-[5-(2-Thiophen-2-yl-vinyl)-thiophen-2-yl]-vinyl}-thiophene-2-carbaldehyde (**7**) [43] were prepared according to the literatures reported earlier.

3.2. Preparation of ligands 12: general procedure

(4,4′-Dimethyl-2,2′-bipyridyl-4-yl) triphenyl phosphonium bromide (**5**) (740 mg, 1.5 mmol) and *trans*-1,2-bis(5-formyl-2-thienyl)ethylene (**11**) (62 mg, 0.25 mmol) were dissolved in CH_3OH (10 mL) and refluxed for 72 h in the presence of NaH (144 mg, 6 mmol). The crude product was purified on silica gel column chromatography with $CHCl_3$–$CH_3COOC_2H_5$–Et_3N (100:100:0.2) as eluent to give **12** as a yellow solid (55 mg, yield 38%). M.p. > 300 °C. ^{1}H NMR (CDCl_3, 400 MHz): δ 2.47 (s, 6H), 6.90 (d, 2H, $J = 16.4$ Hz), 7.01 (d, 2H, $J = 4.0$ Hz), 7.03 (s, 2H), 7.08 (d, 2H, $J = 3.2$ Hz), 7.18 (d, 2H, $J = 4.8$ Hz), 7.33 (d, 2H, $J = 4.4$ Hz), 7.54 (d, 2H, $J = 16$ Hz), 8.28 (s, 2H), 8.50 (s, 2H), 8.58 (d, 2H, $J = 5.2$ Hz), 8.63 (d, 2H, $J = 5.2$ Hz). ^{13}C NMR (CDCl_3, 100 MHz): δ 21.40, 117.99, 120.91, 122.23, 122.32, 125.03, 125.99, 126.36, 127.83, 129.39, 141.25, 143.04, 145.42, 148.43, 149.14, 149.74, 155.97, 156.82. TOF-MS EI[+] Calc. 580.1755; found, 580.1751. API-ES Positive [M+H] = 581.2.

3.3. Preparation of metal complexes 17: general procedure

To a mixture solution of EtOH and H_2O (20 mL, 1:1), *cis*-Ru(bpy)_2Cl_2 · 2H_2O (220 mg, 0.44 mmol) and (**12**) (116 mg, 0.2 mmol) were added and refluxed for 12 h under argon. The color of the solution turned red. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography using acetonitrile–water–saturated KNO_3 (100:10:0.8) as eluent. After removing the solvent until about 5 mL left by evaporation, the

final deep-red solid was precipitated by the addition of saturated aqueous solution of NH_4PF_6, filtered, washed thoroughly with water and dried in vacuum to afford the final product (143 mg, 42%). ^1H NMR (CD_3CN, 400 MHz): δ 2.56 (s, 6H), 7.01 (d, 2H, $J = 16$ Hz), 7.18 (d, 2H, $J = 3.6$ Hz), 7.21 (s, 2H), 7.25 (d, 2H, $J = 4.8$ Hz), 7.28 (d, 2H, $J = 4.0$ Hz), 7.37–7.43 (m, 10H), 7.54 (d, 2H, $J = 5.6$ Hz), 7.58 (d, 2H, $J = 6.0$ Hz), 7.73 (t, 6H, $J = 5.6$ Hz), 7.82 (s, 2H), 7.83 (d, 2H, $J = 16$ Hz), 8.05 (t, 8H, $J = 8.4$ Hz), 8.46 (s, 2H), 8.50 (d, 8H, $J = 8.0$ Hz), 8.55 (s, 2H). ^{13}C NMR (CD_3CN, 100 MHz): 20.50, 120.50, 122.62, 123.56, 124.00, 124.42, 125.24, 127.76, 128.60, 128.92, 129.22, 131.53, 137.89, 140.92, 144.24, 146.30, 150.73, 150.92, 151.54, 151.81, 151.92, 156.68, 157.24. TOF-MS: Calc. for $M^{4+} = 1408.2592$; found, $M^{4+} = 1408.2568$, $[M/4]^+ = 352.0642$. API-ES Positive $[M/4]^+ = 352.0$; $[M^{4+}+PF_6^-]/3 = 517.7$; $[M^{4+}+2PF_6^-]/2 = 848.5$.

4. Conclusion

A concise, acceptable yielding process for the construction of mono- and binuclear complexes with different bridge has been established according to the reaction sequence given above. Although the four ligands have poor stability and bad solubility in different solvents, they have been confirmed by ^1H NMR and TOF-MS and their metal complexes have also been accomplished and characterized by ^1H NMR, ^{13}C NMR and TOF-MS. Additionally, the different protons on the metal complexes have been assigned on the basis of ^1H–^1H COSY spectra. Moreover, a detailed photophysical, electrochemical and ECL properties have been studied. For the monometallic complexes electronic spectra exhibit that the energy levels of π–π^* transition of the bridged ligands and MLCT band all decrease with increase in the length of π-conjugated systems. All the metal complexes have very weak emission compared to that of the reference complex $Ru(bpy)_3^{2+}$. For mononuclear complexes the first reduction potentials are less negative because of oligothienylenevinylenes electron-withdrawing effect. For binuclear ruthenium complexes the oxidation potential of Ru(II/III) is nearly the same to that of $[Ru(bpy)_3]^{2+}$, suggesting that interactions are very weak between two metal centers. It is interesting to note that for the mono-nuclear complexes photoluminescence becomes weak by the introduction of oligothienylenevinylenes, but the intensity of ECL increases instead without any additional reductant. The ECL intensity of all metal complexes follows in the order: **RuTRu** > **Ru3T** > **Ru2T** > **RuT** > **Ru2TRu**.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem. 2007.10.017.

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