

系列含 4,5-二氮杂-9,9'-螺二芴配体的钌配合物的合成及其性能研究

童碧海¹ 刘远远¹ 张 曼¹ 梅群波^{*2} 华中胜¹ 张千峰¹

(¹ 安徽工业大学冶金与资源学院, 分子工程与应用化学研究所, 马鞍山 243002)

(² 南京邮电大学信息材料与纳米技术研究院, 江苏省有机电子与平板显示重点实验室, 南京 210046)

摘要: 合成了 3 个钌(II)配合物, $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$ 、 $[\text{Ru}(\text{bpy})(\text{SB})_2](\text{PF}_6)_2$ 和 $[\text{Ru}(\text{SB})_3](\text{PF}_6)_2$ ($\text{bpy}=2,2'$ -bipyridine, $\text{SB}=4,5$ -diaz-9,9'-spirobifluorene), 通过核磁和元素分析对配合物的结构进行了确定。 $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$ 通过 X 射线单晶衍射确认了结构。研究了配合物的光物理性能。结果表明 $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$ 在乙腈中的发桔红光, 波长为 606 nm, 量子产率约为 0.001 2。在同样条件下 $[\text{Ru}(\text{bpy})(\text{SB})_2](\text{PF}_6)_2$ 和 $[\text{Ru}(\text{SB})_3](\text{PF}_6)_2$ 的发光非常微弱甚至几乎没有发光。还研究了这些配合物的电致化学发光性能。随着配体中 SB 含量的增加, 发光的峰电压从 1.36 V 增加到 1.58 V, 相对发光强度从 731 降低到 52。

关键词: 钌(II)配合物; 氮杂螺二芴; 晶体结构; 磷光; 电致化学发光

中图分类号: O614.82¹

文献标识码: A

文章编号: 1001-4861(2014)05-1174-05

DOI: 10.11862/CJIC.2014.141

Synthesis and Properties of a Series of Ruthenium(II) Complexes with 4,5-Diaza-9,9'-spirobifluorene Ligands

TONG Bi-Hai¹ LIU Yuan-Yuan¹ ZHANG Man¹ MEI Qun-Bo^{*2}

HUA Zhong-Sheng¹ ZHANG Qiang-Feng¹

(¹ College of Metallurgy and Resources, Institute of Molecular Engineering and Applied Chemistry,

Anhui University of Technology, Ma'anshan, Anhui 243002, China)

(² Jiangsu Key Lab of Organic Electronics & Information Displays, Institute of Advanced Materials (IAM),

Nanjing University of Posts & Telecommunications (NUPT), Nanjing 210046, China)

Abstract: Three ruthenium complexes, $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})(\text{SB})_2](\text{PF}_6)_2$ and $[\text{Ru}(\text{SB})_3](\text{PF}_6)_2$ ($\text{bpy}=2,2'$ -bipyridine, $\text{SB}=4,5$ -diaz-9,9'-spirobifluorene), have been synthesized and characterized. $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$ has also been characterized by single-crystal X-ray diffraction. Its crystal belongs to orthorhombic system with $Pbca$ space group, in which $a=1.881\ 8(2)$ nm, $b=1.991\ 3(3)$ nm, $c=2.422\ 1(3)$ nm, $Z=8$. The photophysical properties of these complexes were investigated. $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$ shows orange red emission at around 606 nm with a phosphorescence quantum yield of *ca.* 0.001 2, while $[\text{Ru}(\text{bpy})(\text{SB})_2](\text{PF}_6)_2$ and $[\text{Ru}(\text{SB})_3](\text{PF}_6)_2$ shows rather weak or almost no emission at the same condition. The electrochemiluminescence performance of these complexes has also been studied. With the increase of SB ligand concentration, the peak potential increased from 1.36 V to 1.58 V, and relative peak intensity decreased from 731 to 52. CCDC: 948328.

Key words: ruthenium(II) complex; diazaspirobifluorene; crystal structure; phosphorescence; electrochemiluminescence

收稿日期: 2013-09-05。收修改稿日期: 2013-11-22。

国家自然科学基金(No.50903001, 51204002)和安徽高校自然科学基金项目(No.KJ2013A063)资助项目。

*通讯联系人。E-mail: iamqbmei@njupt.edu.cn, Tel: +86-25-85866396

Ruthenium (II) polypyridyl complexes of 2,2'-bipyridine (bpy) and related ligands have interesting photophysical, photochemical, and electrochemical properties that make them attractive for development of dye-sensitized solar cells^[1], photoinduced switches^[2], and photoactive devices^[3]. Furthermore, Ruthenium(II) polypyridyl complexes have been widely used as electrochemiluminescence (ECL) luminophores^[4]. Since ligand design plays a crucial role in determining and eventually improving both the light-emitting and the electron transfer performances of such systems^[5], a variety of ligands have been included in the coordination spheres of Ru(II) polypyridylmetal fragments.

4,5-Diaza-9,9'-spirobifluorene (SB) is a ligand well-known for its good electron affinity, which has been successfully used to improve the electron injection and transport properties of OLEDs for blue emitters^[6]. This spiro-configured SB ligand can effectively enhance the steric hindrance of iridium(III) complexes and reduce the selfquenching of luminescence^[7-9], a crucial factor for OLEDs. Inspired by the above results, herein we introduce SB as a steric and bulky ligand for the ruthenium(II) complexes, $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})(\text{SB})_2](\text{PF}_6)_2$ and $[\text{Ru}(\text{SB})_3](\text{PF}_6)_2$, and investigate the influence of the SB ligand on the performance of photoluminescence and electrochemiluminescence.

1 Experimental

1.1 General

All solvents were purified by routine procedures and distilled under an atmosphere of dry nitrogen before use. All reagents, unless otherwise specified, were purchased from Aldrich and were used as received. *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and SB were prepared by a published method^[10-11]. UV/Vis absorption spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer. NMR spectra were recorded on a Bruker AV400 spectrometer. Photoluminescence spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. Carbon, hydrogen and nitrogen analysis were carried out on a Vario EL CHNS Elemental Analyzer. The electrochemiluminescence experiments were carried out by using a chemiluminescence analyzer (Xi'an Remax Electronic Science Tech. Co. Ltd., China). Mass spectra

were recorded on a Shimadzu AXIMA-CFR plus MALDI-TOF mass spectrometer.

1.2 Synthesis of complexes

$[\text{Ru}(\text{bpy})_2\text{SB}](\text{PF}_6)_2$: *cis*- $[\text{Ru}(\text{bpy})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (0.13 g, 0.25 mmol) and SB (80 mg, 0.25 mmol) were refluxed in 60 mL of degassed aqueous ethanol ($V_{\text{ethanol}}/V_{\text{water}}=2$) at 90 °C for 14 h under N_2 . An excess of NH_4PF_6 (500 mg) was added, and the mixture was stirred for another 1 h. Thereafter, the solution was concentrated under reduced pressure. The dark red-colored solid was separated from the aqueous solution by filtration, washed with distilled water, and dried under vacuum. Finally, recrystallization of the solid from acetone/dichloromethane provided an orange crystalline complex (194 mg, 76% yield).

^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz): $\delta=6.75$ (d, $J=6.8$ Hz, 2H, PhH), 7.12 (t, $J=7.6$ Hz, 2H, PhH), 7.35~7.41 (m, 6H, PhH and PyH), 7.46 (t, $J=5.6$ Hz, 2H, PyH), 7.68 (t, $J=6.4$ Hz, 2H, PyH), 7.78 (d, $J=4.4$ Hz, 2H, PyH), 7.93 (d, $J=7.6$ Hz, 2H, PyH), 8.07 (t, $J=7.6$ Hz, 2H, PyH), 8.12~8.17 (m, 6H, PyH), 8.48 (d, $J=5.6$ Hz, 2H, PyH), 8.69 (d, $J=8.4$ Hz, 1H, PyH), 8.72 (d, $J=8.4$ Hz, 1H, PyH). ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz): $\delta=162.62$, 158.44, 157.75, 153.12, 152.66, 151.20, 142.93, 141.84, 138.33, 138.06, 133.17, 129.58 (PyH), 128.57, 128.42, 128.33, 127.53, 124.40, 124.31, 123.83, 121.13 (PhH), 67.52 (C(C)₄). Anal. Calcd. for $\text{C}_{43}\text{H}_{30}\text{N}_6\text{P}_2\text{F}_{12}\text{Ru}$ (%): C 50.55, H 2.96, N 8.22. Found (%): C 50.50, H 3.12, N 8.12.

$[\text{Ru}(\text{SB})_2]\text{Cl}_2$: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (2.61 g, 10 mmol), SB (6.36 g, 20 mmol) and LiCl (4.2 g, 100 mmol) were added in 25 mL degassed DMF, and refluxed for 8 h with stirring. After the solution was cooled to room temperature (r. t.), a mixture of 200 mL 1:1 acetone-water was added. A black red microcrystalline solid was obtained by filtration. The solid was added into 200 mL water and stirred for 10 h at r. t. followed by filtration. The crude product $[\text{Ru}(\text{SB})_2]\text{Cl}_2$ was then washed three times with 25-mL portions of water and ether. The yield was 60% based on the ruthenium salt.

^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz): $\delta=6.96$ (d, $J=7.6$ Hz, 4H, PhH), 7.30 (t, $J=8.4$ Hz, 4H, PhH), 7.53 (t, $J=8.0$ Hz, 4H, PhH), 7.67 (d, $J=8.0$ Hz, 4H, PhH), 7.83 (t, $J=7.6$ Hz, 4H, PyH), 8.07 (d, $J=7.6$ Hz, 4H, PyH), 8.35 (d, $J=5.6$ Hz, 4H, PyH). MALDI-TOF MS (m/z): Calcd.

for $C_{46}H_{28}N_4ClRu$ [M-Cl]⁺: 773.264, Found: 776.557.

[Ru(bpy)(SB)₂](PF₆)₂: [Ru(SB)₂]Cl₂ (0.20 g, 0.25 mmol) and 2,2'-bipyridine (39 mg, 0.25 mmol) were refluxed in 60 mL of degassed aqueous ethanol ($V_{\text{ethanol}}/V_{\text{water}}=2$) at 90 °C for 14 h under N₂. An excess of NH₄PF₆ (500 mg) was added, and the mixture was stirred for another 1 h. Thereafter, the solution was concentrated under reduced pressure. The dark red-colored solid was separated from the aqueous solution by filtration, washed with distilled water, and dried under vacuum. Finally, recrystallization of the solid from acetone/dichloromethane provided an orange crystalline complex (166 mg, 56% yield).

¹H NMR ((CD₃)₂CO, 400 MHz): $\delta=6.63$ (d, $J=7.6$ Hz, 2H, PhH), 6.69 (d, $J=7.6$ Hz, 2H, PhH), 7.18~7.23 (m, 6H, PhH), 7.35 (t, $J=7.6$ Hz, 4H, PhH), 7.45~7.50 (m, 4H, PhH and PyH), 7.55 (t, $J=8.4$ Hz, 2H, PyH), 7.76 (d, $J=4.8$ Hz, 4H, PyH), 7.89 (d, $J=7.6$ Hz, 4H, PyH), 8.10 (t, $J=4.8$ Hz, 4H, PyH), 8.44 (d, $J=8.0$ Hz, 2H, PyH), 8.57 (d, $J=5.6$ Hz, 2H, PyH). ¹³C NMR ((CD₃)₂CO, 100 MHz): $\delta=163.60$, 163.17, 158.96, 154.30, 153.34, 152.37, 151.57, 142.85, 142.61, 142.61, 142.05, 142.03, 141.76, 138.15 (PyH), 133.37, 133.27, 133.07, 129.50, 129.48, 128.70, 128.41, 128.04, 127.78, 124.15, 123.85, 123.67, 121.05, 121.02 (PyH), 67.58 (C(C)₄). Anal. Calcd. for C₅₆H₃₆N₆P₂F₁₂Ru(%): C 56.81, H 3.07, N 7.10. Found (%): C 56.61, H 3.11, N 7.00.

[Ru(SB)₃](PF₆)₂: This orange complex was synthesized and purified by the similar procedure described above with the starting materials of [Ru(SB)₂]Cl₂ and SB. The yields were 53%.

¹H NMR ((CD₃)₂CO, 400 MHz): $\delta=6.98$ (d, $J=7.6$ Hz, 6H, PhH), 7.27 (t, $J=7.6$ Hz, 6H, PhH), 7.56 (t, $J=7.6$ Hz, 6H, PhH), 7.62 (d, $J=8.0$ Hz, 6H, PhH), 7.72 (t, $J=8.0$ Hz, 6H, PyH), 8.12 (d, $J=7.6$ Hz, 6H, PyH), 8.57 (d, $J=5.6$ Hz, 6H, PyH). ¹³C NMR ((CD₃)₂CO, 100 MHz): $\delta=164.44$, 153.47, 142.58, 142.14, 141.89 (PyH), 133.34, 129.61, 128.56, 128.54, 123.98, 121.15 (PhH), 67.91 (C(C)₄). Anal. Calcd. for C₆₀H₄₂N₆P₂F₁₂Ru(%): C 61.57, H 3.14, N 6.24. Found(%): C 61.36, H 3.18, N 6.20.

1.3 Crystal structure determination

Single crystals of [Ru(bpy)₂(SB)](PF₆)₂·CH₂Cl₂ were obtained by repeated recrystallization of [Ru(bpy)₂(SB)](PF₆)₂ using a mixture of acetone, CH₂Cl₂ and diethyl ether at room temperature, and then mounted on glass fibers. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with Mo K α radiation at 296 K using a ω scan mode. Crystallographic and experimental data of [Ru(bpy)₂(SB)](PF₆)₂·CH₂Cl₂ is listed in Table 1.

CCDC: 948328.

1.4 Electrochemiluminescence(ECL)

Solutions used to obtain ECL were 0.1 $\mu\text{mol} \cdot \text{L}^{-1}$ ruthenium(II) complexes and 0.05 $\text{mol} \cdot \text{L}^{-1}$ tri-*n*-propylamine (TPA) with 0.2 $\text{mol} \cdot \text{L}^{-1}$ potassium phosphate (aqueous and mixed 50 :50 (V/V) CH₃CN/H₂O) as electrolyte. The photomultiplier tube was biased at 600 V. The ECL cell was placed directly on top of the PMT window and was enclosed in a light-tight box. ECL was measured by cycles from 0 to 2 V versus Ag/AgCl at 0.1 V·s⁻¹ using cyclic voltammetry and the light intensity

Table 1 Crystal data, data collection and structure refinement parameters for [Ru(bpy)₂(SB)](PF₆)₂·CH₂Cl₂

Compound	[Ru(bpy) ₂ (SB)](PF ₆) ₂ ·CH ₂ Cl ₂	$\mu(\text{Mo K}\alpha) / \text{cm}^{-1}$	6.2
Formula	C ₄₄ H ₃₂ Cl ₂ F ₁₂ N ₆ P ₂ Ru	θ range for data collection / (°)	2.25 to 27.54
Formula weight	1 106.67	$F(000)$	4 432
Cryst. Size / mm	0.35×0.23×0.20	hkl range	-24~20, -24~25, -31~31
Crystal system	Orthorhombic	Refl. measured	54 806
Space group	<i>Pbca</i>	Refl. unique	10 390
a / nm	1.881 8(2)	R_{int}	0.074
b / nm	1.991 3(3)	Param. refined	604
c / nm	2.42 1(3)	$R(F)/wR(F^2)^a$ (all refl.)	0.108 7 / 0.181 2
V / nm ³	9.076(2)	GoF (F^2) ^b	0.982
Z	8	Largest diff. peak and hole / (e·nm ⁻³)	770 and -460
D_c / (g·cm ⁻³)	1.62		

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$; ^b $\text{GoF} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

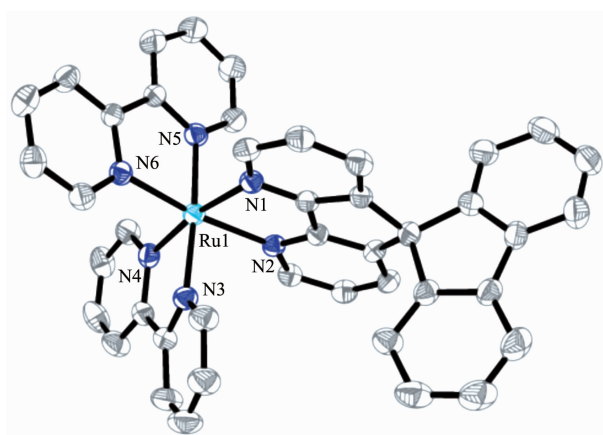
recorded every 0.1 mV. A glass carbon electrode (GCE) (3.0 mm diameter) was used as the working electrode after pre-treated with conventional procedure. The counter electrode was a platinum disc (50 mm²).

2 Results and discussion

2.1 Synthesis and characterization

The new ruthenium complexes, [Ru(bpy)₂(SB)](PF₆)₂, [Ru(bpy)(SB)₂](PF₆)₂ and [Ru(SB)₃](PF₆)₂ were readily prepared from the corresponding intermediates and ligands. The structure of intermediate [Ru(SB)₂]Cl₂ was validated by ¹H NMR spectrum and mass spectrum. The regular ¹H NMR spectrum indicate the Ruthenium elements were not paramagnetic Ru³⁺ cations. At the same time, the mass-to-charge ratio of the molecular ion peak is 776.557 corresponding to [Ru(II)(SB)₂Cl]⁺. These results indicate that in this intermediate, the Ru(III) atoms are reduced into Ru(II) atoms by solvent. All the complexes were characterized by NMR spectroscopy and elemental analysis.

The structure of [Ru(bpy)₂(SB)](PF₆)₂ which exists in the form of solvation ([Ru(bpy)₂(SB)](PF₆)₂ · CH₂Cl₂), has been further confirmed by X-ray crystallography. The



Displacement ellipsoids are shown at the 25% probability level; H-atoms, PF₆⁻ anions and CH₂Cl₂ solvent molecules are omitted for clarity; Selected distances (nm) and angles (°): Ru1 N4 0.203 7(3), Ru1 N6 0.205 1(3), Ru1 N3 0.205 6(3), Ru1 N5 0.205 8(3), Ru1 N1 0.210 8(3), Ru1 N2 0.214 4(3), N4-Ru1-N6 95.54 (13), N4-Ru1-N3 79.02 (14), N6-Ru1-N3 98.90 (14), N4-Ru1-N5 97.30(14), N6-Ru1-N5 78.75(14), N3-Ru1-N5 175.48(13), N4-Ru1-N1 170.76 (13), N6-Ru1-N1 90.84 (13), N3-Ru1-N1 93.42 (13), N5-Ru1-N1 90.49 (13), N4-Ru1-N2 91.62 (13), N6-Ru1-N2 172.11(12), N3-Ru1-N2 85.70(13), N5-Ru1-N2 97.08(13), N1-Ru1-N2 82.45(12)

Fig.1 Perspective view of [Ru(bpy)₂(SB)]²⁺

molecular structure of complex cation is shown in Fig.1, PF₆⁻ anions are omitted for clarity. The crystal data, data collection and structure refinement parameters are given in Table 1. The compound crystallizes in orthorhombic space group *Pbca*. [Ru(bpy)₂(SB)]²⁺ cations are situated in general positions with no crystallographically imposed symmetry. The complex cation features distorted octahedral coordination around the Ru atom through hexadentate coordination of two bipyridines and one SB ligand. The Ru-N bond lengths of bpy ligands ranging from 0.203 7 to 0.205 8 nm are shorter than that of SB ligands, which are spanning from 0.210 8 to 0.214 4 nm. However, the N-Ru-N bond angles in this structure are all deviated from either 90° or 180°. Similar bond lengths and angles were also observed in formerly reported ruthenium polypyridyl complexes^[12-15].

2.2 Photophysical and electrochemiluminescence properties

The UV/Vis absorption spectra of those new ruthenium(II) complexes in CH₃CN (Fig.2) are mainly dominated by two intense absorption at ca. 190~380 nm and a comparatively less intense band at ca. 380~500 nm. The former is assigned to a typical spin-allowed ¹π-π* transition of the ligands, and the later to MLCT transition. With the increase of SB ligand concentration, the sharp band at 286 nm gradually grows wider and the band at 212 nm enhanced.

The room temperature photoluminescence spectra of the ruthenium(II) complexes in CH₃CN solution are illustrated in Fig.3. [Ru(bpy)₂(SB)](PF₆)₂ emits a weak luminescence with the emission wavelength at 606 nm

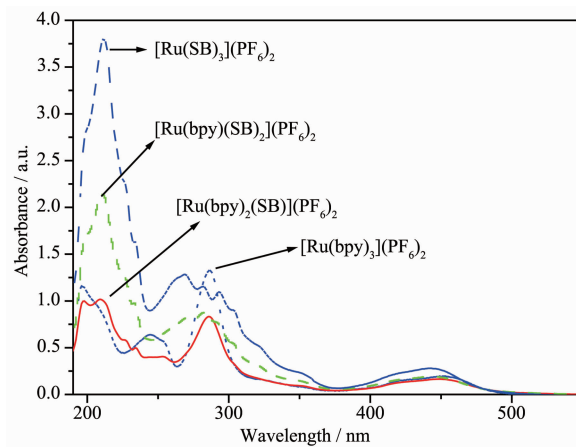


Fig.2 UV/Vis absorption spectra of the ruthenium(II) complexes in CH₃CN

which has a 6 nm red-shift compared to that of reference $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. The phosphorescence quantum efficiency of $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$ in CH_3CN is *ca.* 0.001 2, using $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ ($\Phi=0.062$) as the standard^[16]. $[\text{Ru}(\text{bpy})(\text{SB})_2](\text{PF}_6)_2$ and $[\text{Ru}(\text{SB})_3](\text{PF}_6)_2$ have rather weak or almost no light under the same excitation condition. A plausible explanation is the presence of interligand steric repulsions which weaken the ligand field. As a consequence, the metal centered (^3MC) state may approach the $^3\text{MLCT}$ state, so that emission of $^3\text{MLCT}$ state is quenched by the nonradiative decay of ^3MC state to the ground state^[17].

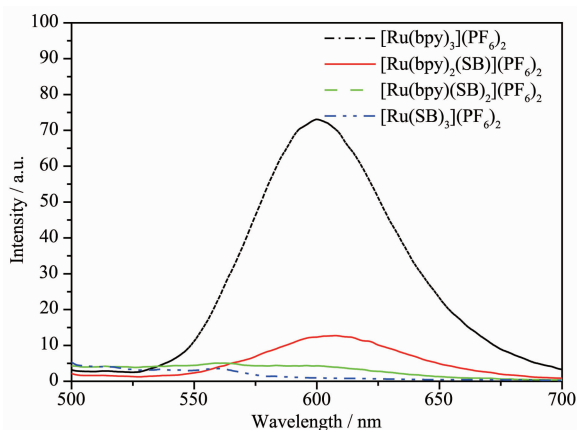


Fig.3 Room-temperature photoluminescence spectra of the ruthenium(II) complexes ($1 \mu\text{mol} \cdot \text{L}^{-1}$) in CH_3CN ($\lambda_{\text{ex}}=480 \text{ nm}$)

The I_{ECL}/E curves of ruthenium(II) complexes are shown in Fig.4. Under the same conditions, $[\text{Ru}(\text{bpy})_2(\text{SB})](\text{PF}_6)_2$ has the strongest light among the three complexes but is much lower than the reference $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. $[\text{Ru}(\text{SB})_3](\text{PF}_6)_2$ has very weak light. With the increase of SB ligand concentration, the peak

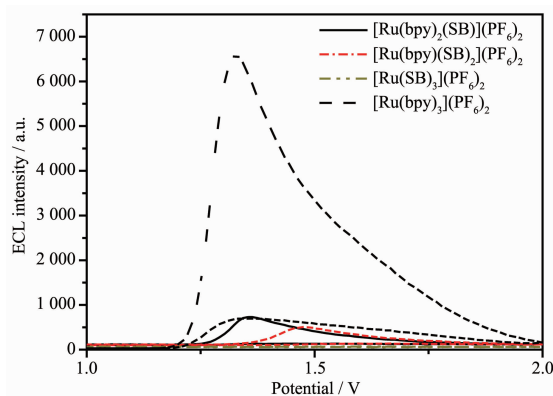


Fig.4 ECL intensity-potential curves of ruthenium(II) complexes

potential increased from 1.36 V to 1.58 V, and relative peak intensity decreased from 731 to 52 which are consistent with the photoluminescence result. These results indicate that the ECL comes from the radiation transition of triple state $^3\text{MLCT}$ ^[18].

4 Conclusions

In summary, we have synthesized three ruthenium(II) complexes with SB as ligand. These complexes have a reduced room-temperature photoluminescence and ECL with increased SB concentration. Thus, the present results have shown that SB is not a good ligand for luminescent ruthenium(II) complexes, and need for further modification for the energy level matching.

References:

- [1] Mishra A, Pootrakulchote N, Wang M K, et al. *Adv. Funct. Mater.*, **2011**, *21*:963-970
- [2] Sun W L, Yao T M, Shi S, et al. *Analyst*, **2012**, *137*:1550-1552
- [3] Hirahara M, Masaoka S, Sakai K, et al. *Dalton Trans.*, **2011**, *40*:3967-3978
- [4] Liu D Y, Xin Y Y, He X W, et al. *Biosens Bioelectron*, **2011**, *26*:2703-2706
- [5] Stagni S, Palazzi A, Zacchini S, et al. *Inorg. Chem.*, **2006**, *45*:695-709
- [6] Chi C C, Chiang C L, Liu S W, et al. *J. Mater. Chem.*, **2009**, *19*:5561-5571
- [7] Su H C, Fang F C, Hwu T Y, et al. *Adv. Funct. Mater.*, **2007**, *17*:1019-1027
- [8] Su H C, Wu C C. *Appl. Phys. Lett.*, **2006**, *89*:261118-261118-3
- [9] Su H C, Chen H F, Fang F C, et al. *J. Am. Chem. Soc.*, **2008**, *130*:3413-3419
- [10] Sullivan B P, Salmon D J, Meyer T J, et al. *Inorg. Chem.*, **1978**, *17*:3334-3341
- [11] Wong K T, Chen R T, Fang F C, et al. *Org. Lett.*, **2005**, *7*:1979-1982
- [12] Khatua S, Samanta D, Bats J W, et al. *Inorg. Chem.*, **2012**, *51*:7075-7086
- [13] Bhaumik C, Das S, Saha D, et al. *Inorg. Chem.*, **2010**, *49*:5049-5062
- [14] Das S, Saha D, Bhaumik C, et al. *Dalton Trans.*, **2010**, *39*:4162-4169
- [15] Saha D, Das S, Maity D, et al. *Inorg. Chem.*, **2011**, *50*:46-61
- [16] Caspar J V, Meyer T J. *J. Am. Chem. Soc.*, **1983**, *105*:5583-5590
- [17] Sauvage J P, Collin J P, Chambrion J C, et al. *Chem. Rev.*, **1994**, *94*:993-1019
- [18] Wilson G. J, Sasse W H F, Mau A W H, et al. *Chem. Phys. Lett.*, **1996**, *250*:583-588