

## 含席夫碱桥联配体的双核金属钌配合物的合成及其性能研究

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**摘要:** 合成了 3 种双核钌配合物  $[\text{Ru}(\text{bpy})_2]_2\{[(\text{PyCHN})\text{-Ph-O-C}_6\text{H}_4\text{-}]_2\text{R}\}(\text{ClO}_4)_4$ ,  $\text{bpy}=2,2'$ -联吡啶,  $\text{PyCHN}=\text{N}$ -2-吡啶亚甲基,  $\text{R}=\text{无}(\mathbf{1})$ ,  $-\text{C}(\text{CH}_3)_2(\mathbf{2})$ ,  $-\text{SO}_2(\mathbf{3})$  并进行了有关表征。电化学研究表明: 配合物  $\mathbf{3}$  的  $\Delta E$  和  $K_c$  值最大, 说明苯环和硫原子之间存在着较强的  $(p(\pi)\text{-}d)\pi$  相互作用, 有助于获得较强的金属-金属相互作用。配合物  $\mathbf{1}, \mathbf{2}, \mathbf{3}$  都有混合价, 通过 Hush 方程可以得到  $V_{ab}$  的值大概为  $320\sim 420\text{ cm}^{-1}$ 。这些结果表明: Schiff 碱作为桥配体对于调配金属-金属相互作用并将其作为分子导线起着特殊的作用。

**关键词:** 双核钌配合物; 金属-金属相互作用; 分子导线

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## Synthesis and Properties of Dinuclear Ruthenium Complexes with Schiff Base Bridging Ligands

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**Abstract:** Binuclear ruthenium complexes  $[\text{Ru}(\text{bpy})_2]_2\{[(\text{PyCHN})\text{-Ph-O-C}_6\text{H}_4\text{-}]_2\text{R}\}(\text{ClO}_4)_4$ , where  $\text{bpy}=2,2'$ -bipyridine,  $\text{PyCHN}=\text{N}$ -2-pyridylmethylene,  $\text{R}=\text{none}$  for  $\mathbf{1}$ ,  $-\text{C}(\text{CH}_3)_2$  for  $\mathbf{2}$  and  $-\text{SO}_2$  for  $\mathbf{3}$ , have been prepared and characterized. Electrochemical studies reveal that the  $\Delta E$  and  $K_c$  for complexes  $\mathbf{1}$ ,  $\mathbf{2}$  and  $\mathbf{3}$  are surprisingly and unprecedentedly large. However, the complex  $\mathbf{3}$  gives larger  $\Delta E$  and  $K_c$ . It is suggested that the strong  $(p(\pi)\text{-}d)\pi$  interactions between the phenyl rings and the sulfur atom should be helpful to achieve stronger metal-metal interaction. For mixed-valence species of complexes  $\mathbf{1}$ ,  $\mathbf{2}$  and  $\mathbf{3}$ ,  $V_{ab}$  can be obtained by Hush equation with a value of  $320\sim 420\text{ cm}^{-1}$ . These results indicate that the Schiff base bridging ligands show particular efficiency for mediating the metal-metal interactions and for using as molecular wires.

**Key words:** binuclear ruthenium complexes, metal-metal interaction, molecular wires

## 0 Introduction

Molecular electronics may be considered a combined effort from chemists and physicists to replace wires, switches, transistors, etc. of current microelectronic technology by single molecular devices<sup>[1]</sup>. One of the areas of basic research, molecular wires, has become an exciting, challenging,

and rapidly expanding field in this area, crossing the borders between many areas of physics, chemistry, and engineering<sup>[2-3]</sup>. Mixed-valence compounds with at least two redox sites (D and A) linked by a bridge which mediates the transfer of electrons from one site to the other are excellent candidates for such studies, and give new insights into natural processes, such as photosynthesis, respiration, nitrogen fixation, DNA

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biosynthesis and repair, etc.<sup>[4-5]</sup>. In addition, mixed-valence compounds can be simple models for the expanding domain of nanojunctions, in which a single molecule is bridging two nanoscale metallic conductors<sup>[6]</sup>. For such systems, experimental studies have increased over the past few years as a result of recent developments in nano-fabrication, self-assembly, and scanning tunneling microscopy techniques<sup>[7]</sup>.

A key point in providing guidelines for the design of such nanoscale electronic devices is a deeper understanding of the relation between structure and electrical conductivity of molecular wires, and significant research efforts are currently being made to achieve progress in this direction<sup>[8]</sup>. Polyaromatic bridges provide relatively strong intercomponent electronic coupling and, therefore, are very convenient connectors for the construction of polynuclear metal complexes, especially for the study of long-range energy-/electron-transfer processes<sup>[9]</sup>. However, as the sizes of compounds increase, synthetic problems become more severe, particularly, with a decrease in solubility. Thus the new classes of compounds that would be more easily accessible and would exhibit stronger metal-metal coupling are required. Schiff base compounds are excellent chelating ligands. The ease of synthesis and high yield in a single-step reaction from commercial and inexpensive reagents allow us to systematically probe the effect of modifications to the ligand backbone through which we are attempting to control the precise topography and the electronic properties defined molecular wires. Here we design several flexible bridging ligands (Scheme 1) containing saturated spacers that link two Ru(bpy)<sub>2</sub> ends with metal-metal separations up to several nm for the study of the long-distance intervalence transitions.

## 1 Experimental

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a Perkin-Elmer 240C

elemental analyzer at the Analysis Center of Nanjing University. Electrospray mass spectra were recorded on a LCQ system (Finnigan MAT, USA) using methanol as mobile phase. 500 MHz <sup>1</sup>H NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS (SiMe<sub>4</sub>) as an internal reference at 25 °C. Differential pulse voltammetry (DPV) was done with an EG and GPAR model 273 instrument in a three-electrode cell with a pure Ar gas inlet and outlet. The working electrode and counter electrode were Pt spirals, and the reference electrode was a saturated calomel electrode (SCE). The experiments were carried out in the presence of CH<sub>3</sub>CN. DPV experiments were performed with a scan rate of 20 mV·s<sup>-1</sup>. UV-Vis-NIR spectra were obtained at room temperature on Shimadzu 3100 spectrophotometer in acetonitrile solution.

### 1.1 Preparation of BL<sup>1</sup>

4, 4'-Bis (4-aminophenoxy)biphenyl (0.37 g, 1.0 mmol) and 2-pyridinecarboxaldehyde (0.54 g, 5.0 mmol) were mixed in methanol (35 mL) and heated at reflux for 8 h. The yellow solid (0.48 g, 0.88 mmol, yield 88%) was filtered and dried under vacuum. Anal. Found: C, 79.2; H, 4.8; N, 10.4. Calcd. for C<sub>36</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>: C, 79.1; H, 4.8; N, 10.3. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 8.80 (2H, d, Py), 8.64 (2H, s, CH), 8.19 (2H, d, Py), 7.81 (2H, t, Py), 7.54 (4H, d, Ph), 7.37 (2H, t, Py), 7.36 (4H, d, Ph), 7.12 (8H, d, Ph). IR (cm<sup>-1</sup>): 3 060 (ν<sub>C-H</sub>), 1 625, 1 578, 1 476, 1 463, 1 279 (ν<sub>C=C</sub>, ν<sub>C=N</sub>, ν<sub>C-N</sub>), 1 243, 1 279 (ν<sub>Ph-O</sub>), 833, 777, 739 (δ<sub>C-H</sub>).

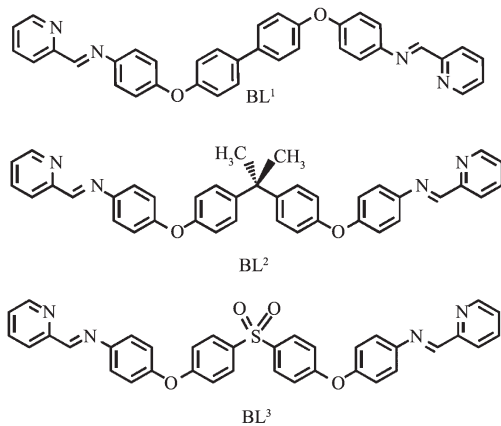
### 1.2 Preparation of BL<sup>2</sup>

2,2'-Bis[4-(4-aminophenoxy)phenyl]propane (0.41 g, 1.0 mmol) and 2-pyridinecarboxaldehyde (0.54 g, 5.0 mmol) were mixed in methanol (35 mL) and heated at reflux for 4.5 h. The solution was then evaporated to 5 mL, and 15 mL petroleum ether was added. After cooling to 0 °C, the yellow precipitate (0.42 g, 0.72 mmol, yield 72%) was filtered and dried under vacuum. Anal. Found: C, 79.6; H, 5.4; N, 9.6. Calcd. for C<sub>39</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>: C, 79.6; H, 5.5; N, 9.5. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 8.80 (2H, s, Py), 8.64 (2H, s, CH), 8.19 (2H, d, Py), 7.81 (2H, t, Py), 7.54 (4H, d,

Ph), 7.37 (2H, t, Py), 7.36 (4H, d, Ph), 7.12 (8H, d, Ph), 1.70 (6H, s, CH<sub>3</sub>). IR (cm<sup>-1</sup>): 3 060 (ν<sub>C-H</sub>), 1 625, 1 578, 1 476, 1 463, 1 279 (ν<sub>C=C</sub>, ν<sub>C=N</sub>, ν<sub>C-N</sub>), 1 243, 1 279 (ν<sub>Ph-O</sub>), 833, 777, 739 (δ<sub>C-H</sub>).

### 1.3 Preparation of BL<sup>3</sup>

Bis [4-(4-aminophenoxy)phenyl]sulfone (0.44 g, 1.0 mmol) and 2-pyridinecarboxaldehyde (0.54 g, 5.0 mmol) were mixed in methanol (35 mL) and heated at reflux for 4.5 h. The solution was then evaporated to 5 mL, and the yellow product (0.51 g, 0.83 mmol, yield 83%) was filtered and dried under vacuum. Anal. Found: C, 70.7; H, 4.3; N, 9.3. Calcd. for C<sub>36</sub>H<sub>26</sub>N<sub>4</sub>O<sub>4</sub>S: C, 70.8; H, 4.3; N, 9.2. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 8.64 (2H, d, Py), 8.23 (2H, s, CH), 7.98 (2H, d, Py), 7.86 (4H, d, Ph), 7.83 (4H, t, Ph), 7.41 (4H, d, Ph), 7.36 (8H, d, Ph). IR (cm<sup>-1</sup>): 1 629, 1 585, 1 488, 1 296 (ν<sub>C=C</sub>, ν<sub>C=N</sub>, ν<sub>C-N</sub>), 1243 (ν<sub>Ph-O</sub>), 833, 777, 742 (δ<sub>C-H</sub>).



Scheme 1

### 1.4 Preparation of complex 1

Ligand BL<sup>1</sup> (0.27 g, 0.5 mmol) and Ru<sub>2</sub>(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (0.52 g, 1.0 mmol) were mixed in ethanol (100 mL) and heated at reflux for 12 h. The solution was then evaporated to 15 mL, and added to a saturated ethanol solution of NaClO<sub>4</sub>. The yellow solid product (0.63 g, 0.36 mmol, yield 72%) was filtered, purified by washing with hot methanol and dried under vacuum. Anal. Found: C, 51.6; H, 3.4; N, 9.7. Calcd. for Ru<sub>2</sub>C<sub>76</sub>H<sub>58</sub>N<sub>12</sub>O<sub>18</sub>Cl<sub>4</sub>: C, 51.5; H, 3.3; N, 9.5. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO) δ(ppm): 8.89 (2H, t, Py), 8.69 (2H, d, Py), 8.64 (2H, m, Py), 8.51 (2H, t, bpy), 8.21 (6H, m, bpy), 8.01 (4H, t, Py), 7.86 (2H, d, Py), 7.79 (2H, s, CH), 7.72 (12H, m, bpy), 7.50 (4H, d, Ph), 7.38 (4H, d, Ph),

6.80~7.00 (4H, m, bpy), 6.69 (4H, d, bpy), 6.64 (4H, d, bpy). IR (cm<sup>-1</sup>): 1 603, 1 489 (ν<sub>C=C</sub>, ν<sub>C=N</sub>), 1 240 (ν<sub>Ph-O</sub>, ν<sub>C-N</sub>), 768, 625 (δ<sub>C-H</sub>), 1106 (ν<sub>Cl-O</sub>).

### 1.5 Preparation of complex 2

Ligand BL<sup>2</sup> (0.29 g, 0.5 mmol) and Ru<sub>2</sub>(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (0.52 g, 1.0 mmol) were mixed in ethanol (100 mL) and heated at reflux for 12 h. The solution was then evaporated to 15 mL, and added to a saturated ethanol solution of NaClO<sub>4</sub>. The yellow solid product (0.65 g, 0.37 mmol, yield 74%) was filtered, purified by washing with hot methanol and dried under vacuum. Anal. Found: C, 52.4; H, 3.9; N, 9.1. Calcd. for Ru<sub>2</sub>C<sub>79</sub>H<sub>64</sub>N<sub>12</sub>O<sub>14</sub>Cl<sub>4</sub>: C, 52.3; H, 3.6; N, 9.3. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO) (ppm): 8.89 (2H, t, Py), 8.66 (2H, d, Py), 8.62 (2H, d, Py), 8.49 (2H, d, bpy), 8.24 (8H, m, bpy), 7.96 (4H, m, Ph), 7.86 (2H, s, CH), 7.79 (2H, d, Py), 7.69 (6H, m, bpy), 7.64 (4H, m, bpy), 7.54 (4H, d, Ph), 7.35 (4H, d, Ph), 7.27 (4H, d, Ph), 6.76 (6H, d, bpy), 6.67 (6H, m, bpy), 1.65 (6H, s, CH<sub>3</sub>). IR (cm<sup>-1</sup>): 1 625, 1 578, 1 476, 1 463, 1 279 (ν<sub>C=C</sub>, ν<sub>C=N</sub>, ν<sub>C-N</sub>), 1243, 1279 (ν<sub>Ph-O</sub>), 833, 777, 739 (δ<sub>C-H</sub>), 1118 (ν<sub>Cl-O</sub>).

### 1.6 Preparation of complex 3

Ligand BL<sup>3</sup> (0.30 g, 0.5 mmol) and Ru<sub>2</sub>(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (0.52 g, 1.0 mmol) were mixed in ethanol (100 mL) and heated at reflux for 12 h. The solution was then evaporated to 15 mL, and added to a saturated ethanol solution of NaClO<sub>4</sub>. The yellow solid product (0.75 g, 0.41 mmol, yield 82%) was filtered, purified by washing with hot methanol and dried under vacuum. Anal. Found: C, 49.7; H, 3.2; N, 9.2. Calcd. for Ru<sub>2</sub>C<sub>76</sub>H<sub>58</sub>N<sub>12</sub>SO<sub>20</sub>Cl<sub>4</sub>: C, 49.7; H, 3.2; N, 9.2. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO) δ(ppm): 8.87 (2H, t, Py), 8.67 (2H, d, Py), 8.62 (2H, d, Py), 8.50 (4H, t, bpy), 8.22 (8H, m, bpy), 8.01 (4H, d, Ph), 7.96 (4H, m, bpy), 7.86 (2H, d, Py), 7.79 (2H, d, CH), 7.72 (4H, d, bpy), 7.68 (4H, d, Ph), 7.64 (4H, d, Ph), 7.53 (4H, d, Ph), 7.35 (2H, t, bpy), 6.90 (2H, d, bpy), 6.84 (4H, d, bpy), 6.69 (4H, d, bpy). IR (cm<sup>-1</sup>): 1 603, 1 583, 1 487, 1 465, 1 294 (ν<sub>C=C</sub>, ν<sub>C=N</sub>, ν<sub>C-N</sub>), 1244 (ν<sub>Ph-O</sub>), 1108 (ν<sub>Cl-O</sub>), 768, 626, 558 (δ<sub>C-H</sub>).

## 2 Results and discussion

### 2.1 Synthesis and characterization of the ligands

The bridging ligands BL<sup>1</sup>, BL<sup>2</sup> and BL<sup>3</sup> were

synthesized by reaction of the 2-pyridinecarboxaldehyde and the corresponding diamines (2:1 molar ratio) in methanol under refluxing conditions. The BL<sup>1</sup>, BL<sup>2</sup> and BL<sup>3</sup> were obtained as yellow precipitate in good yield and purified by washing with hot methanol, in which reactants are highly soluble. The ligands BL<sup>1</sup>-BL<sup>3</sup> gave satisfactory elemental analysis. The IR spectra of all the ligands show the presence of the band around 1 625 cm<sup>-1</sup>, indicating the formation of C=N in the Schiff base. The <sup>1</sup>H NMR spectra of BL<sup>1</sup>-BL<sup>3</sup> were recorded in CDCl<sub>3</sub>. The observed spectra of BL<sup>1</sup>-BL<sup>3</sup> indicate that each half of the ligand is equivalent due to internal symmetry, therefore it may be assumed that the trans configuration of the ligands is predominant in solution or that there is a fast equilibrium between the cis and trans isomers of BL<sup>1</sup>-BL<sup>3</sup>. The <sup>1</sup>H NMR spectrum of BL<sup>1</sup> shows eight sets of signals in the aromatic region, as illustrated in Fig.1a. The signal assignment is rather straightforward by the comparison of chemical shifts with those of similar Schiff-base ligands. The chemical shifts of H<sub>e</sub> and H<sub>i</sub> are observed at about 8.71 ppm and 8.80 ppm, respectively. The py-CH=N is an electron-withdrawing group, and close to H<sub>e</sub> and H<sub>d</sub>, so the chemical shifts of H<sub>e</sub> and H<sub>d</sub> were downfield

in comparison with H<sub>a</sub> and H<sub>b</sub>. In <sup>1</sup>H NMR spectra of the ligand BL<sup>2</sup> and BL<sup>3</sup>, similar cases were observed.

## 2.2 Synthesis and characterization of the complexes

CAUTION! Although no problems were encountered in this work, perchlorates are potentially explosive, and should be handled with care.

Dinuclear ruthenium complexes **1**, **2** and **3** were prepared by reacting Ru(bipy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O [10] with the relevant bridging ligands BL<sup>1</sup>, BL<sup>2</sup> or BL<sup>3</sup> in a 2:1 ratio. The products were isolated as perchlorate salts. The elemental analyses suggested the formation of the completely reduced forms of the dinuclear ruthenium compounds. <sup>1</sup>H NMR spectra of complexes **1-3** were recorded in (CD<sub>3</sub>)<sub>2</sub>SO, as illustrated in Fig.1b for the complex **3**. Since the electronic environments of many aromatic hydrogen atoms are very similar, their signals may appear in a narrow chemical shift range. On the other hand, the complicated NMR spectra for the diruthenium complexes should be mainly due to the formation of the two diastereomers, because the ruthenium centers are chiral. In fact the aromatic regions of the spectra are complicated, however, direct comparisons of the intensity of the aromatic proton signals with that of the clearly observable singlet due to the CH=N proton for complexes **1**, **2** and **3** (δ=9.0) reveal the presence of the calculated number of aromatic protons. The partial overlapping of the signals makes it difficult to assign all the individual signals. The structures of dinuclear complexes were further established by electrospray mass spectrometry (ESI-MS) in CH<sub>3</sub>CN-CH<sub>3</sub>OH. This technique has proven to be very helpful for identifying polynuclear transition metal complexes with high molecular masses. ESI-MS spectra of the three ruthenium complexes exhibit only one strong peak with *m/z* at 343.6 for 1<sup>4+</sup>, 354.2 for 2<sup>4+</sup>, and 359.3 for 3<sup>4+</sup>, respectively, which are in excellent agreement with the calculated values (Fig.2). The observed peaks for 1<sup>4+</sup>, 2<sup>4+</sup> and 3<sup>4+</sup> reveal that the dinuclear ruthenium species are stable in the solution.

## 2.3 Electrochemical properties of the complexes

For the experimental evaluation of a molecular

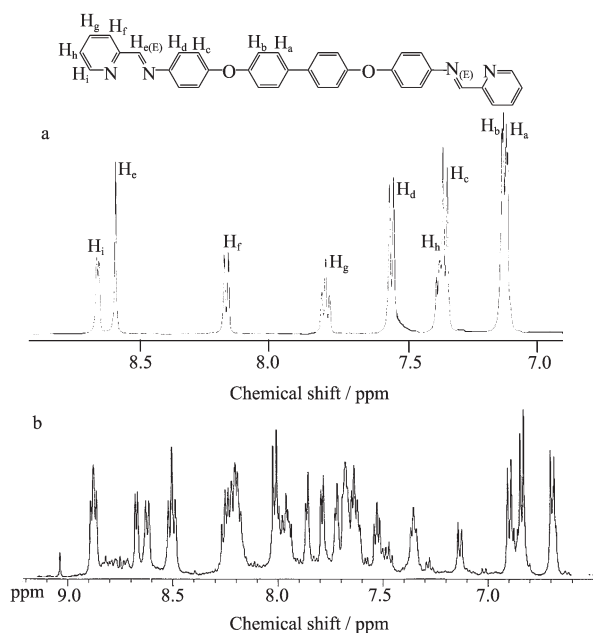
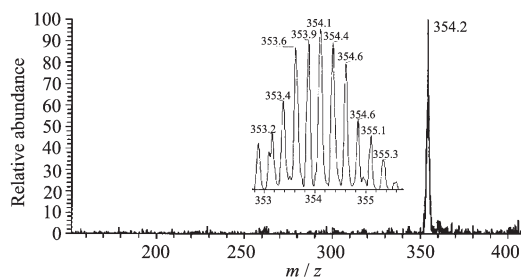


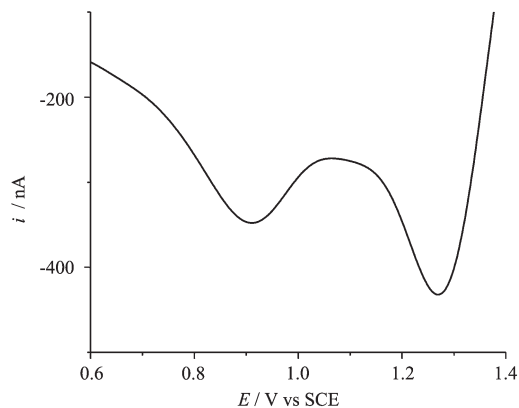
Fig.1 <sup>1</sup>H NMR spectrum of the bridging ligand BL<sup>1</sup> in CDCl<sub>3</sub> (a) and the complex **3** in (CD<sub>3</sub>)<sub>2</sub>SO(b)

Fig.2 ESI-MS spectra for the  $2^{+}$  in  $\text{CH}_3\text{OH}$ 

wire as a device that allows exchange of an electron or hole between its terminal redox centers, there are in principle four different methods available: measurement of the (i) bulk conductivity, (ii) conductivity of a single molecule, (iii) intervalence transition by NIR spectroscopy, and (iv) electronic interaction by cyclic voltammetry. The first approach is highly dependent on the actual solid state structure of the material and gives only a statistical figure of merit, which is dominated by intermolecular and not necessarily by intramolecular interactions. The second method would be the most accurate test, but the experimental setup is quite difficult (measurement of the current/voltage response of a single molecule inserted between an electrode and a STM tip) and has been realized only for very few systems<sup>[7]</sup>. The third method gives the electron coupling as a function of the energy and half-width of the optical intervalence transition in weakly coupled systems, but often it is difficult to deconvolute the spectra due to very broad signals and/or overlapping metal-to-ligand charge transfer bands. The fourth approach is the most convenient and the commonly used practice. It allows an indirect measurement of the “electronic communication” between the redox termini of a molecule in solution and has been applied to many intramolecular electron transfer systems.

The differential pulse voltammetry (DPV)

technique is employed to obtained well-resolved potential information, while the individual redox processes for the multinuclear complexes are poorly resolved in the CV experiment, in which individual  $E_{1/2}$  potentials cannot be easily or accurately extracted from the data. Differential pulse voltammetry (DPV) of the complexes **1-3** were recorded in acetonitrile, the data are summarized in Table 1, and a representative is shown in Fig.3. All the three complexes exhibit two oxidations in the range of 0~1.5 V. Since the bridging ligands does not exhibit any obvious peaks at the range of 0~1.5 V under the same condition, these peaks of the complexes are all assigned to the redox of the  $\text{Ru}^{\text{II}}$  moieties. In Fig.3, the oxidations at 0.90 and 1.28 V correspond to the couples  $3^5+/3^4+$  and  $3^6+/3^5+$ , respectively. The 380 mV separation of the oxidation process of the complex **3** corresponds to a comproportionation constant ( $K_c$ ) of  $10^6$ . However, complex **1** and **2** show smaller separate oxidation as 220 and 180 mV, respectively. It is suggested that strong ( $p(\pi)$ -d) $\pi^{[11]}$  interactions between the phenyl rings and the sulfur atom should be helpful to achieve stronger metal-metal interaction. Generally, despite of the long



0.1 mol·L<sup>-1</sup>  $\text{NBu}_4\text{ClO}_4$ ; scan rate of 20 mV·s<sup>-1</sup>

Fig.3 DPV of the complexes **3** in  $\text{CH}_3\text{CN}$  solution

Table 1 DPV and intervalence transitions data for the species mentioned

	$E / \text{V}$	$K_c$	$\nu_{\text{max}} / \text{cm}^{-1}$	$\epsilon_{\text{max}}$	$V_{\text{ab}} / \text{cm}^{-1}$	$d_{\text{MM}} / \text{nm}$
<b>1</b>	1.13, 1.35	$5.4 \times 10^3$	13 200	1 800	340	2.1
<b>2</b>	1.12, 1.20	$1.1 \times 10^3$	13 500	1 500	320	2.2
<b>3</b>	0.90, 1.28	$3.6 \times 10^6$	13 000	3 200	415	2.4

$d_{\text{MM}}$ : calculated from molecular model.

distance ( $d_{\text{Ru-Ru}} > 2 \text{ nm}$ )<sup>[12]</sup> and the saturated -O-C<sub>6</sub>H<sub>4</sub>-R-C<sub>6</sub>H<sub>4</sub>-O- spacers, the  $\Delta E$  and  $K_c$  for complexes **1**, **2** and **3** are surprisingly and unprecedentedly large<sup>[13]</sup>. The large  $K_c$  values may suggest that the mixed-valence complex can be prepared and studied effectively from its complete reduction and oxidation states.

## 2.4 UV-Vis spectra of the complexes

In order to obtain more detailed information about the electronic interaction between the two Ru centers in this type of complexes, NIR-Vis spectra of the complexes upon chemical oxidation<sup>[14]</sup> were measured. Fig.4 shows the UV-Vis-NIR spectra of the oxidation titration process of compound **1**. During the titration started from the fully reduced species, the metal-to-ligand-charge-transfer (MLCT) band located near 450 nm moves a little to the shorter wavelength while its intensity decreases. In the near infrared region, the intervalence band at about 800 nm grows to maximum when **1** equiv. of oxidant added and then decays. It seems that the ligand-to-metal-charge transfer (LMCT) band of the Ru<sup>III</sup> appears as weaker shoulder or extra absorption on the short-wavelength side. The LMCT, MLCT and MMCT (metal-to-metal-charge transfer) bands overlapped each other, which is helpful to the electron-transfer. Experimental results on the intervalence transitions (position, extinction coefficient, width) are gathered in Table 1. The energy of the transition decreases slightly with the  $K_c$  value

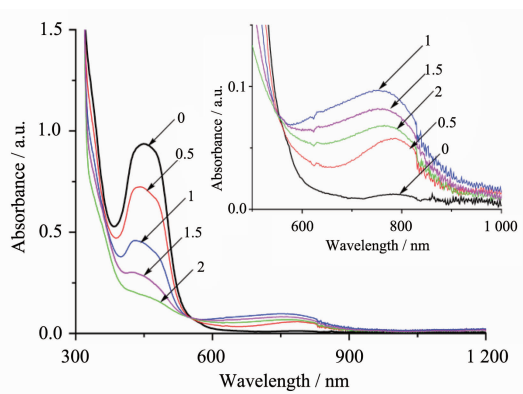
increases, which is expected from the standard model of the solvent reorganization energy. Bandwidths were compared with the theoretical values coming from Hush's expression<sup>[15]</sup>. Consequently,  $V_{ab}$  can be obtained by Hush equation with a value of 320~420 cm<sup>-1</sup> for mixed-valence species of complexes **1**, **2** and **3**. Such a mixed-valence behavior is an exciting example with a long metal-metal separation, especially for compound **2**, in which the two ruthenium centers are obstructed by distorted and flexible saturated parts. It could be concluded that the Schiff base bridging ligands show particular efficiency for mediating the metal-metal interactions and approach as molecular wires. Considering the repeated Ar-O units in the bridges, a multistep hopping mechanism with electron transfer to and from the bridge, like those in the biological systems, is possible<sup>[16]</sup>.

Considering the higher energy absorption band of the mixed-valence species and the overlapped MLCT, LMCT and MMCT bands, a superexchange mechanism may be used to explain the present results. That is, the electron moves from the HOMO of the Ru<sup>II</sup> to the LUMO of the bridging ligands (MLCT), then from the the HOMO of the bridging ligands to the LUMO of the Ru<sup>III</sup> (LMCT). However, the large distance between the two ruthenium ions appears not to support this hypothesis.

The presence of the repeat group O-Ar in the bridging ligands instead suggests a multistep hopping mechanism with electron transfer to and from the bridge rather than a single-step mechanism applied in this system. That is, the one-step charge transfer via a superexchange mechanism between Ru<sup>II</sup>(Ru<sup>III</sup>) and the first repeat group O-Ar, is turned into a two-step hopping process in the ligand. The alternative is that the Schiff base bridging ligands makes the electron transfer efficient for such a long metal-metal distance, and that the presence of the group Ar-O makes the electron transfer prefer to a single-step tunneling process through the bridge<sup>[16]</sup>.

## 3 Conclusions

The easy-to-prepare Schiff-base ligands BL<sup>1</sup> to BL<sup>3</sup> provide a useful starting point to study the



The inset shows the change of the near-IR spectra of the complex **1**. The LMCT of the Ru<sup>III</sup> and the intervalence transition are coupled each other at about 550~900 nm

Fig.4 UV-Vis-NIR spectra of complex **1** with the successive additions of Ce(IV)



long-range intramolecular electron transfer using a modular strategy with a systematic application of intervalence coupling. It is postulated that intervalence electron transfer can be monitored in distance >2.0 nm between two metal centers, which are bridged by several saturated groups, like the electron transfer in the biological system. We are in the process of synthesizing longer bridges with the repeated Ar-O units to study the distance-dependence of the metal-metal coupling and validate the possible multistep hopping mechanism.

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