# SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF TWO BINUCLEAR RHENIUM (I) COMPLEXES

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# ABSTRACT

Rhenium(I) complexes of 1,4-bis(4'-methyl-2,2'-bipyrid-4-yl)buta-1,3-diene and 1,4-bis(4'-methyl-2,2'bipyrid-4-yl)benzeneligands,hereafter denoted as **bbdb** and **bphb** respectively,were synthesised, characterised, and investigated for redox and luminescence properties involving ligand-localized phosphorescence with the aim of verifying their ability in photosensitization. The expected ligand localized phosphorescence was not observed in the **bbdb** complex, most probably due to the flexibility of the bridging ligand. The ligand itself shows no luminesce in room temperature solutions, but at 77 K, it exhibits fluorescence with no structured phosphorescence even in the presence of ethyl iodide. The **bphb**complex,however, exhibits phosphorescence at 77 K, but the ligand does not show structured phosphorescence, suggesting the **bphb**complexa good candidatefor photosensitizer application. These complexes showedirreversible oxidative cyclic voltammograms and the reductive cyclic voltammogramsconsist of several overlapping waves, indicating aggregation of the complexes at the electrode surfaceand reduction of the bridging-ligand.

Keywords: Rhenium, Phosphorescence, Luminescence, MLCT, Electrochemical, Structureless

#### **1.0 INTRODUCTION**

The complex fac-[(bpy)Re(CO)<sub>3</sub>Cl] (where bpy = 2,2'-bipyridine) and its derivatives, which were introduced by Wrighton and co-workers (Wrighton and Morse, 1975; Wrighton and Morse, 1974; Kirganet al, 2007), are generally (Metal-to-charge-transfer) <sup>3</sup>MLCT light emitters, typified by a broad, structureless emission band that is sensitive to temperature, pH, and other environmental changes (Lees, 1987;Leasureet al, 1991). The emission energies, lifetimes, and quantum yields of these complexes can be tuned by derivatizing the 2,2'-bipyridine (**bpy**) ligand or replacing the chloride with other ligands such as acetonitrile, triphenyl phosphine, pyridine or its derivatives (Fernández-Moreira et al, 2010; Bhuvaneswariet al, 2014). In addition, Re(I) diimine complexes are relativelyeasy to synthesize

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electron transfer. These properties have made them potentially useful as photocatalysts, sensors and detectors (Hawekeret al, 1986; Christ et al, 1992; MacQueen and Schanze, 1991). However, as with the Ru (II) diimine complexes, the efficiency of <sup>3</sup>MLCT emission depends on the <sup>3</sup>MLCT state being lower in energy than the ligand localised <sup>3</sup>IL state (Gonçalves and Frin, 2015; Kumar et al, 2010). Although most Re(I) diimine complexes emit from the <sup>3</sup>MLCT states, there have been instances where emission was observed from both <sup>3</sup>MLCT and <sup>3</sup>IL states (Lippard, 1983). In this work, rhenium(I) complexes of 1,4bis(4'-methyl-2,2'-bipyrid-4-yl)buta-1,3-diene and 1,4-bis(4'-methyl-2,2'-bipyrid-4-y1) benzeneligands, denoted as bbdb and bphb respectively, were synthesised, characterised, and investigated for the relative energies of the <sup>3</sup>MLCT and <sup>3</sup>IL states, and the presence of ligand-localized phosphorescence.

#### 2.0 MATERIALS AND METHODS

4,4'-dimethyl-2,2'-bipyridine (**dmb**), purchased from Reily Tar and Chemical Company was recrystallized from tetrahydrofuran. All other

How to cite this paper:Baba, A.I., Atiga, S., &Ocheni, A. (2018). Spectroscopic and electrochemical studies of two binuclear rhenium (I) complexes. *Confluence Journal of Pure and Applied Sciences (CJPAS)*, **2**(1), 1-10.

reagents were purchased as analytical grade from Aldrich and were used without further purification.

Redox potentials were obtained by cyclic voltammetry (using EG and G Princeton Applied Research (PAR) model 173 Potentiostat) and differential pulse polarography, FAB-MS were acquired using the Kratos Analytical (Manchester England) Concept 1-H mass spectrometer, luminescence and luminescence lifetime measurements were recorded using a SpexFluorolog equipped with a 450 W Xenon arc lamp and a cooled photomultiplier tube. Proton NMR spectra were recorded on GE200 spectrometer. Transient absorption spectra measurements were made at the Centre for Fast Kinetics Research, Austin, Texas.

# Synthesis of 1,4-bis(4'-methyl-2,2'-bipyrid-4yl)buta-1,3-diene (bbdb)

A mixture of 10g (0.054 moles) of 4,4'-dimethyl-2,2'-bipyridine, 11.53g (0.064 moles) of Nbromosuccinamide (NBS) and 1.1g of azoisobutyro-nitrile (AIBN) were refluxed in 200ml carbon tetrachloride on an oil bath for 3 hours (under nitrogen). The mixture was cooled to 40°C and the precipitated succinimide was filtered and washed with 80 mlof carbon tetrachloride. The crude halogenated intermediatewas dissolved in 250 ml of benzene containing 14.15g (0.054 moles) of triphenyl phosphine and the mixture was refluxed on an oil bath for 3 hours under  $N_2$ . The solution was cooled and filtered and the precipitate was washed with 120 ml of benzene and 100 ml of ether, in sequence, to remove unreacted **dmb**, halides and triphenyl phosphine. The phosphonium salt was dried in a vacuum at room temperature and used within 24 hours of drying.

1.71g (8.17 mmoles) of glyoxaltrimericdihydrate was added to 23.59g (0.049 moles) of the phosphonium salt dissolved in 200ml of absolute ethanol. The mixture was refluxed for 45 minutes before 5.29g (0.097 moles) of sodium methoxide was slowly and carefully added, and the refluxing was continued for 1 hour after which the mixture was cooled to room temperature, and the solvent removed by rotary evaporation. The dark brown solid was treated with 30 ml of 12M HCl and the protonated bipyridinium salts were precipitated from the solution by the addition of 150 ml of acetone. The precipitate was filtered, washed with 50 ml more acetone, dried and dissolved in water. The aqueous solution was filtered and the filtrate treated with saturated Na<sub>2</sub>CO<sub>3</sub> to precipitate the product, bbdb. After standing for 2 hours, the crude butadiene product was filtered, washed with water and dried and later purified by flash chromatography on silica gel (230-400 mesh) using CHCl<sub>3</sub>:EtOAc:Et<sub>3</sub>N (4:4:1) solvent mixtures as eluent. Overall yield was 20.30%. Melting point: 220°C. HRMS 390.18479 (deviation: 0.87 ppm, peaks: 390, 221, 170). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.62 (2H, d); 8.56 (2H, d); 8.43 (2H, s); 8.23 (2H, s); 7.29 (2H, d); 7.25 (2H, d of d); 7.15 (2H, d); 6.75 (2H, d of d); 2.43 (6H, s).

# Synthesis of 1,4-bis(4'-methyl-2,2'-bipyrid-4-yl)benzene, bphb

1.4g (2.75 mmol) of 1,4-bis(4'-methyl-2,2'-pyrid-4-yl)2-cyclohexenyl-5,6-dicarboxylic acid (earlier prepared in a different process) and 2.43g (5.50 mmol) Pb(OAC)<sub>4</sub> were dissolved in 2 ml of acetic acid under N<sub>2</sub>. The mixture was refluxed on an oil bath for 20 minutes after which 5 ml of dimethyl formamide was added from a syringe and the refluxing continued for an additional 3.5 hours. Refluxing was then discontinued and the mixture allowed to cool to room temperature before been poured into 50 ml of water. The resulting turbid solution was extracted with CHCl<sub>3</sub> which was later washed with saturated Na<sub>2</sub>CO<sub>3</sub> solution.

The CHCl<sub>3</sub> extract was rotovaped to 5 ml and purified of any unreacted diacid by column separation on silica gel (230-400 mesh) using chloroform (CHCl<sub>3</sub>), ethyl acetate (EtOAc) and triethyl amine (ET<sub>3</sub>N) in the ratio, CHCl<sub>3</sub>:EtOAc:Et<sub>3</sub>N (4:4:1) as eluent solvent. This reaction was tried many times with product yields ranging from 17-20%, not considering the unreacted diacid that was recovered by flushing the column with methanol. Melting point: 203°C. HRMS: 414.18 (deviation: 1.12 ppm, Peaks: 414.201). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.75 (2H, d); 8.71 (2H, s); 8.60 (2H, d); 8.30 (2H, s); 7.89 (4H, s); 7.60 (2H, d); 7.15 (2H, d); 2.42 (6H, s).

# Synthesis of{[(CO)<sub>3</sub>(CH<sub>3</sub>CN)Re]<sub>2</sub>(bphb)}(PF<sub>6</sub>)<sub>2</sub>

This was prepared using apublished method (Sahaiet al, 1989). Re(CO)<sub>5</sub>Cl (600 mg, 1.65 mmoles) was sonicated to dissolve in 100 ml MeOH and was poured into 80 ml refluxing solution of **bphb**(300 mg, 0.78 mmoles). The mixture was refluxed for additional 2 hours, cooled and the solution rotary evaporated to 30 ml and cooled for 25 mins at room temperature. The yellow precipitate,  $\{[(CO)_3(Cl)Re]_2(bphb)\}(PF_6)_2$ was collected on a minimum porosity fritted funnel, washed with 40 ml of diethyl ether and airdried. Yield (400 mg, 51.4%). FAB-MS: 1298.4 (M); 1153.4  $(M - PF_6)$ . The  $\{[(CO)_3(Cl)Re]_2(bphb)\}(PF_6)_2$  (400 mg, 0.40 mmoles) was refluxed with  $AgPF_{6}$  (300 mg) in 40 ml of CH<sub>3</sub>CN for 12 hours. The solution was cooled, filtered to remove precipitated AgCl and chromatographed on neutral alumina (ALCOA F20) using CH<sub>3</sub>CN. Product yield was quantitative.

#### Synthesis of

# {[(CO)<sub>3</sub>(CH<sub>3</sub>CN)Re]<sub>2</sub>(bbdb)}(PF<sub>6</sub>)<sub>2</sub>

The complex was prepared from  $[\text{Re}(\text{CO})_5\text{Cl}]$ (150 mg, 0.414 mmoles) and **bbdb**(65 mg, 0.165 mmoles) in a similar method to that used for preparing {[(CO)<sub>3</sub>(CH<sub>3</sub>CN)Re]<sub>2</sub>(bphb)}(PF<sub>6</sub>)<sub>2</sub>. The product yield was 52%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.94 (2H, d); 8.86 (2H, d); 8.53 (2H, s); 8.46 (2H, s); 7.77 (2H, d); 7.71 (2H, d of d); 7.56 (2H, d); 7.11 (2H, d of d); 2.63 (6H, s); 2.06 (6H, s): FAB-MS: 1303 (M); 1158 (M-PF<sub>6</sub>).



Structure of  $\{[(CO)_3(CH_3CN)Re]_2(bphb)\}(PF_6)_2$ 



Structure of  $\{[(CO)_3(CH_3CN)Re]_2(bbdb)\}(PF_6)_2$ 

#### **3.0 RESULTS AND DISCUSSION**

The products were characterised by FAB-MS, FT-IR, and <sup>1</sup>H-NMR. The FT-IR spectrum of the b b d b complex,  $\{[(CO)_3(CH_3CN)Re]_2(bbdb)\}(PF_6)_2$  exhibits typical C=O stretching peaks at 2036, 2021 and 1921 cm<sup>-1</sup>. However, the **bphb**complex, {[(CO)<sub>3</sub>(CH<sub>3</sub>CN)Re]<sub>2</sub>(bphb)}(PF<sub>6</sub>)<sub>2</sub> showed only two main peaks at 2033 and 1915 cm<sup>-1</sup>. The peak at 2033 cm<sup>-1</sup> is sharp while that around 1920 is broad. Rillema and co-workers (Wallendaelet al, 1990) reported similar behaviour for bimetallic complexes that were bridged by mebpy (1,2bis(4'-methyl(2,2'-)bipyridyl-4-yl)ethane, **bpm**(2,2'-bipyrimidine) and **bpp** (2,3-bis(2pyridyl)pyrazine. These complexes had two peaks compared to three peaks for the monometallic complexes. Such differences could be due to peak broadening and the presence of isomers in the bimetallic complex. Charged rhenium complexes have less electron density to back donate to the carbonyl bond, therefore increasing the CO bond strength and thus result in a shift in the stretching frequencies. (Nakamoto, 1986).

#### NMR Data

The <sup>1</sup>H-NMR spectrum obtained for  $\{[(CO)_3(CH_3CN)Re]_2(bbdb)\}(PF_6)_2$  show well resolved resonances that were due to the **bbdb** bridging ligand and the CH<sub>3</sub>CN ligands. As expected for the pure complex, the number of proton resonances and the splitting patterns were the same as in the **bbdb**ligand, plus additional resonance due to the CH<sub>3</sub>CN ligand. Compared to the bridging ligand, the proton resonances in the complex are shifted to lower field.

On the contrary, the spectrum obtained for  $\{[(CO)_3(CH_3CN)Re]_2(bphb)\}(PF_6)_2$  was poorly resolved and exhibited more complexity than the spectrum

# FAB-MS Data

Major peaks in the FAB-MS result from losses of PF-  $_{6}$ , CO and CH<sub>3</sub>CN groups. The complex, {[(CO)<sub>3</sub>(CH<sub>3</sub>CN)Re]<sub>2</sub>(bphb)}(PF<sub>6</sub>)<sub>2</sub>, with a molecular mass of 1298.42 has FAB-MS peaks at 1153.42 and 986.4 which are due to the loss of PF<sub>6</sub> and 6CO molecules respectively. The **bbdb**complex has a molecular mass of 1303 while FAB-MS showed peaks at 1158, 990.37 and 947.45, corresponding to the loss of PF<sub>6</sub>, 6CO and CH<sub>3</sub>CN groups respectively. No peak due to [Re(CO)<sub>3</sub>(CH<sub>3</sub>CN)]<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> was observed.

# Electrochemistry

Electrochemical data for the complexes are given in Table 1. The metal-centred one electron oxidation potential (Re(II/I)) is nearly the same for the two complexes. Oxidative cyclic voltammograms were irreversible. Irreversibility of the Re(II/I) waves have been ascribed to reactions with water and/or other impurities in the solvent (Sahai*et al*, 1989; Shaw and Schmehl, 1991; Tapol*et al*, 1990). The reductive cyclic voltammograms for these complexes consist of several overlapping waves. The first reductive wave is quasi-reversible and is assigned to the bridging-ligand based reduction.

#### Absorption and Luminescence properties

The spectroscopic properties of the complexes are given in Table 2. In room temperature solutions, the **bphb** and **bbdb** complexes have absorption maxima of 354nm and 388 nm respectively. Fig. 1 is the absorption spectrum of **bphb** ligand and its complex, while Fig. 2 is the absorption spectrum of the **bbdb** ligand and its complex. These values are within the absorption maxima for **bdvbb** and **dmb**Re (I) complexes as reported elsewhere (Shaw and Schmehl, 1991).

The emission of the **bphb** complex at room temperature (Fig. 3A) is structureless with a maximum at 556 nm. At 77 K, the spectrum exhibits some structure with a maximum at 514 nm (Fig. 3B). Its emission lifetimes at both room temperature (1.55 and 3.98  $\mu$ s) and 77 K (3.66 and 17.42  $\mu$ s) are biexponential. Multiexponential behaviour has also been observed in other complexes (Zipp*et al*, 1993) and may be due to the presence of multiple excited

states. The transient absorption spectrum has a maximum at 497 nm (Fig. 4) which is similar to that of the **dmb** and **bpy**complexes, both emitting solely from the <sup>3</sup>MLCT state. This similarity is suggestive that th e  $\{[(CO)_3(CH_3CN)Re]_2(bphb)\}(PF_6)_2 \text{ complex}$ emits mainly from the <sup>3</sup>MLCT. However, a timeresolved emission of this bphb dimer at 77 K which was taken at 0 s delay, Fig. 5A, after laser excitation was broad and featureless. At longer delays (30 µs) (Fig. 5B), the spectrum showed some structure and has a maximum at 510 nm. This strongly suggests that for this complex, the <sup>3</sup>MLCT and <sup>3</sup>IL states are close in energy and at 77 K emission is from both states.

The time-resolved phosphorescence spectrum of the **bphb**ligand taken at 77K (Fig.6) showed no structure. Absence of observed structured phosphorescence was a bit surprising, since its related hydrocarbon, *p*-terphenyl was reported to show some structure in frozen ethyl iodide: ether: ethanol: toluene (2:2:1:1) matrices (Marchetti and Kearns, 1967).

The room temperature emission spectrum of the **bbdb** complex has a maximum at 546 nm and appears to have some structure (Fig. 7A). The room temperature lifetime is low and biexponential (41 and 609 ns). Comparatively, the emission spectrum at 77 K (Fig. 7B) has the same maximum, shows more structure and the lifetimes increase to 3.66 and 18.9  $\mu$ s. Transient absorption spectrum exhibits strong absorption beyond 580 nm (Fig. 8). Such strong absorption in the red has being observed for [(CO)<sub>3</sub> (CH<sub>3</sub>CN) Re]<sub>2</sub>(bdvbb) (PF<sub>6</sub>)<sub>2</sub> and has been assigned as the <sup>3</sup>IL state (Jones *et al*, 1992; Watanabe and Honda, 1982).

The ligand **bbdb** does not luminesce in room temperature solutions. At 77 K, it shows fluorescence but no structured phosphorescence (Fig. 9) even in the presence of 10% ethyl iodide. A possible explanation for this is that the ligand undergoes isomerisation from a*trans-trans* to a *cis-cis* and/or *cis-trans* conformation prior to intercolation in the frozen matrix. Change in planarity from *ortho*to *para*-substituted biphenyls is known to shift the energy of observed phosphorescence to the blue. Similar change in conformation from the planar *trans-trans* isomer in **bbdb** ligand would be expected to result in a blue shift in the phosphorescence peak which may then overlap with the fluorescence peaks (Marchetti and Kearns, 1967).

Based on (1) short room temperature emission lifetime, (2) low emission quantum yield, (3) structured room temperature emission and, (4) strong transient absorption in the red, the <sup>3</sup>IL state is expected to be lower than the <sup>3</sup>MLCT state for  $[(CO)_3(CH_3CN)Re]_2(bbdb)(PF_6)_2$ . However, for  $[(CO)_3(CH_3CN)Re]_2(bphb)(PF_6)_2$  the <sup>3</sup>MLCT state is lower in energy than the <sup>3</sup>IL state at room temperature. Both states may be close in energy at 77 K.

From the spectroscopic properties of the **bbdb** complex, it may be expected that if the <sup>3</sup>IL state is lower in energy than the <sup>3</sup>MLCT state the emission maximum should be at 688 nm. Quite surprisingly, the emission maximum lies further to the blue, although a careful look at the emission spectra

both at room temperature and 77 K shows a shoulder at about 700 nm. Also, the time-resolved emission spectrum obtained for this complex at 77 K (using 0 delay and 20  $\mu$ s), Fig. 10, does not show structured phosphorescence but has shoulders around 700 nm. Similar shoulders were also observed for the **bbdb**ligand. Based on these results, it is possible that the emission peak around 700 nm may be due to the <sup>3</sup>IL state.

# 4.0 CONCLUSION

Re (I) complexes with <sup>3</sup>IL state lower in energy than the <sup>3</sup>MLCT state should exhibit phosphorescence and the bridging ligand would be expected to show structured phosphorescence. Our results indicate that the **bphb** complex shows phosphorescence at 77 K but the ligand itself does not show structured phosphorescence. Based on its luminescence characteristics, the **bbdb** complex was expected to exhibit ligand localized phosphorescence but its absence is probably due to the bridging ligand flexibility.

Table 1: Reduction potentials of compounds examined in CH<sub>3</sub>CN

	Oxidation	Reduction			
Compound	E1, V	E <sub>2</sub> , V	E3, V	E4, V	
{[(CO) <sub>3</sub> (CH <sub>3</sub> CN)Re] <sub>2</sub> (bphb)} <sup>2+</sup>	1.80(irr)	-1.26			
${[(CO)_3(CH_3CN)Re]_2(bbdb)}^{2+}$	1.79(irr)	-0.90	-1.42(irr)	-1.20(irr)	

Table 2: Spectroscopic properties of the complexes

Compound	λ <sub>max</sub> , nm (log ε)	λ <sub>max</sub> , nm (298K)	λ <sub>max</sub> , nm (77K)	Φ <sub>em</sub> (298K)	τ <sub>em</sub> , ns (298K)	τ <sub>em</sub> , ns (77K)	n <sub>ISC</sub> k <sub>r</sub>
$\{[(CO)_3(CH_3CN)Re]_2(bphb)\}^{2+}$	354 (4.46)	556	514 560	0.267	1550 3980	3870 17420	17X10 <sup>4</sup> 10X10 <sup>4</sup>
$\{[(CO)_3(CH_3CN)Re]_2(bbdb)\}^{2+}$	388 (4.65)	517	525 541	<10 <sup>-3</sup>	41 609	3660 18900	1.7X10 <sup>4</sup> 1149





 $[(CO)_3(CH_3CN)Re]_2(bphb)]^{2+}$  in acetonitrile using a quartz cell



**Figure 2:** Room temperature absorption spectra of (A) bbdb in MeOH and (B)

 $[(CO)_3(CH_3CN)Re]_2(bbdb)](PF_6)_2$  in acetonitrile using a quartz cell



Figure 3: Emission spectra of  $[(CO)_3(CH_3CN)Re]_2(bphb)(PF_6)_2$  (A) at room temperature in deaerated acetonitrile and

(B) at 77K in EtOH:MeOH (4:1) matrix



**Figure 4:** Transient Absorption spectrum of [(CO)<sub>3</sub>(CH<sub>3</sub>CN)Re]<sub>2</sub>(bphb)(PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>CN at room temperature at various times (in seconds) after excitation at 308 nm



#### Wavelength, nm

Figure 5: Time-resolved emission spectra of  $[(CO)_3(CH_3CN)Re]_2(bphb)(PF_6)_2$  in EtOH:MeOH (4:1) at 77K with delay of 0 s, gate = 2µs for (A) and delay = 30µs, gate = 20µs



Figure 6: Time-resolved emission spectra of bphb in EtOH:MeOH (4:1) containing 10% EtI at 77K with delay of 2 s, gate = 1 ms for (A) and with delay =  $5\mu$ s, gate = 1 ms



Figure 7: Emission spectra of  $[(CO)_3(CH_3CN)Re]_2(bbdb)(PF_6)_2$  (A) at room temperature in deaerated acetonitrile and (B) at 77K in EtOH:MeOH (4:1) matrix



Figure 8: Transient Absorption spectrum of [(CO)<sub>3</sub>(CH<sub>3</sub>CN)Re]<sub>2</sub>(bbdb)(PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>CN at room temperature at various times (in seconds) after excitation at 308 nm



# Figure 9: Time-resolved emission spectra of bbdb in EtOH:MeOH (4:1) containing 10% EtI at 77K with delay of 2 s, gate = 1 ms for (A) and with delay = $50\mu$ s, gate = 1 ms



Figure 10: Time-resolved emission spectra of  $[(CO)_3(CH_3CN)Re]_2(bbdb)(PF_6)_2$  in EtOH:MeOH (4:1) at 77K with delay of 2  $\mu$ s, gate = 1 ms for (A) and with delay =  $50\mu$ s, gate = 1 ms

#### 5.0 ACKNOWLEDGEMENT

Aaron Baba thanks the donors of the Petroleum Research Fund administered by the American Chemical Society for financial assistance in support of this research. He equally acknowledges Ray Hoff of Tulane University, USA, for technical assistance.

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