Synthesis of asymmetric supramolecular compounds using a Ni(0) catalysed homo-coupling approach

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Received 13th October 2008, Accepted 4th December 2008
First published as an Advance Article on the web 11th February 2009
DOI: 10.1039/b817896h

The synthesis and characterisation of a series of dinuclear ruthenium and osmium polypyridyl metal complexes based on the bridging ligands [5-(5′-bipyridin-2’,2’-yl)-3-(pyridin-2-yl)]-1,2,4-triazole (Hpytr-bipy), 2,2′-bis(pyridin-2’-yl)-5,5′-bis(pyridin-3’-yl) (bipy-bipy) and 5,5′-bis(pyridin-2’-yl)-3,3′-bis(1,2,4-triazole) (Hpytr-Hpytr) are reported. The dinuclear complexes have been synthesised via a Ni(0) catalysed cross-coupling reaction from brominated precursors. With this approach a mixture of three products is obtained, which are separated by chromatographic methods. The compounds obtained are characterised by elemental analysis, 1H NMR, absorption and emission spectroscopy. The synthetic approach developed offers a new route to asymmetric multinuclear supramolecular structures that is complimentary to the complexes as ligands/complexes as metal approaches.

Introduction

The development of supramolecular chemistry based on ruthenium and, increasingly, osmium, polypyridyl metal complexes witnessed over the past four decades has led to the definition of molecular entities useful for the construction of multifunctional systems. Their robust tuneable photophysical, photochemical and electrochemical properties constitute the primary basis of interest in these complexes and have led to widespread development and investigation into their application as artificial antenna systems, charge separation devices for photochemical solar energy conversion, and molecular electronics.1 The development of such applications is greatly dependent on the availability of a synthetic approach capable of delivering organised structures of metal-based molecular components with specific supramolecular properties.2 The challenges encountered in the preparation of pure, structurally well-defined metal complexes increases with the size of the structure and although the complexes as metals/complexes as ligands approaches have proven remarkably effective there remains a need for the development of alternative synthetic approaches.3

We are at present interested in intramolecular processes in asymmetric dinuclear metal complexes, containing two M(bipy) units, where M is Ru(II) or Os(II), incorporating a bridging ligand consisting of two different chelating moieties, one bipy and one triazole based, as shown in Fig. 1.

In this contribution we report the syntheses, separation and characterisation of the target dinuclear complexes using a homo-coupling reaction. The decision to utilise a nickel catalysed homogeneous coupling approach for the synthesis of asymmetric dinuclear complexes seems, in the first instance, counter-intuitive. The results obtained show, however, that such an approach can prove to be fruitful provided that the mixture of products obtained can be separated in a facile manner. Coupling was carried out employing the ruthenium and osmium precursors [M(bipy)](bipy-Br)]+ (1a/1b), [M(bipy)(pytr-Br)]+ 2a/2b and their selectively deuteriated analogues 1d and 2d containing bromo-substituted ligands. With this method binuclear complexes of the types [M(bipy)(bipy-M(bipy))]+ (3, 4), [M(bipy)(pytr-pytr)M(bipy)]+ (5, 6), and [M(bipy)(pytr-bipy)M(bipy)]1+ (7, 8, 9) the target complexes, where (bipy-bipy) is 2,2′-bis(pyridin-2’-yl)-5,5′-bis(pyridin-3’-yl), (Hpytr-Hpytr) is 5,5′-bis(pyridin-2’-yl)-3,3′-bis(1,2,4-triazole) and (Hpytr-bipy) is [5-(5′-bipyridin-2’,2’-yl)-3-(pyridin-2-yl)]-1,2,4-triazole and M is either Ru(II) or Os(II) were isolated (Fig. 2).

The deuteriated ruthenium isopologues 3d, 5d and 7d are reported also. All compounds are characterised using NMR, UV/Vis and emission spectroscopy.

Experimental

Materials

All solvents used for spectroscopy were of spectroscopic grade (Sigma-Aldrich). All other reagents were of HPLC or Analar grade. cis-[Ru(bipy)Cl2]2H2O, cis-[Os(bipy)Cl2] and cis-[Ru(d4(bipy)Cl2]2H2O and the ligands 5-bromo-1,2,4-triazole (HBrpytr), and 5-bromo-2,2′-bipyridyl (Brbipy) and complexes 2a, 2b and 2d were prepared by methods reported previously.
Ni(0) coupling reactions using 1a and 2a as precursors

\[ \text{[Ru(bipy)](pyr-trpy)Ru(bipy)\cdot PF}_6 \] (5. \[ \text{[Ru(bipy)](pyr-trpy)Ru(bipy)\cdot PF}_6 \] (7) and \[ \text{[Ru(bipy)](bipy-bipy)Ru(bipy)\cdot PF}_6 \] (3). 2.29 g (8.72 mmol) of triphenylphosphine and 10 cm³ of dry DMF were added to 514.51 mg (2.17 mmol) of nickel(II) chloride. The blue mixture was stirred for 30 min under N₂. 142 mg (2.17 mmol) of zinc powder was added and the mixture was stirred for 1 h, at which stage the solution was brown.

842 mg (1.09 mmol) of \([\text{Ru(bipy)(Brpy)]\cdot PF}_6\) (1a) and 1.02 g (1.09 mmol) of \([\text{Ru(bipy)(Brpy)]\cdot PF}_6\) (2a) were added to this solution. The mixture was heated at 95 °C for 6 h after which the mixture was diluted with 30 cm³ of acetonitrile, filtered and flash precipitated from diethyl ether with rapid stirring. The crude product was isolated by filtration. Crude yield: 1.12 g. The crude product was then purified by column chromatography on silica gel with acetonitrile–saturated aqueous NaNO₃ solution (7 : 5 v/v) to yield three fractions which were identified by ESI-MS. The third fraction contained a mixture of the desired products.

This fraction was further purified by column chromatography on Sephadex-Sp C-25 with NaCl solution (0.05–0.1 M for first band, 0.17–0.25 M for second band, 0.4–0.45 M for third band). Three fractions were obtained with the first fraction being identified as \([\text{Ru(bipy)](pyr-trpy)Ru(bipy)\cdot PF}_6\) (5) the second fraction as \([\text{Ru(bipy)](pyr-trpy)Ru(bipy)\cdot PF}_6\) (7) and the final fraction as \([\text{Ru(bipy)](bipy-bipy)Ru(bipy)\cdot PF}_6\) (3). On occasion the third band required further purification on a silica column with acetonitrile–water (4 : 1, v/v) with 0.05 M KNO₃ buffer as eluent. The solutions obtained were reduced in vacuo and the product precipitated by the addition of aqueous NH₄PF₆. The products were collected by filtration and washed with diethyl ether and recrystallised from methanol–water (1 : 1).

**Fraction 1.** \([\text{Ru(bipy)](pyr-trpy)Ru(bipy)\cdot PF}_6\) (5. Isolated yield: 8.1%. \(^1\)H NMR (CD, CN, 298 K) \(\delta 8.42 (8H, m), 8.06 (dd, 2H), 7.83–8.02 (m, 14H), 7.78 (m, 4H), 7.27–7.40 (m, 5H), 7.10 (dd, 2H). Elem. anal. Ru₃C₂H₁₀N₁₂P₂F₁₈·5H₂O: Calc: C 43.37%, H 3.34%, N 14.99%. Found: C 42.84%, H 3.38%, N 14.94%. ESI-MS [M – 2PF₆ + H⁺]⁺ m/z = 556.7. \([\text{M – 2PF}_6 + H^+]^{+}\) m/z = 556.7.

**Fraction 2.** \([\text{Ru(bipy)](pyr-trpy)Ru(bipy)\cdot PF}_6\) (5. 2NaNO₃, (7). Isolated yield: 7.6%. \(^1\)H NMR (CD, CN, 298 K) \(\delta 8.72–8.48 (m, 12H), 8.29 (d, 1H), 8.11–7.95 (m, 10H), 7.84–7.67 (m, 9H), 7.55 (dd, 1H), 7.48–7.37 (m, 9H), 7.24 (dd, 1H). Elem. anal. Ru₃C₂H₁₀N₁₂P₂F₁₈·2NaNO₃: Calc: C 39.53%, H 2.48%, N 12.94%. Found: C 38.38%, H 2.44%, N 12.46%.

**Fraction 3.** \([\text{Ru(bipy)](bipy-bipy)Ru(bipy)\cdot PF}_6\) (5. 2KNO₃, (3). Isolated yield: 8.0%. \(^1\)H NMR (CD, CN, 298 K) \(\delta 8.46–8.59 (m, 12H), 7.78 (d, 2H), 7.70 (d, 4H), 7.43–7.35 (m, 10H). Elem. anal. Ru₃C₂H₁₀N₁₂P₂F₁₈·2KNO₃: Calc: C 37.54%, H 2.40%, N 10.22%. Found: C 37.43%, H 2.97%, N 9.60%.

Ni(0) coupling reactions using 1d and 2d as precursors

\[ \text{[Ru(d-bipy)](pyr-trpy)Ru(d-bipy)\cdot PF}_6 \] (5d. \[ \text{[Ru(d-bipy)](pyr-trpy)Ru(d-bipy)\cdot PF}_6 \] (7d and \[ \text{[Ru(d-bipy)](bipy-bipy)Ru(d-bipy)\cdot PF}_6 \] (3d were obtained from \([\text{Ru(d-bipy)](Brpy)]\cdot PF}_6\) (0.16 mmol) and \([\text{Ru(d-bipy)](Brpy)]\cdot PF}_6\).

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**Fig. 2** Structures of the dinuclear complexes and their precursor complexes. The compounds 1d, 2d, 3d, 5d and 7d were prepared using [Ru(d-bipy)]Cl₂·2H₂O.

**Syntheses**

\[ \text{[Ru(bipy)](Brbipy)\cdot PF}_6\] (1a). 185 mg (0.36 mmol) of cis-[Ru(bipy)]Cl₂·2H₂O was added to 127 mg (0.54 mmol) Brbipy in 50 cm³ of a 1 : 1 water–ethanol mixture. The solution was heated at reflux overnight turning the reaction mixture from deep purple to clear red. The solution was reduced in vacuo and the product precipitated upon the addition of aqueous NH₄PF₆. The crude product was collected by filtration and washed with diethyl ether.

The complex was purified by column chromatography on neutral alumina with acetonitrile as eluent. The product was obtained upon evaporation of the solvent and recrystallised from methanol–water (1 : 1). Yield: 269 mg (0.29 mmol), 76%. \(^1\)H NMR (CD, CN, 298 K) \(\delta 8.50 (5H, m), 8.38 (1H, s), 8.24 (1H, dd), 8.05 (5H, m), 7.80 (2H, d), 7.74 (1H, d), 7.70 (1H, t), 7.65 (1H, dd), 7.40 (6H, m). Elem. anal. C₅₆H₃₂Ni₆Ru₃P₆F₁₈·H₂O: Calc: C 38.38%, H 2.45%, N 8.95%. Found: C 38.49%, H 2.44%, N 8.71%. ESI-MS [M – 2PF₆ + H⁺]⁺ m/z = 324.

\[ \text{[Ru(d-bipy)](Brbipy)\cdot PF}_6 \] (1d) was prepared as reported for 1a above. Yield: 271 mg, 0.24 mmol, 67.6%. \(^1\)H NMR (CD, CN, 298 K) \(\delta 8.51 (H3’, d), 8.41 (H4’, d), 8.25 (H3, d), 8.08 (dd, H4), 7.77 (H6’, s), 7.73 (H6, d), 7.43. (H5, dd).

\[ \text{[Os(bipy)](Brbipy)\cdot PF}_6 \] (1b). This complex was obtained from cis-[Os(bipy)Cl₂] as for 2a. Yield: 135 mg (0.13 mmol), 68%. \(^1\)H NMR (CD, CN, 298 K) \(\delta 8.52–8.5 (m, 5H), 8.4 (d, 1H), 8.05 (dd, 1H), 7.92–7.87 (m, 5H), 7.72 (m, 2H), 7.66–7.57 (m, 4H), 7.36–7.32 (m, 5H). Elem. anal. C₃₀H₂₀Ni₆Os₃P₆F₁₈: Calc: C 35.05%, H 2.23%, N 8.18%. Found: C 35.05%, H 2.19%, N 7.93%.
(0.16 mmol) using the method described above. Crude yield: 0.174 g (95%).

**Fraction 1.** [Ru(d4-bipy)(pytr-pytr)Ru(d4-bipy)](PF6)6 (5d). Yield after purification: 6.0%. 1H NMR (CDCl3, 298 K) δ 8.12 (dd, 2H), 7.89 (dd, 2H), 7.46 (d, 2H), 7.10 (dd, 2H).

**Fraction 2.** [Ru(d4-bipy)(pytr-pytr)Ru(d4-bipy)](PF6)6 (7d). Yield after purification: 5.4%. 1H NMR (CDCl3, 298 K) δ 8.71–8.65 (m, 2H), 8.54 (m, 1H), 8.31 (d, 1H), 8.07–8.12 (m, 2H), 7.97 (dd, 1H), 7.79 (d, 1H), 7.58 (d, 1H), 7.45 (t, 1H), 7.25 (dd, 1H).

**Fraction 3.** [Ru(d4-bipy)(bisbipy)Ru(d4-bipy)](PF6)6 (3d). Yield after purification: 5.8%. 1H NMR (CDCl3, 298 K) δ 8.62 (dd, 4H), 8.07 (dd, 4H), 7.73 (d, 4H), 7.43 (dd, 2H).

Ni(0) coupling reactions using 1a and 2b as precursors

[Ru(bipy)(pytr-pytr)Os(bipy)](PF6)6 (8) [Os(bipy)(bipy-bipy)-Os(bipy)](PF6)6 (4) and [Ru(bipy)(pytr-pytr)Ru(bipy)](PF6)6 (5) were prepared from [Ru(Bpppy)(bipy)](PF6)6 (1a) (0.71 mmol) and [Os(Br(bipy))](PF6)6 (2b) (0.71 mmol) using the method described above. Crude yield: 0.82 g (95%).

**Fraction 1.** This compound was identified (vide supra) as [Ru(bipy)(pytr-pytr)Ru(bipy)](PF6)6 (5). Yield after purification: 8.2%.

**Fraction 2.** [Ru(bipy)(pytr-pytr)Os(bipy)](PF6)6-NaNO3 (8). Yield after purification: 8.5%. 1H NMR (CDCl3, 298 K) δ 8.58–8.46 (m, 12H), 7.95–7.75 (m, 12H), 7.71–7.52 (m, 8H, 7.62 (d, 4H), 7.39–7.28 (m, 10H). Elem. anal. RuOsC9H6N6P4F6NaNO3:

**Fraction 3.** [Os(bipy)(bipy-bipy)Os(bipy)](PF6)6-KNO3 (4). Yield after purification: 7.9%. 1H NMR (CDCl3, 298 K) δ 8.58–8.46 (m, 12H), 7.95–7.75 (m, 12H), 7.71–7.52 (m, 8H, 7.62 (d, 4H), 7.39–7.28 (m, 10H). Elem. anal. OsC9H6N6P4F6KNO3:
Calc: C 36.29%, H 2.31%, N 9.17%. Found: C 35.85%, H 2.46%, N 8.88%.

Ni(0) coupling reactions using 1b and 2a as precursors

[Os(bipy)(pytr-pytr)Ru(bipy)](PF6)6 (9) [Ru(bipy)(bipy-bipy)-Ru(bipy)](PF6)6 (3) and [Os(bipy)(pytr-pytr)Os(bipy)](PF6)6 (6) were prepared from [OsBr(bpy)](PF6)6 (1b) (0.7 mmol) and [Ru(bipy)](PF6)6 (2a) (0.7 mmol) using the method described above. Crude yield: 0.81 g (95%).

**Fraction 1.** [Os(bipy)(pytr-pytr)Os(bipy)](PF6)6-H2O (6). Yield after purification: 7.9%. 1H NMR (CDCl3, 298 K) δ 8.44–8.36 (m, 8H), 8.06 (dd, 2H), 7.81–7.62 (m 16H), 7.39 (d, 2H), 7.27–7.20 (m, 8H), 7.16 (t, 2H), 7.01 (t, 2H). Elem. anal. OsC9H6N6P4F6H2O: Calc: C 40.50%, H 2.62%, N 14.00%. Found: C 40.59%, H 2.51%, N 13.57%.

**Fraction 2.** [Os(bipy)(pytr-pytr)Ru(bipy)](PF6)6 NaNO3 (9). Yield after purification: 8.4%. 1H NMR (CDCl3, 298 K) δ 8.60–8.43 (m, 11H), 8.14–8.03 (m, 6H), 7.97 (t, 1H), 7.89–7.77 (m, 12H), 7.61 (d, 1H), 7.52 (d, 1H), 7.42–7.24 (m, 10H), 7.08 (dd, 1H). Elem. anal. RuOsC9H6N6P4F6NaNO3: Calc: C 39.44%, H 2.47%, N 12.11%. Found: C 38.91%, H 2.43%, N 12.44%, ESI-MS [M – 3PF6]1+, m/z = 405.

**Fraction 3.** This material was identified as [Ru(bipy)2(bipy-bipy)Ru(bipy)](PF6)6 (3). Yield after purification: 7.9%.

**Physical measurements**

1H NMR spectra were recorded on a Bruker (AC) (400 MHz) NMR spectrometer. All measurements were carried out in CDCl3 for ligands and in d1-acetonitrile for complexes. Peak positions are relative to residual solvent peaks. UV/vis absorption spectra were recorded on a JASCO 570 UV/Vis-NIR or a JASCO 630 UV/Vis spectrophotometer with 1 cm pathlength quartz cells. Absorption maxima are ±2 nm: molar absorptivities are ±10%. Emission spectra were recorded at 450 nm at 278 K in spectroscopic grade solvents using a JASCO-7200 spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 detector. Emission lifetime measurements were carried out using Time Correlated Single Photon Counting (Edinburgh Analytical Instruments) in a T setting, consisting of a n9000 (N2 filled) flashlamp, J-yA monochromators, a Single Photon Photomultiplier Detection System, model S 300 detector, with a Norland N5000 MCA card. The F900 Program, (Version 5.13) is used for data processes, with the quality of its determined by examination of the χ2 and residual plots of the fitted functions. Lifetimes were recorded in aerated acetonitrile and are ±10 ns. Mass spectra were recorded using a Bruker-EsquireLC_00050 using electrospray ionisation using a cap-exit voltage of 167 V. Spectra were recorded in the scan range of 50–2200 m/z with an acquisition time of between 300 and 900 μs and a potential of between 30 and 70 V. Each spectrum was recorded by the summation of 20 scans. Elemental analysis was carried out at the Microanalytical Laboratory at University College Dublin.

**Results and discussion**

**Synthetic aspects**

The synthesis of large supramolecular assemblies is by no means straightforward, especially when the desired product is heteronuclear in nature and is based upon an asymmetric bridging ligand such as the bipyridine-triazole based ligand shown in Fig. 1. When such ligands, which can be prepared without great difficulty, are reacted directly with M(bipy)3-type precursor complexes, a range of products may be expected. Triazole based systems, in addition, two positional coordination isomers can be expected also, since the metal ions may coordinate at the N2 or the N4 atom of the triazole ring. For example, direct reaction of Hpytr-Hpytr to form dinuclear compounds leads to the formation of up to eight isomers.9 However, despite repeated attempts to proceed via this route using a range of precursors, catalysts and conditions, the target products were not obtained, possibly because of the electronic properties of the triazole moiety. However, it we demonstrated previously that with Ni(0) as a catalyst a homogenous cross-coupling of triazole containing precursors can be achieved.10,20 It was, therefore, decided that this route would be pursued. The M(bipy)3-type precursor complexes 1 and 2 (Fig. 2).
were used as bromo-precursors. Importantly, such compounds are readily accessible. The results obtained show that the bromine functional group allows for efficient coupling of the mononuclear complexes using this Ni(0) catalysed reaction. Furthermore, the presence of the bromine substituent at the 3' position of the triazole ring results in the preferential formation of the N2 isomer (>95%) of complexes 1a, 1b and 1d. This reduces the number of isomers that may be obtained for the mononuclear precursors and hence the dinuclear complexes formed in subsequent reactions. One disadvantage of this method is that, since the Ni(0) catalysed coupling reaction is in essence a homogeneous cross-coupling reaction, three different compounds will be obtained each containing a different bridging ligand as shown in Fig. 3. As outlined in the Experimental section the compounds obtained may be separated using silica and Sephadex based column chromatography based on their respective charges with the dicationic complex as the first fraction, the target tricationic complex as the second fraction, and finally the tetracationic complex.

In general yields after purification were moderate, with ruthenium and osmium dinuclear complexes being obtained in approximately 5–8.5% isolated yield with respect to the crude yield under non-optimised conditions. Considering that three different products are formed the expected statistical yield for each product will be about 33% assuming that the reactivity of both reaction components is similar. A similar synthetic approach has been reported by Scandola and co-workers who isolated one of the three possible products.

The effect of variation of the concentration of the reactants on the reaction product distribution was investigated to assess the reactivity of the two reaction partners 1a and 2a as shown in Table 1. The data obtained indicate that by increasing the molar equivalents of precursor complex [Ru(bipy)₂(bipy-bipy)Ru(bipy)₂](PF₆)₄ (3) remain the same, while a decrease in the percentage yield of complex 5, [Ru(bipy)₂(pytr-pytr)Ru(bipy)₂](PF₆)₄, is observed. When the ratio of reactants is reversed the yield of compound 3 is reduced while that of the others is maintained.

These results indicate that the percentage yield of one of the dinuclear products may be reduced significantly by control of the concentration of the precursor complexes, which simplifies the purification process. These results furthermore indicate that the reactivity of the reactants used is similar.

**'H NMR Spectroscopy**

The 'H NMR data obtained for all compounds are listed in the Experimental section. The 'H NMR spectra of the asymmetric compound [Ru(bipy)₂(pytr-bipy)Ru(bipy)₂]³⁺ (7), and its d₅-bipy isotopologue 7d are shown in Fig. 4.

The interpretation of the resonances observed is made by comparison with related compounds, COSY and deuteriation of the bipy ligands. Overall the results obtained for the bipy ligands are as expected² and are not considered further. The spectra obtained for the asymmetric compounds are more complex than those of the symmetric dinuclear complexes. However, as shown in Fig. 4, the spectra can be simplified considerably by preparing the partly deuteriated complexes. Using the spectra obtained for these deuteriated compounds the 'H NMR absorptions of the bridging ligand can be determined accurately (Fig. 5).

![Fig. 3](image-url)  
**Fig. 3** Synthetic approach used for the synthesis of the dinuclear complexes.

![Fig. 4](image-url)  
**Fig. 4** 'H NMR spectra of 7 (top) and 7d (bottom) in d₆-acetonitrile.

<table>
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<th>Precursor</th>
<th>Molar ratio</th>
<th>Yield 7</th>
<th>Yield 3</th>
<th>Yield 5</th>
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<tr>
<td>1a/2a</td>
<td>1 : 1</td>
<td>7.6% (92 mg)</td>
<td>8.0% (96 mg)</td>
<td>8.1% (97 mg)</td>
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<tr>
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<td>7.6% (14 mg)</td>
<td>2.4% (4.5 mg)</td>
<td>9.1% (16 mg)</td>
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Table 1  Effect of ratio of reactants on isolated yields
Fig. 5 ¹H NMR spectroscopic data for bridging ligands in the dinuclear complexes.

The ¹H NMR spectra support the formation of the dinuclear compounds. In addition, the utilisation of deuteriated bipy ligands facilitates the full assignment of the bridging ligand ¹H NMR absorption bands.

Electronic properties

Electronic absorption and emission data for all complexes are presented in Table 2. All complexes exhibit absorption and emission properties which are characteristic of Ru(II) and Os(II) based polypyridyl complexes with triazole and/or bipyridyl bridging ligands (Fig. 7). ¹ The characteristic dπ–π* metal to ligand charge transfer (¹MLCT) absorption bands are observed in the visible region (350–520 nm). For the bis-1,2,4-triazolato containing complex 5 the ¹MLCT absorption bands are red-shifted compared with those complexes containing one (7) or no (3) 1,2,4-triazolato units due to the increased σ-donor capacity of this moiety. Similar spectral features are observed for the corresponding Os(II) complexes (4, 6 and 8). However additional absorption bands are observed in the 500–700 nm region characteristic of ³MLCT absorption bands typical of Os(II) polypyridyl compounds.

All complexes exhibit the expected ³MLCT based luminescence at room temperature in acetonitrile solution (Table 2 and Fig. 7). As observed for the absorption spectra there is a general shift to lower energy with increasing number of σ-donor triazolato moieties. For the heteronuclear complexes, 8 and 9, emission is observed only from the osmium centre. This indicates that in the excited state interaction between the two metal centres is significant. At this stage it is however not possible to identify the ligand localisation of the emitting ³MLCT state definitively. For the compounds based either on the Hpytr-Hpytr bridging ligand the emissive ³MLCT state is most probably based on peripheral bipy ligands. However for the bipy-pytr and bipy-bipy bridged complexes the situation is less clear. In these compounds the emitting state may be based on the bridging ligand or on the peripheral bipyridyl ligands.

Table 2  Electronic properties of dinuclear complexes

<table>
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<th>λmax(abs)/nm (10⁻⁴c/M⁻¹cm⁻¹)</th>
<th>λmax(em)/nm (τ/μs)</th>
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<tr>
<td>3</td>
<td>440 (2.53)</td>
<td>663 (215)</td>
</tr>
<tr>
<td>4</td>
<td>463 (2.57), 625 (0.47)</td>
<td>792 (85)</td>
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<tr>
<td>5</td>
<td>478 (1.90)</td>
<td>686 (62)</td>
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<tr>
<td>6</td>
<td>496 (2.67), 652 (0.61)</td>
<td>811 (15)</td>
</tr>
<tr>
<td>7</td>
<td>447 (1.76)</td>
<td>668 (80)</td>
</tr>
<tr>
<td>8</td>
<td>445 (1.23), 622 (0.16)</td>
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<td>9</td>
<td>456 (1.68), 501 (1.18)</td>
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<td>[Os(bipy)]³⁺</td>
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<td>732 (60)</td>
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Fig. 6 UV/Vis absorption spectra of [(bipy)₂Ru(bis-bipy)Ru(bipy)]²⁺ (3) (solid line), [(bipy)₂Ru(pytr-pytr)Ru(bipy)]²⁺ (5) (dashed line) and [(bipy)₂Ru(pytr-bipy)Ru(bipy)]³⁺ (7) (dotted line) in acetonitrile. Spectral intensities were adjusted for comparison.

Fig. 7 Emission spectra of compounds 7–9 in CH₃CN. Solutions were isoabsorptive at the wavelength of excitation (450 nm). Counter-anion of complexes 7–9 is PF₆⁻.
Conclusions

The results reported in this study show that homogeneous coupling technologies can facilitate direct access to asymmetric bimetallic compounds which cannot be obtained in other ways. Because of the homogeneous nature of this approach, three compounds are obtained from a single reaction: the target compound with the asymmetric bridging ligand, and two reference compounds based on the symmetric analogues. In this way a series of related compounds can be made where not only the nature of the bridging ligand, but also that of the two metal centres attached can be changed systematically. It is also important to note that in this manner new bridging ligands can be prepared in situ. To the best of our knowledge the bpy-bpy, or 2,2′,5′,5″,2″′-quaterpyridine, and Hpytr-bpy ligands have not been prepared before, while for the Hpytr-Hpytr bridging ligand pure compounds can only be obtained by this synthetic approach. A number of related quaterpyridine ligands such as 2,2′,4′,4″-quaterpyridine and 2,2′,4′,4″-quaterpyridine have appeared in the literature.3 Our interest in these compounds is aimed at the investigation of the electronic properties and interaction between metal centres in dinuclear assemblies, both in the ground and excited state. With the compounds presented here, a systematic investigation of these supramolecular aspects as a function of the HOMO and LUMO properties of the bridge and those of the metal centres will be carried out. Importantly the distance between the metal centres in the compounds remains the same but the electronic properties of the bridge are very different. Further investigation of the intramolecular interaction of these dinuclear compounds in the excited state using emission and resonance Raman spectroscopy and in the ground state by applying electrochemical and spectro-electrochemical techniques, will be reported in due course.

Acknowledgements

The authors thank the Irish Research Council (IRCSET, L. C.) the Netherlands Organisation for Scientific Research (NWO-vidi, W. R. B.) and Science Foundation Ireland (Grant 06/RFP/029) (Lynda Cassidy) for supporting this work.

Notes and references

8 Y. Q. Fang and G. S. Hanan, Synlett, 2003, 6, 852.