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Bipyridine–porphyrin conjugates with a conjugated connection†

Jacinda L. Allwood,[a] Anthony K. Burrell,*[a] David L. Officer,*[a] Sonya M. Scott,[a] Kirstie Y. Wild[a] and Keith C. Gordon[b]

[a] *IFS-Chemistry, Massey University, Private Bag 11222, Palmerston North, New Zealand. E-mail: a.k.burrell@massey.ac.nz*

[b] *Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand*

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A bisporphyrin substituted bipyridine ligand and several metal derivatives are described.

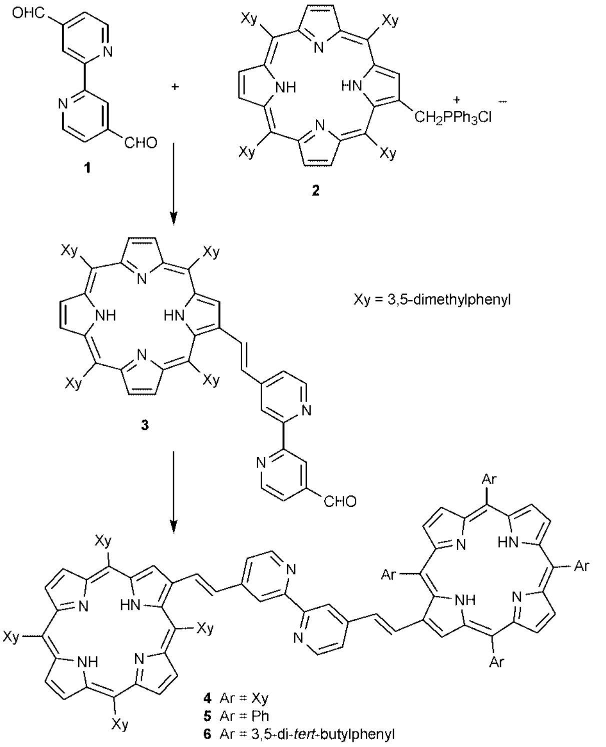
There has been great interest in recent years in the photochemical and electrochemical properties of supramolecular assemblies composed of mononuclear metal polypyridyl complexes.[1] Such systems have applications in solar energy harvesting[2] and in molecular device technology.[3] These functions may be achieved by programming such assemblies, through molecular design, so they transduce energy in one particular direction. This is possible by using binuclear complexes with different metals or by having different terminal ligand substituents.[4]

We have a particular interest in the assembly of polychromophore systems, especially those involving porphyrins.[5] More recently we have been investigating the chemistry of porphyrins that have pendant groups such as pyridine capable of acting as ligands.[6] Here, we report the expansion of this work to include the bipyridyl ligand.

Treatment of 4,4′-diformyl-2,2′-bipyridine **1** with 1 equivalent of tetraxylylporphyrin phosphonium salt (TXP-CH_2PPh_3Cl) **2** proceeds to give the porphyrin functionalised bipyridine **3** in 91% yield (Scheme 1). The remaining aldehyde group can be treated with a further equivalent of **2** to give the bisporphyrin–bipyridine compound **4**. Alternatively, **3** can be treated with other Wittig reagents such as the tetraphenylporphyrin or variants[7] of **2** such as tetra(di-*tert*-butylphenyl)porphyrin[5] to give the hetero-bisporphyrin–bipyridines **5** and **6**. All of the compounds **3**–**6** are insoluble in hexane or alcohols but are very soluble in most other organic solvents.

The ^1H NMR spectrum of **4** is consistent with a symmetrical compound. In particular the symmetry is demonstrated by the presence of only three signals associated with the bipyridyl group. A doublet at δ 7.30 (^3J 5.2 Hz) identified as the two equivalent 5-position protons ($H_{5,5'\text{-bpy}}$), the two 3-position bipyridine protons ($H_{3,3'\text{-bpy}}$) appear as a singlet at δ 8.41 while protons of the 6-position ($H_{6,6'\text{-bpy}}$) give rise to a doublet (^3J 5.2 Hz) at δ 8.81. The lack of steric restrictions apparent from the spectrum of **4** is confirmed by its CPK model with no unfavorable steric interactions being apparent.

Treatment of **4** with suitable transition metal complexes results in the formation of stable coordination complexes where it acts as a bidentate ligand. Thus, heating $ReCl(CO)_5$ and **4** in benzene at reflux temperature gives the rhenium complex **7** in



Scheme 1

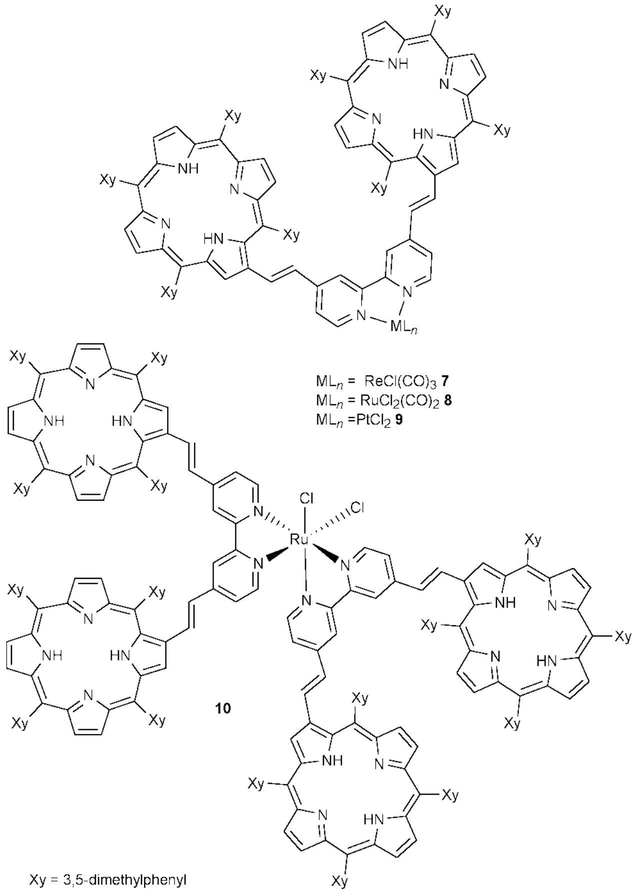


Fig. 1 Molecular structures of compounds.

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† Electronic supplementary information (ESI) available: characterisation data for **3**–**10**. See http://www.rsc.org/suppdata/cc/b0/b000364f/

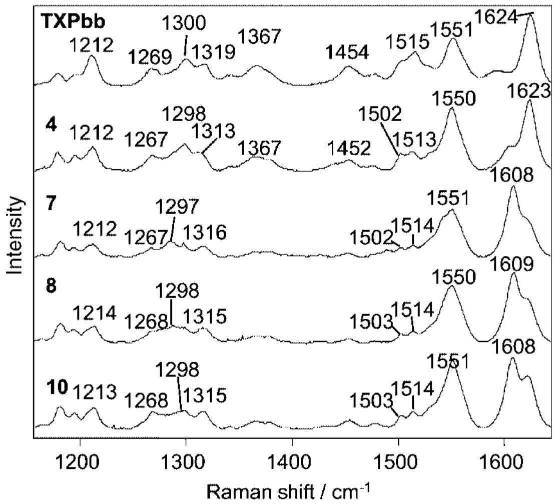

Fig. 2 Resonance Raman spectra of **4**, **7**, **8** and **10** in dichloromethane (1 mM). Excitation wavelength was 457.9 nm (20 mW).

74% yield. Similar complexes of ruthenium **8** and platinum **9** can be obtained by treating **4** with $[Ru(CO)_2Cl_2]_n$ and $PtCl_2(Me_2SO)_2$, respectively (Fig. 1). The ^1H NMR spectra for **7–9** are little changed from **3**, with only slight shifts observed in the positions of the resonances.

The reaction of **4** with $RuCl_2(Me_2SO)_4$ results in the formation of a complex **10** where 2 equivalents of **4** are coordinated. The yield is 28%, but all of the unreacted **4** can be recovered and reused. The ^1H NMR spectrum of **10** is particularly interesting as it enables the geometry of the metal complex to be established unequivocally. In contrast to **4** and the complexes **7–9** where the resonances of the protons attached to the bipyridyl rings give only three signals as expected for symmetrical coordination, six signals are observed for these protons in the ^1H NMR spectrum of **10**. This indicates that the chloride ligands must be *cis* to each other, imposing an asymmetry in the bipyridine ligand.

The electronic absorption spectra of the ligands **4–6** show porphyrin character with the $\pi \longrightarrow \pi^*$ band of the bpy evident at 299 nm in **4**. The metal complexes **7**, **8** and **10** appear to possess only porphyrin character in their visible spectra but close examination of the spectra shows a broadening and asymmetry in the Soret band owing to the presence of the metal to ligand charge transfer under the Soret. The spectra are effectively the sum of the spectra of the porphyrin and $M(bpy)_3$ components.[8] Emission studies on these systems show similar results to other bpy–porphyrin complexes[8] with significantly reduced porphyrin emission, and no emission attributable to the M(bpy) portion of the system observed. The emission quenching observed in these systems is thought to be energy transfer similar to that observed in terpy based systems by Flamigni *et al.*[8b,c] The resonance Raman spectra of **4**, **7**, **8** and **10** are shown in Fig. 2. Also present is the spectrum of TXPbb, which is a vinyl-phenyl substituted tetraxylyl porphyrin, for comparative studies. The spectra for **4**, **7**, **8** and **10** are largely porphyrin in nature, with the only feature attributable to the MLCT transition the band at 1608 cm^{-1} in **7**, **8** and **10**. In **7** a band due to the carbonyl can be observed at 2020 cm^{-1}. An investigation of systems such as these in solar energy conversion is currently underway in our laboratory.

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