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Preliminary Communication

Novel ditopic terpyridine and phenylterpyridine ligands bridged by one or two ethynyl bonds: syntheses of rigid rod-like multinuclear complexes

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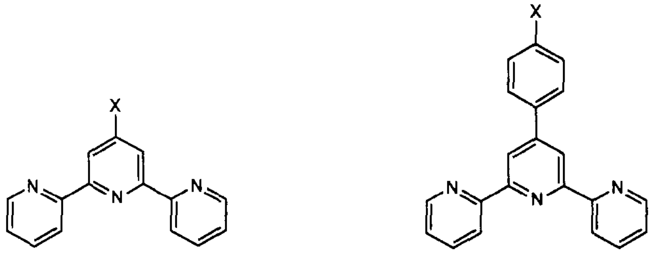
Abstract

A novel series of ditopic ligands bearing two 2,2′:6′,2″-terpyridine or two 4′-phenyl-2,2′:6′,2″-terpyridine subunits and an ethynyl (**3a** and **3b**) or a diethynyl (**4a** and **4b**) bridge has been synthesised from 4′-ethynyl-2,2′ : 6′,2″-terpyridine (**1d**) and 4′-(4-ethynylphenyl)-2,2′:6′,2″-terpyridine (**2c**) by coupling with the corresponding triflate- or bromo-substituted substrates, or by self-coupling of the ethynyl substituted precursors, respectively. They form rigid rod-like homodinuclear and heterotrinuclear ruthenium(II) and iron(II) complexes.

Widespread interest in polypyridine complexes of transition metals is principally a consequence of their potential use in electron and energy transfer processes. They are often used as photosensitisers in model systems for the photochemical conversion of solar energy, as photocatalysts for the light-driven transformation of small molecules [1], and they have been recently considered as good candidates for components in molecular devices [2]. Intramolecular electron transfer is the basic process involved in molecular electronics and, in this respect, bridging ligands of various lengths have been employed since the pioneering work of Creutz and Taube with 1,4-pyrazine-bridged Ru^{II}/Ru^{III} mixed-valence complexes [3]. Recently a cyclometalated 3,3′,5,5′-tetrapyridylbiphenyl bridge has been shown to allow strong coupling in Ru^{II}/Ru^{III} mixed-valence systems [4]. Surprisingly, to our knowledge only one example of the use of an acetylenic bridged bis(pyridine) type ligand has been reported in mixed-valence systems [5]. Polyalkyne substituted bipyridine or terpyridine subunits are of considerable interest as molecular building blocks for the preparation of polymeric photosensitive metal complexes. A possible use of these materials is to control photochemical processes in which optical excitation is followed by a spatially directed energy or electron migration along the π-delocalized polymeric chain [6].



1a : X = OTf

1b : X = Br

1c : X = ≡—TMS

1d : X = ≡—H

2a : X = Br

2b : X = ≡—TMS

2c : X = ≡—H

Scheme 1.

As part of a project for the synthesis and study of new molecular systems allowing electronic communication between metal centres, we have recently developed the chemistry of aromatic polyimine ligands functionalised by polyalkyne chains [7]. Here we describe the synthesis of a new class of alkyne-substituted terpyridine compound **1c**, **1d**, **2b**, **2c** as well as novel homoditopic materials **3a**, **3b**, **4a**, **4b**. Their coordination and spectroscopic properties towards Ru^{II} and Fe^{II} cations are also described. Compounds **1c** was prepared either from the triflate [8] **1a** or the bromo [9,10] derivative **1b**, in 75% and 87% yields, respectively, by reaction of trimethylsilylacetylene in the presence of diisopropylamine as base and a mixture of $[Pd(PPh_3)_2Cl_2]/CuI$ as catalyst precursor [11]. Compound **2b** was prepared quantitatively from the bromo-substituted phenylterpyridine [12] under similar conditions (Scheme 1). Removal of the TMS group using KF in MeOH/THF afforded the corresponding terminal alkynes (87% for **1d** and 92% for **2c**) *.

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* All compounds were obtained as white powders and were characterised by NMR, mass, electronic, infrared and Raman spectroscopies and melting point. All data were consistent with the proposed structures (Scheme 1 and 2).

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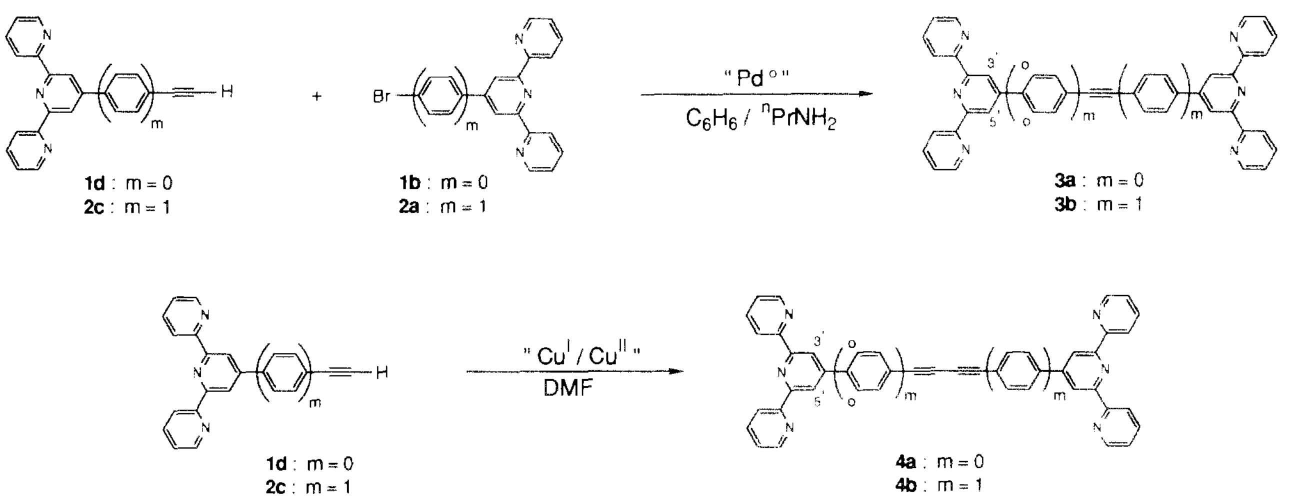
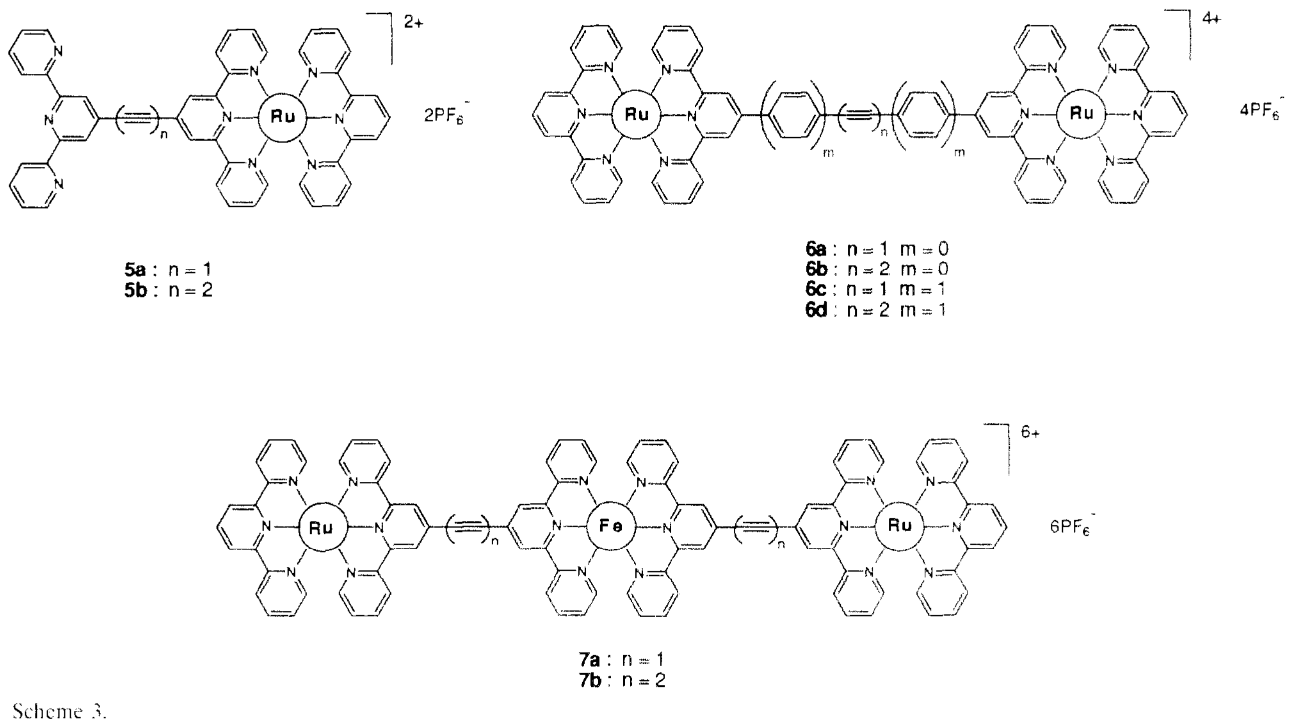


Scheme 2.

The monoethynyl-bridged compounds **3a** and **3b** were prepared by reaction of a stoichiometric quantity of the bromo-substituted species with the corresponding ethynyl substituted compound in the presence of [Pd(PPh$_3$)$_4$] and n-propylamine (Scheme 2, 71% for **3a** and 79% for **3b**). The absence of copper in these reactions, compared to the previous experimental conditions, avoided undesired side-reactions.

The diethynyl-bridged compounds **4a** and **4b** were prepared by dimerization of the ethynyl substituted precursors **1d** and **2c**, respectively, at room temperature in the presence of a mixture of CuCl and CuCl$_2$ [13] (Scheme 2, 50% for **4a** and 46% for **4b**).

These new multinucleating materials containing terpyridine domains are interesting molecules for the controlled assembly of coordination oligomers and



Scheme 3.

Table 1. Selected data for the Ru^{II}, Ru^{II}/Fe^{II} complexes depicted in Scheme 3

Compound	Isolated yield (%)	R_f [a]	FAB$^+$ [b] (nature of the cluster)	λ_{max}, nm [c] (ϵ, dm^3 mol^{-1} cm^{-1})
5a	68	0.46	968{[Ru(terpy)(**3a**)]$^{2+}$, PF_6^-}	490(19 200)
5b	60	0.40	992{[Ru(terpy)(**4a**)]$^{2+}$, PF_6^-}	490(23 000)
6a	25	0.23	1593{[Ru_2(terpy)$_2$(**3a**)]$^{4+}$, $3PF_6^-$}	515(32 800)
6b	28	0.15	1617{[Ru_2(terpy)$_2$(**4a**)]$^{4+}$, $3PF_6^-$}	512(39 300)
6c	18	0.47	1745{[Ru_2(terpy)$_2$(**3b**)]$^{4+}$, $3PF_6^-$}	488(48 500)
6d	22	0.20	1769{[Ru_2(terpy)$_2$(**4b**)]$^{4+}$, $3PF_6^-$}	489(62 000)
7a	91	0.32	2427{[(**5a**)$_2$Fe]$^{2+}$, PF_6^-}	596(57 500)/497(43 200)
7b	90	0.10	2475{[(**5b**)$_2$Fe]$^{2+}$, PF_6^-}	596(59 300)/499(48 600)

[a] Retention front determined using alumina TLC sheets and CH_2Cl_2/MeOH (9:1) as eluent for **5a**, **5b**, **6a**, **6b**, **6c**, **6d** and CH_2Cl_2/MeOH (8:2) as eluent for **7a** and **7b**. [b] Using *meta*-nitrobenzylalcohol as matrix. [c] Metal-to-ligand charge transfer absorption measured in acetonitrile.

polymers. We therefore studied the interaction of Ru^{II} cations with these novel ditopic ligands, using a new Ru^{II}-terpy precursor. Classical ruthenium/terpyridine complexation reactions require forcing conditions (*e.g.* glycerol, 180°C) to reduce the starting Ru^{III} to Ru^{II} *in situ* and to favour complexation [14]. Reaction of the ditopic bis(terpyridine) compounds (Scheme 2) using [Ru^{III}(terpy)Cl_3] gave a mixture of insoluble polymeric complexes. Under mild conditions, however, the reaction, of the hitherto unreported [Ru^{II}(terpy)(DMSO)Cl_2] * with the bis-terpyridine ligands **3a** and **4b** afforded, after work-up and chromatography, the pure orange mononuclear complexes **5a** (68%) and **5b** (60%) as well as the pure red homodinuclear complexes **6a** (25%) and **6b** (28%) (Scheme 3) **. The complexes exhibited in their FAB$^+$ mass spectra, a molecular ion peak with the expected isotopomer distributions and no significant peaks at higher mass (see Table 1 for selected data). Interestingly, in the case of the ditopic phenyl-terpyridines **3b** and **4b** only the dinuclear complexes are formed: **6c** (28%) and **6d** (32%) (Scheme 3).

The mononuclear complexes **5a** and **5b** are of interest in their own right and as potential precursors for more elaborate molecular architectures in which the electronic communication between the two redox centres could, in principle, be modulated by the oxidation state of the central metal. Indeed, reaction of complexes **5a** and **5b** with $FeSO_4 \cdot 7H_2O$ allowed the straightward synthesis of heterotrinuclear complexes (Scheme 3): **7a** (91%) and **7b** (90%). These two trinuclear complexes exhibit two charge-transfer absorption bands, the red shifted band corresponding to the Fe to terpy transition and the second to the Ru to terpy, as compared with authentic samples of [M(terpy)$_2$]$^{2+}$ M = Fe or Ru. Electrospray mass spectroscopy (eluent H_2O/CH_3CN 1:1) exhibited the expected molecular peaks *m/z*, 284 for [Fe{Ru(terpy)(**3a**)}$_2$]$^{6+}$ and 292 for [Fe{Ru(terpy)(**4a**)}$_2$]$^{6+}$, respectively, for complexes **7a** and **7b**. This result has also been futher confirmed by FAB$^+$ mass spectrometry (see Table 1).

A significant bathochromic shift (25 nm) was observed in the dinuclear complexes **6a** and **6b** compared to the related mononuclear complexes **5a** and **5b**. These new compounds represent an interesting example where extensive ground-state π-electronic delocalization is evident, as previously observed in polyenes [16], merocyanines [17], carotenoïds [18]. This effect is not observed in the diphenylethynyl dinuclear Ru^{II} complexes **6c** and **6d**, because of a decrease of π-overlap. A twisted conformation of the terpyridine and the phenylethynyl fragments in **3b** and **4b** is expected in order to minimize steric interactions between the protons in the 3′ and 5′ positions of the terpyridine and the *ortho* protons of the phenyl subunits (labelling given in Scheme 2).

In summary, we have synthesised novel rigid rod-like cationic, bimetallic complexes in a stepwise fashion from appropriate ditopic oligopyridine ligands. These ditopic ligands and related compounds should be useful precursors for a variety of new oligomer chain complexes using a "complexes as ligand/complexes as metals" approach [19]. Complete studies of their photophysical and electrochemical properties and the extension of this methodology to tetraacetylenic compounds are currently under active investigation and will be the subject of future reports.

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* Prepared in 80% yield from [Ru(DMSO)$_4$$Cl_2$] [15] and 2,2′:6′,2″-terpyridine in $CHCl_3$; FAB$^+$ MS *m/z* (m-NBA) 482.9/484.9 [M$^+$], 447.9 [M−Cl], 404.9 [M-DMSO], 369.9 [M-DMSO-Cl], 333.9 [M-DMSO-2Cl-H].

** All complexes were obtained as highly coloured, crystalline compounds and were characterized by NMR, FAB$^+$, electronic, infrared and Raman spectroscopies. All data were consistent with the proposed structures (Scheme 3).

Acknowledgements

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