Synthesis, Characterization and Properties of Novel Covalently Linked Binuclear Ruthenium(II) and Trinuclear Ruthenium(II)–Copper(I) Bipyridyl Complexes

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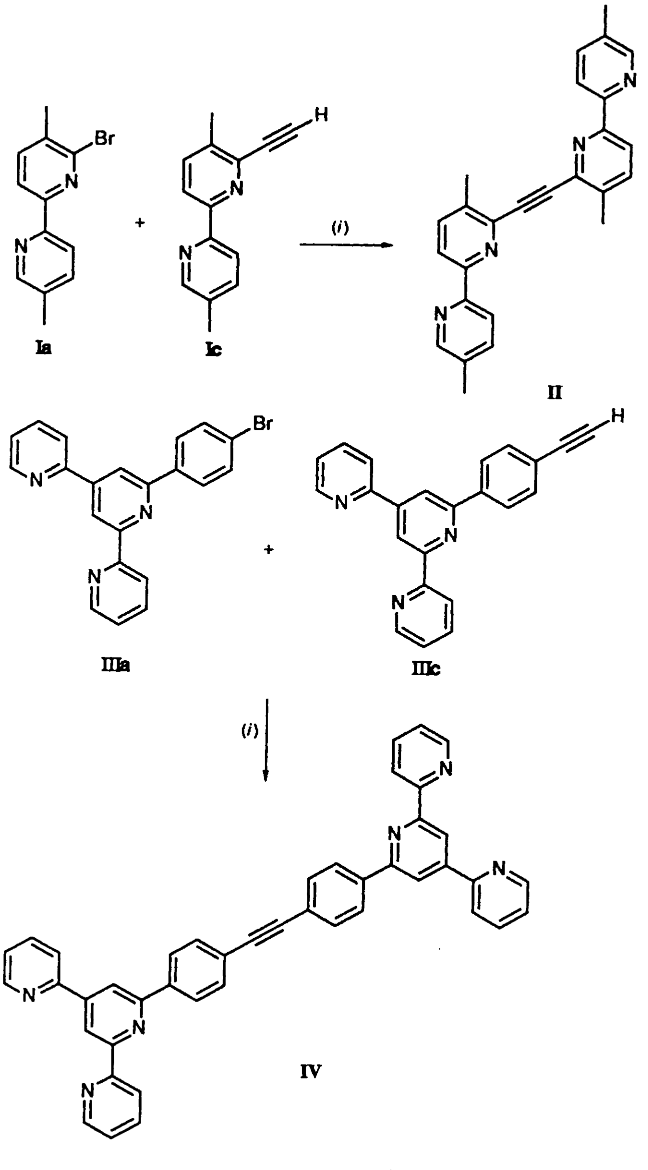
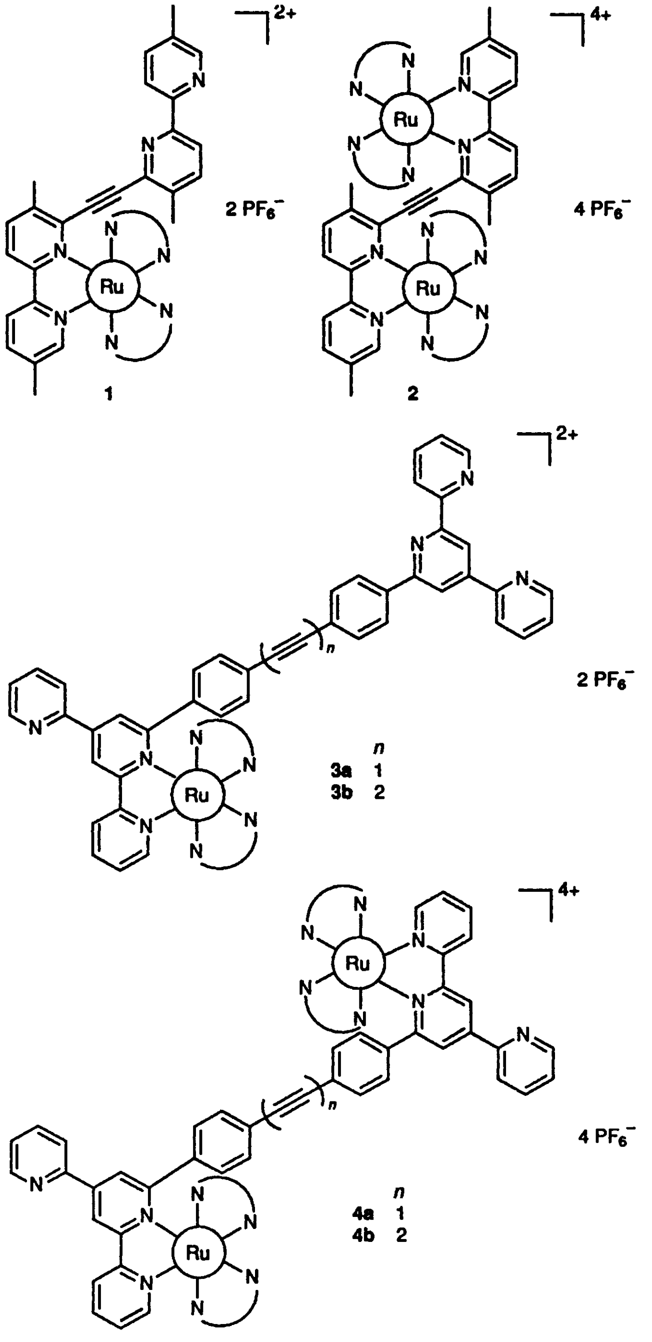
New ditopic ligands bearing two bipyridine subunits and an ethynyl or diethynyl bridge have been synthesised and shown to form a series of novel cationic mononuclear ruthenium(II) and copper(I), dinuclear ruthenium(II) and trinuclear ruthenium(II)–copper(I) complexes.

There is a growing interest in interfacial photoprocesses, in the photochemistry of large aggregated chromophores and in supramolecular systems capable of performing photoinduced energy transfer and/or charge separation.[1] The preparation and spectroscopic characterization of small clusters of luminophores may serve as models for larger and more elaborate systems.[2] Ruthenium–polypyridine complexes can be used as building blocks to synthesise luminescent and redox-active polynuclear complexes where energy- and/or electron-transfer processes can be induced by light.[3] Recently, covalently linked bipyridine derivatives have been synthesised;[4,5] however, most of the systems described in the literature are based on ditopic ligands linked by an alkyl or polyene chain.[6,7] In the latter case the presence of low-energy ligand-centred transitions shielded the photophysical processes associated with metal-to-ligand transitions.[8] It can therefore be anticipated that ditopic ligands (Schemes 1 and 2), bridged by polyalkyne chains, could in principle overcome this problem and favour electronic and/or energetic interactions between two chromophores in close proximity. Polyalkyne-substituted bi- or ter-pyridine subunits are also 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. Herein we report the synthesis, characterization and preliminary properties of the hitherto unknown mono- and di-ethynyl linked ruthenium(II)–polypyridine complexes **2**, **4a** and **4b**, as well as the preparation of novel ruthenium(II)–copper(I) trinuclear complexes **6a** and **6b** prepared from the related mononuclear ruthenium(II) complexes **3a** and **3b** (Schemes 2 and 3).

The trimethylsilylacetylene-substituted compounds **Ib** and **IIIb** were prepared by quantitative reaction of trimethylsilylacetylene with the bromo-substituted starting materials **Ia** and **IIIa**, using [$Pd(PPh_3)_2Cl_2$] as catalyst, CuI as reducing agent and diisopropylamine as base.[9] Removal of the $SiMe_3$ group with KF in methanol gave the terminal alkyne compounds **Ic** and **IIIc** in good yield (97 and 86%, respectively). The dimeric monoethynyl-bridged ligands **II** (52%) and **IV** (85%) were synthesised respectively from **Ic** and **IIIc** by reaction with compounds **Ia** and **IIIa**, using [$Pd(PPh_3)_4$] as catalyst and an excess of $NPr^i{}_2H$ as base (Scheme 1). The dimeric diethynyl-bridged ligand **V** was prepared by dimerization of the ethynyl-substituted precursor **IIIc** in the presence of CuCl, $Me_2NCH_2CH_2NMe_2$ and O_2 (97%).[10]

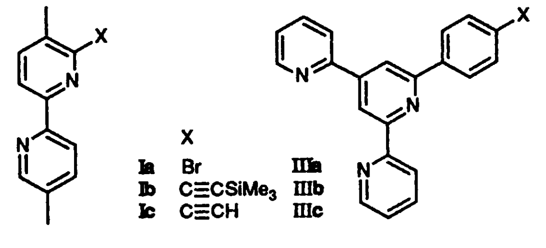


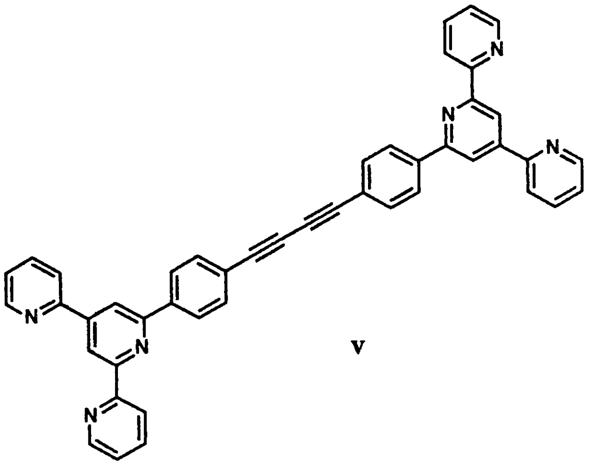
Scheme 1 (*i*) 'Pd⁰'



Scheme 2

The preparation of the ruthenium(II) complexes involved substitution of solvent for chloride ion in the co-ordination sphere of [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (bipy = 2,2′-bipyridine) (2 equivalents) by reaction with AgBF$_4$ in methanol.[11] The AgCl formed was filtered off under argon and the filtrate allowed to react under reflux with 1 equivalent of the ditopic ligands **II**, **IV** and **V**. After a few hours of heating the resultant bright orange solution was strongly luminescent. The crude product was precipitated with aqueous NH$_4$PF$_6$. The complexes were purified by column chromatography [neutral alumina eluted with CH$_2$Cl$_2$–MeOH (9:1)]. All complexation reactions resulted in a mixture of the mono- and di-ruthenium(II) complexes (Scheme 2 and Table 1) with chemical yields as high as 82% for the former. All complexes were obtained as crystalline materials and characterized by ^{1}H, ^{13}C-{^{1}H} NMR, IR, Raman, mass, absorption and emission spectroscopy (for selected data see Table 1).





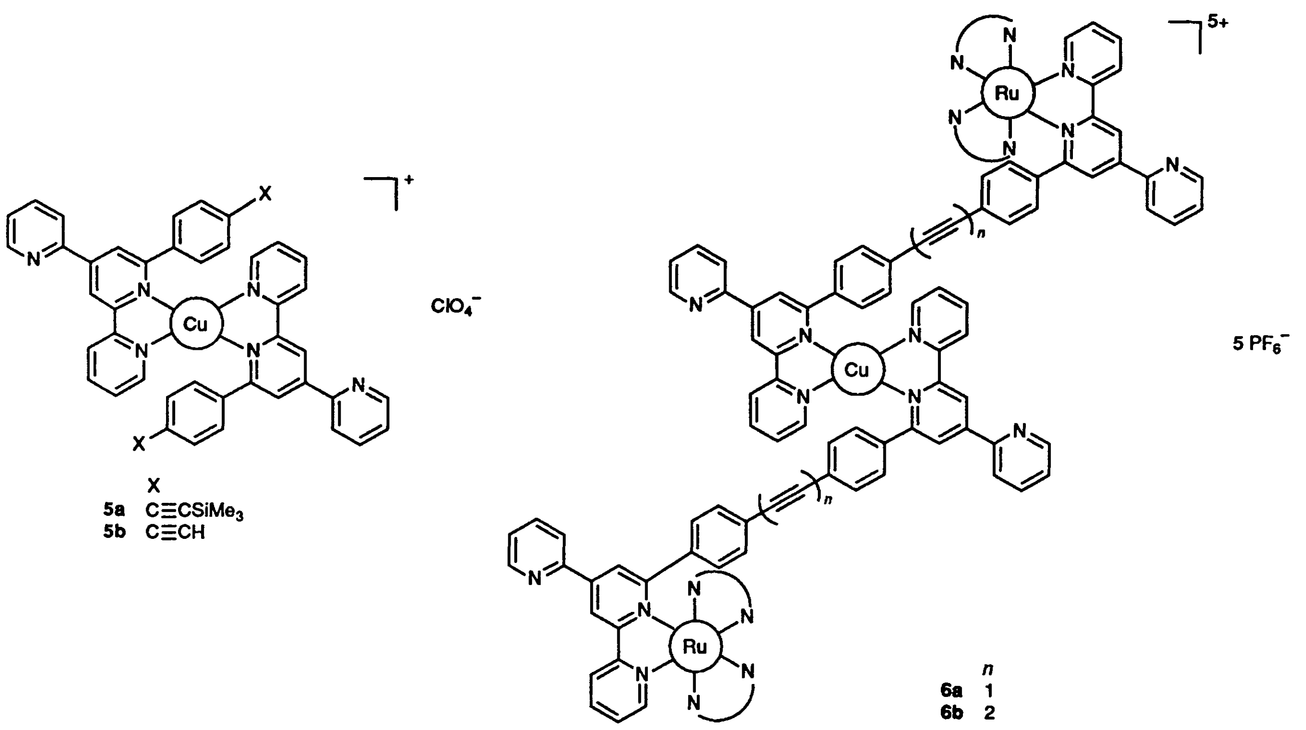
The observed carbon chemical shifts are in good agreement with those reported for other ethynyl derivatives.[9,12] Furthermore, in their FAB$^+$ mass spectra all complexes exhibited intense peaks with the expected isotope distribution. The mononuclear complexes **3a** and **3b** are of interest in their own right and as potential precursors to more elaborate molecular architectures in which the electronic interaction between the two chromophores could, in principle, be modulated by the nature and/or oxidation state of the central metal (*i.e.* a molecular photoswitch). Copper(I) seems to be a good candidate mostly because it forms stable complexes when a bulky group is present *ortho* to the nitrogen atom of a polypyridine ligand.[13] Indeed, ligands **IIIb** and **IIIc** form stable deep violet and air-stable copper(I) complexes with a stoichiometry of two ligands to one copper (**5a** and **5b**). Reaction of the monoruthenium(II) complexes **3a** and **3b** with [Cu(CH$_3$CN)$_4$]ClO$_4$[14] allowed the straightforward synthesis of the deep red heterotrinuclear complexes **6a** and **6b** in excellent yields (Scheme 3 and Table 1 for characterization). The electronic absorption and luminescence spectra show some general trends and features: (*i*) all complexes exhibit strong absorption bands which are ascribed to metal-to-ligand charge transfer (m.l.c.t.) transitions (the m.l.c.t. of Ru^{II} being by far the most intense compared to that of Cu^I); (*ii*) except for Cu^I, all complexes exhibit an m.l.c.t. emitting state as usually observed for [Ru(bipy)$_3$]$^{2+}$ complexes. It is worth noting that a significant decrease (70%) in the intensity of luminescence was observed for the trinuclear complexes **6a** and **6b**, compared to **3a** and **3b**. This could be due to the change in bipyridine geometry (*cis* conformation) during complexation of Cu^I. This may, at least in part, perturb the emission of the Ru–bipy moiety. Indeed, copper decomplexation with cyanide in MeOH restores the initial emission intensity of the mononuclear ruthenium(II) species. These new compounds **6a** and **6b** represent interesting examples where fluorescence could be modulated by subsequent complexation.

In summary, we have synthesised and characterized novel highly coloured cationic bi- and tri-metallic complexes in a stepwise fashion from appropriate polyalkyne-substituted ligand precursors. The study of their photophysical and electrochemical properties and the extension of this methodology to more delocalized systems are currently in progress.

Table 1 Selected data for the complexes of Ru^{II} and Cu^{I} depicted in Schemes 2 and 3

Complex	Isolated yield (%)	^{13}C-{^{1}H} NMR^a (δ)	FAB^{+b} {nature of the cluster}	$\lambda_{max}{}^c$/nm (ε/dm^3 mol^{-1} cm^{-1})	$\lambda_{em}{}^d$/nm
1	82	100.41/86.67	949 {[**II**, Ru(bipy)$_2$]$^{2+}$, PF$_6{}^-$}	448 (12 100)	615
2	16	96.82	1653 {[**II**, Ru$_2$(bipy)$_4$]$^{4+}$, 3PF$_6{}^-$}	445 (23 000)	618
3a	32	91.65/90.47	1199 {[**IV**, Ru(bipy)$_2$]$^{2+}$, PF$_6{}^-$}	454 (10 700)	639
3b	30	83.05/81.83 75.51/75.28	1223 {[**V**, Ru(bipy)$_2$]$^{2+}$, PF$_6{}^-$}	455 (13 500)	639
4a	21	90.34	1903 {[**IV**, Ru$_2$(bipy)$_4$]$^{4+}$, 3PF$_6{}^-$}	455 (19 300)	639
4b	36	81.90/75.20	1927 {[**V**, Ru$_2$(bipy)$_4$]$^{4+}$, 3PF$_6{}^-$}	455 (24 900)	640
5a	80	104.18/94.65	873 {[2 **IIIb**, Cu]$^+$}	437 (3 600) 560 (2 100)	—
5b	98	82.87/79.34	729 {[2 **IIIc**, Cu]$^+$}	436 (4 000) 560 (2 400)	—
6a	92	90.79/90.27	2751 {[2 **3a**, Cu]$^+$}	455 (28 200)	639^e
6b	90	82.34/81.97	2799 {[2 **3b**, Cu]$^+$}	454 (28 600)	643^e

[a] Chemical shifts for C≡C and for C≡CH (complex **5b**), measured in CD$_3$CN except for **5a** and **5b** (CD$_2$Cl$_2$); **6a** and **6b** in argon-degassed CD$_3$CN solutions. [b] Using *m*-nitrobenzyl alcohol as matrix. [c] For m.l.c.t. absorption measured in acetonitrile, except for **5a**, **5b**, **6a** and **6b** (argon-degassed methanol). [d] Emission measured in acetonitrile, except for **5a, 5b, 6a** and **6b** (argon-degassed methanol), at 25 °C using 3×10^{-5} to 1×10^{-4} mol dm^{-3} solutions. [e] Weak fluorescence [*ca.* 30% of the emission observed for the related mononuclear ruthenium(II) complexes].



Scheme 3

Acknowledgements

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