Making photoactive molecular-scale wires

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A synthetic strategy is described that provides access to oligopyridine-based ditopic ligands bridged by an alkyne spacer comprising one to four ethynyl groups. The spacer serves as both a rigid girder to maintain structural integrity and a conduit for electron flow. These ditopic ligands, bearing 2,2'-bipyridine, 1,10-phenanthroline or 2,2':6',2''-terpyridine coordination sites, are used to construct a dichotomous series of polynuclear metal complexes. Judicious selection of ligand and metal cation permits the assembly of novel molecular architectures incorporating a logical gradient of redox units along the molecular axis. Different molecular shapes become possible by changing the position at which the alkyne bridge is connected to the terminal ligand and by varying the nature of the complexing cation. The electrochemical and photochemical properties of many such molecular arrays are enumerated with a view to the future design of molecular electronic devices. The alkyne bridge actively promotes long-range electronic coupling between remote cationic units, especially under illumination with visible light. Intramolecular triplet energy transfer, photon migration and light-induced electron transfer occur by way of extremely rapid superexchange involving LUMO and HOMO states localized on the bridge. It is also shown that facile electron delocalization over an extended π^* orbital takes place in the triplet excited states of symmetrical binuclear complexes. This process extends the triplet lifetime and thereby facilitates secondary reactions that are otherwise unattainable. The level of electronic communication along the molecular wire can be controlled by insertion of suitable insulating groups into the bridge, these groups also providing further means by which to manipulate the stereochemistry. In certain cases, the alkyne bridge undergoes reductive electropolymerization to generate molecular films having metallo centres dispersed along a conjugated backbone.

Introduction

The idea of a molecular-scale wire is not new; its origins can be traced to the so-called 'soliton theory' of electronic conduction in DNA.[1] The most effective one-dimensional organic conductors are doped polyacetylenes or polypyrroles and this realisation has led to the extensive study of polyenes as electron carriers. Many such systems have been investigated, especially those having electron donor and acceptor units as terminals for short polyene chains.[2–5] Significantly different electronic conduction has been anticipated for odd- and even-alternant and non-alternant hydrocarbons.[6] The old belief that β-carotenes provide an electronic pathway through lipid membranes has been re-examined in a non-biological context and there is little doubt that such molecules promote long-range electronic coupling between terminal subunits.[7–10] Other types of organic-based molecular wires have been proposed, including poly-phenyls,[11] polyynes,[12–16] polycondensed aromatics,[17,18] and π stacks,[19] but progress has been slower than with polyenes. The maximum permitted length of the polyenic bridge is set by the

nature of the terminal subunits and by the mode of activation, although in the ideal case it will be limited by the Peierls distortion.[20]

To identify appropriate redox-active end groups it is necessary to consider (*i*) how to couple the terminus to the bridge and (*ii*) how to activate the system. Usually, the bridge is attached directly to an aromatic ligand (*e.g.* cyclopentadiene, pyridine) coordinated to the metal centre. This provides for extended π-electron conjugation running along the molecular axis, spanning the gap between the terminal metal centres, but complicates definition of where the actual bridge begins and ends. Activation can be provided by way of electrochemical (or chemical) oxidation/reduction of one of the terminal groups or by selective illumination into a preferred chromophore. In either case, it is necessary that the energies of LUMO and HOMO states localised on the bridge exceed those of the terminal groups so as to avoid their direct participation in the overall redox reaction. Consequently, most end groups have been chosen from low-potential, redox-active transition-metal centres. Photoactivation is highly selective, extremely versatile and rapid but we need to bear in mind that conjugated polyenes are excellent triplet state quenchers.[21]

It is also necessary to consider how to quantify electronic coupling between remote sites situated along the wire. The most common method involves formation of a mixed-valence species in which a covalently linked dyad comprising two identical, redox-active (*e.g.* ferrocene) termini is subjected to one-electron oxidation or reduction. Electronic interaction between the end groups may result in the appearance of an intervalence
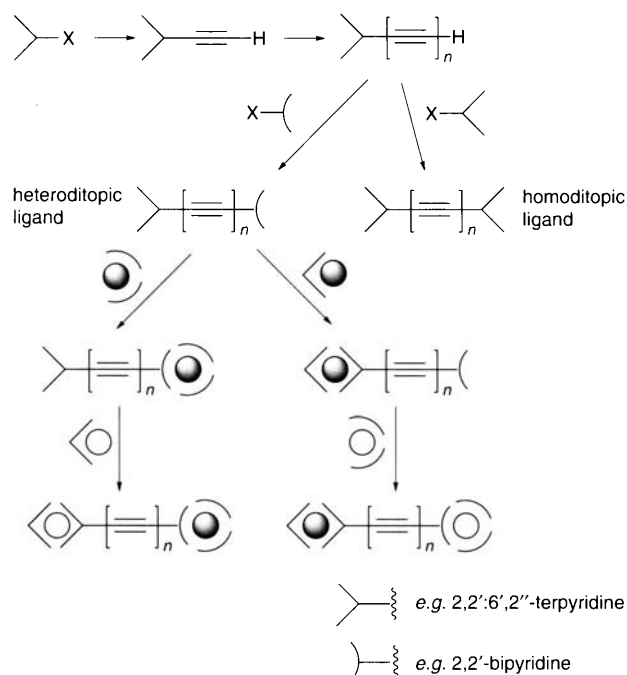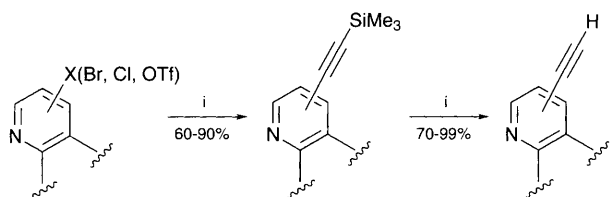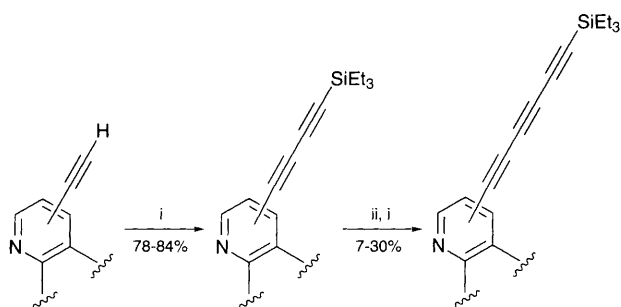

Fig. 1 Programmed layering approach used to assemble the elemental carbon-bridged polynuclear complexes studied in this project

charge-transfer absorption band that can be used to estimate the electronic coupling matrix element.[22] Similar studies can be made by photoelectron and electron-transmission spectroscopy.[23] In certain cases, mutual interaction between terminal metal complexes can be monitored by magnetic susceptibility measurements and/or by EPR spectroscopy. A more general technique for monitoring electronic interactions involves cyclic voltammetry whereby addition or removal of electrons from one terminus affects the potential at which identical processes occur at the second terminus.

We have made extensive use of laser spectroscopy to measure the rates of light-induced, intramolecular energy and/or electron transfer between specific partners. This approach is
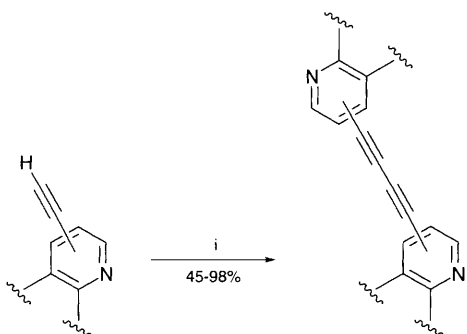
attractive in that it provides direct kinetic information for electron-transfer reactions under conditions where the temperature, driving force, and environment can be changed readily. However, relating the derived kinetic data to electronic terms is not always straightforward and requires confidence in particular theoretical models.

Constructing the wires

Because of their exceptional coordinative properties, chemical stability and synthetic versatility, we chose to use oligopyridino ligands as the key molecular building blocks by which to construct multicomponent molecular-scale wires. The second critical aspect of this work concerns the application of Pd[0] catalysis for building elemental carbon–carbon bridges between adjacent oligopyridino ligands in such a manner as to permit selective metallation.[24] The final, and perhaps most important, element in our approach involves the identification of polyynes

Scheme 1 *Reagents and conditions*: i, HC≡CSiMe₃, [Pd(PPh₃)₂Cl₂] (3%), CuI (6%), Pri₂NH; ii, K₂CO₃ or KF

Scheme 2 *Reagents and conditions*: i, BrC≡CSiEt₃, CuCl (7%), NH₂OH·HCl, PrⁿNH₂; ii, NaOH
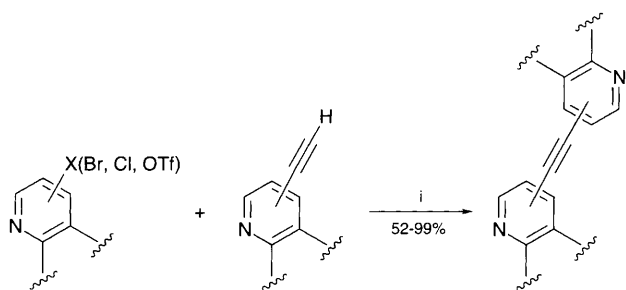
Scheme 3 *Reagents and conditions*: i, [Pd⁰(PPh₃)₄] (6%), Pri₂NH or PrⁿNH₂

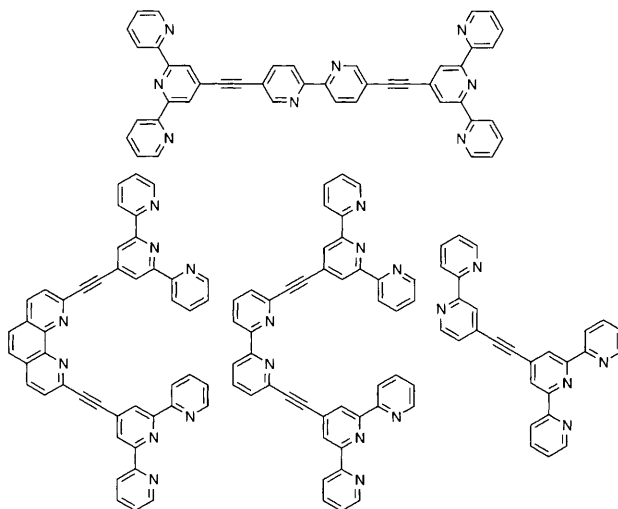**Scheme 4** *Reagents and conditions*: i, CuCl₂, CuCl, O₂ or CuCl, tmeda, O₂
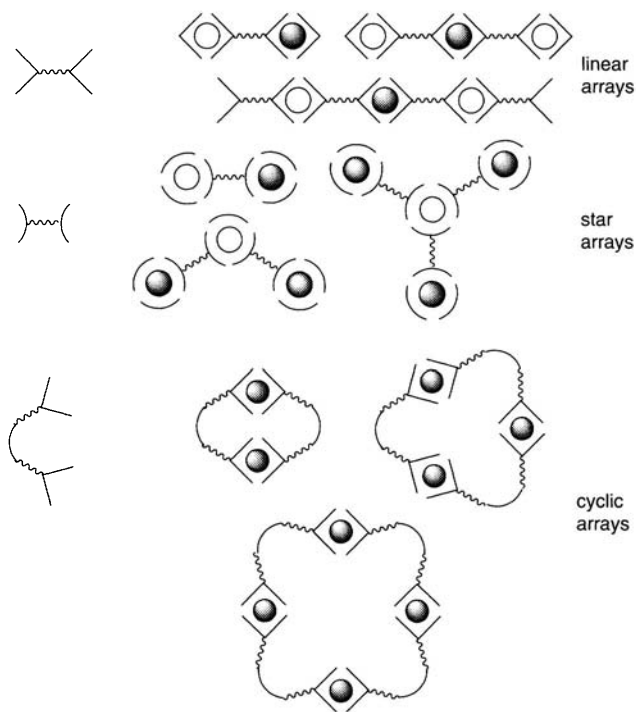

Fig. 2 Ligands used during this project

Fig. 3 Selection of the molecular structures prepared and fully characterized during this project

as appropriate spacer groups for maintaining strong electronic communication between remote metal centres over extended distances.[25] Following this rationale, a general strategy was devised that permits isolation of alkyne-bridged polynuclear metal complexes in reasonable yield by a stepwise synthetic procedure as outlined in Fig. 1. The first step requires functionalisation of oligopyridino ligands with an ethynyl substituent at a predetermined site (Scheme 1).[26] By making judicious use of successive Cu[I]-catalysed Cadiot–Chodkiewicz reactions, it becomes possible to extend the length of the alkyne spacer until hampered by reactivity and solubility restrictions (Scheme 2).[27] Many functionalized oligopyridino ligands bearing a carbon chain comprising one to four ethynyl groups have now been synthesized and fully characterized using this sequential approach: in particular, ^{13}C NMR, UV–VIS and IR spectroscopies provide convenient tools for monitoring pro-

gressive elongation of the spacer.[28] Chain termination with a second oligopyridino species, leading to formation of ditopic ligands, can be realized by way of Heck-type cross-coupling, for ethynyl-linked systems (Scheme 3),[29] or via oxidative Glaser coupling, for buta-1,3-diynyl-bridged systems (Scheme 4).[30] The synthetic methodology is readily extended for the preparation of novel multitopic ligands having various poly-pyridino coordination sites situated along the wire.

These coupling reactions are highly versatile, and, for example, allow synthesis of di- and tri-topic ligands having identical, similar, or dissimilar coordination sites available for complexation with suitable metal cations. A few selected examples of mixed 2,2′-bipyridine–2,2′:6′,2″-terpyridine and 1,10-phenanthroline–2,2′:6′,2″-terpyridine multitopic ligands synthesized during this programme are show in Fig. 2.[31] This strategy, in turn, provides for a gradient of redox or photoactive

Table 1 Photophysical and electrochemical properties of some alkyne-substituted metal polypyridine complexes measured in acetonitrile at 22 °C

Compound	n^a	$\lambda_{EM}{}^b$/nm	$\tau_T{}^c$/ns	$E'_{red}{}^d$/V vs. SCE		$E'_{ox}{}^e$/V vs. SCE
[Ru(terpy)₂]²⁺	–	640	0.56	−1.25	−1.52	1.30
1	1	722	565	−0.97	−1.19	1.42
2	2	735	720	−0.92	−1.15	1.41
3	1	670	3.2	−1.16	−1.40	1.34
4	2	665	5.5	−1.08	−1.32	1.39
5	1	700	180	−1.02	−1.33	1.43
6	2	715	190	−0.98	−1.25	1.34
[Ru(bpy)₃]²⁺	–	620	980	−1.35	−1.54	1.27
16	1	690	1850	−0.94	−1.19	1.31
	2	705	2400	−0.86	−1.04	1.29
17	1	680	1270	−0.92	−1.16	1.38
	2	695	2200	−0.90	−1.12	1.35
18	1	615	4.1	−1.02	−1.26	1.35
	2	625	8.6	−1.00	−1.18	1.31
[Os(bpy)₃]²⁺	–	745	60	−1.25	−1.54	0.83
11	1	805	65	−1.04	−1.14	0.82
12	1	835	52	−0.97	−1.11	0.81
13	1	755	58	−1.11	−1.21	0.85

a Number of ethynyl groups in bridge. *b* Emission maximum, ±5 nm. *c* Triplet lifetime, ±5%. *d* First and second reduction potentials of the coordinated ligand, ±20 mV. *e* Oxidation potential of the metal centre, ±20 mV.

5 M = Zn, n = 1   6 M = Zn, n = 2
9 M = Fe, n = 1   10 M = Fe, n = 2
14 M = Co, n = 1   15 M = Co, n = 2
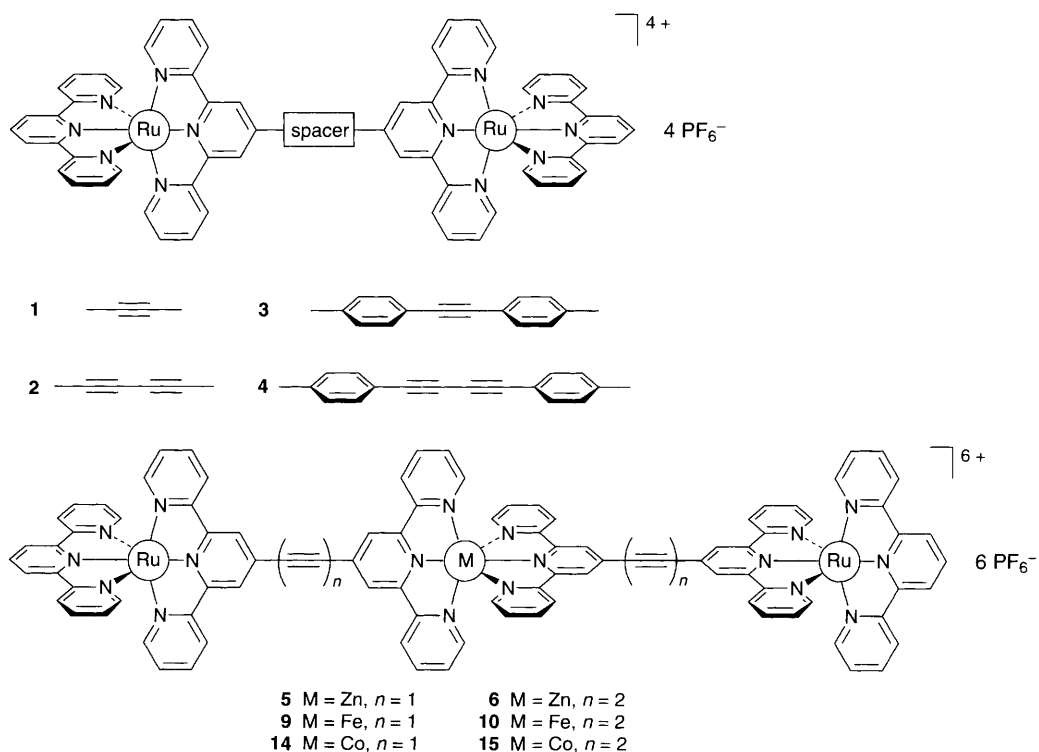
metal complexes arranged in a logical and predetermined sequence along the chain. Different metal cations can be inserted into the vacant coordination sites, allowing for a cruder variation in electronic properties. The ditopic ligands can be capped with metalloligands, forming symmetric and asymmetric binuclear complexes, or reacted with additional ditopic ligands before capping, forming multinuclear complexes. Many such mono-, di-, tri-, tetra- and hepta-nuclear metal complexes are now available, having a wide range of metal cations (e.g. Ru^{II}, Os^{II}, Re^{I}, Co^{II}, Zn^{II}, Fe^{II}) bound to the oligopyridino ligands. Selective oxidation of certain cations extends the range of available complexes. Furthermore, the site at which the alkyne substituent is attached to the oligopyridino ligand can be varied in many cases, thereby providing for subtle tuning of the
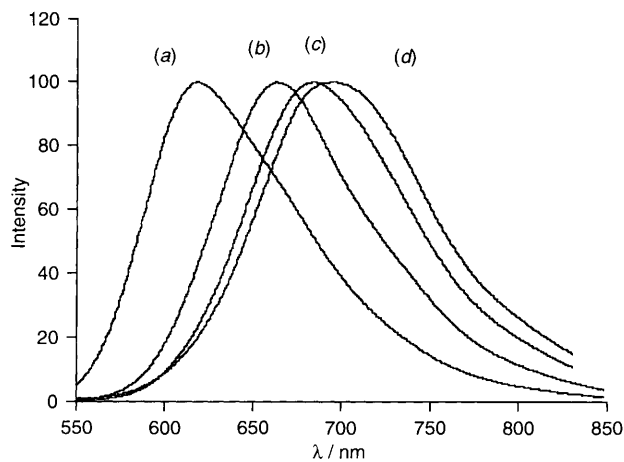
electronic properties and facilitating construction of exotically shaped molecular arrays.[32] Additional structures become possible by varying the ratio of parent and ditopic ligands. Some of the structures attainable with this approach are illustrated in Fig. 3.

Clearly, a plethora of multicomponent molecular systems can be engineered in this way and, because of (i) preferential binding properties, (ii) the use of pre-organized modules, and (iii) the programmed layering of successive molecular units, the resultant metal complexes are amenable to detailed characterization by advanced spectroscopy. Relative to the free ligands the metal complexes are highly soluble in common organic solvents. The applied modality increases the electronic charge resident on the molecule at each step in the synthetic scheme. This provides for easy chromatographic separations and ensures that electrospray mass spectrometry is indispensable for proper analysis.[33]

This piecewise synthetic approach, although tedious in operation, permits systematic variation of nuclearity, electronic spin, magnetic susceptibility, molecular polarizability, dipole moment, colour, and conductivity. The size, shape and solubility of the molecule can be easily modulated. In turn, these changes are reflected in marked variations in the magnetic, electrochemical and photochemical properties. The compounds are now being investigated with respect to their possible use as *molecular magnets, selective sensors, homogeneous catalysts*, and *optical relays or switches*. A key feature of each potential application concerns the level of electronic communication along the carbon wire.

Fig. 4 Normalized luminescence spectra recorded in acetonitrile at 22 °C for (a) $[Ru(bpy)_3]^{2+}$, (b) corresponding mononuclear form of **16** with $n = 1$, (c) **16** with $n = 1$, and (d) **16** with $n = 2$
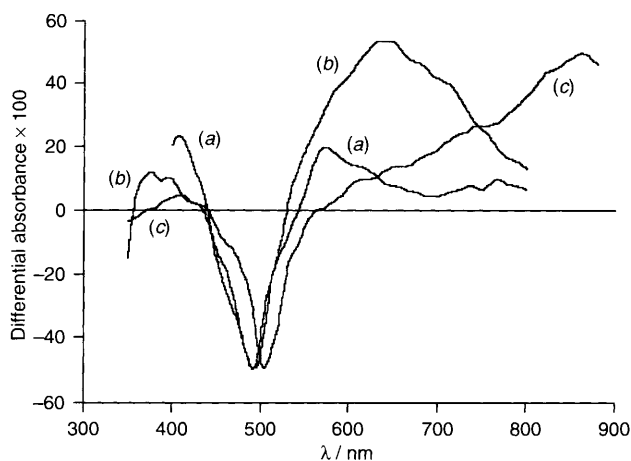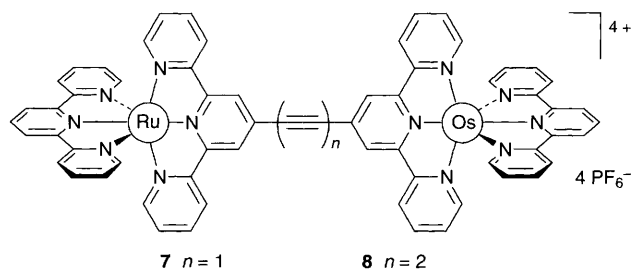

Fig. 5 Differential absorption spectra recorded in deoxygenated acetonitrile at 22 °C for the triplet excited states of (a) $[Ru(terpy)_2]^{2+}$, (b) the corresponding mononuclear form of complex **2**, and (c) **2**

Table 2 Rate constants for photoinduced electron exchange (electron transfer for compounds **14** and **15**) and the appropriate energy gaps measured in acetonitrile solution at 22 °C
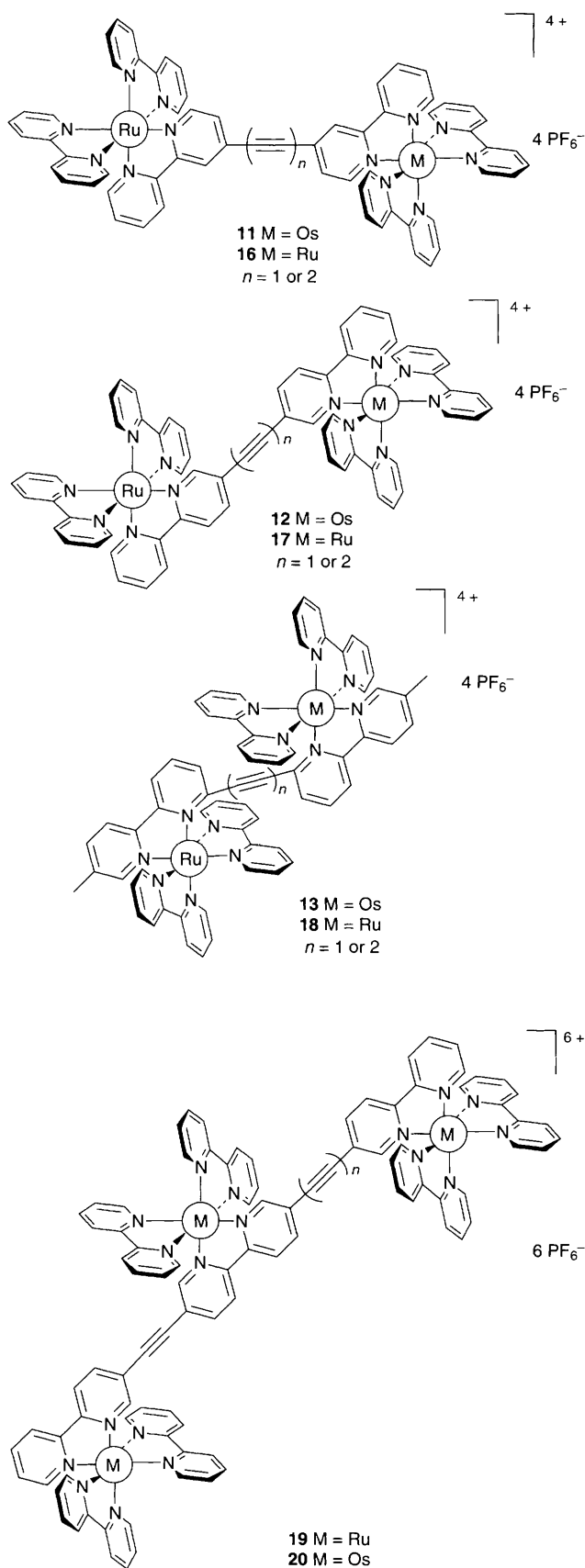
Compound	n^a	$10^{-7}\ k^b/s^{-1\,b}$	$\Delta E^c/eV$	$R_{MM}{}^d$	M/M'^e
7	1	7 100	0.13	1.38	Ru/Os
8	2	5 000	0.11	1.62	Ru/Os
9	1	8 300	—	1.52	Ru/Fe
10	2	6 250	—	1.78	Ru/Fe
14	1	16 700	0.37	1.50	Ru/Co
15	2	12 500	0.37	1.75	Ru/Co
11	1	2 500	0.34	1.38	Ru/Os
12	1	2 700	0.37	1.25	Ru/Os
13	1	1 780	0.45	0.91	Ru/Os
21	2	1.3	0.35	1.92	Ru/Os
22	2	1.0	0.35	1.37	Ru/Os

^{a} Number of ethynyl groups in the bridge. ^{b} rate constant, ±10%. ^{c} Energy gap, ±0.02 eV. ^{d} Metal-to-metal separation, ±0.01 nm. ^{e} Nature of the metal centres.

Scheme 5

7 $n = 1$ **8** $n = 2$
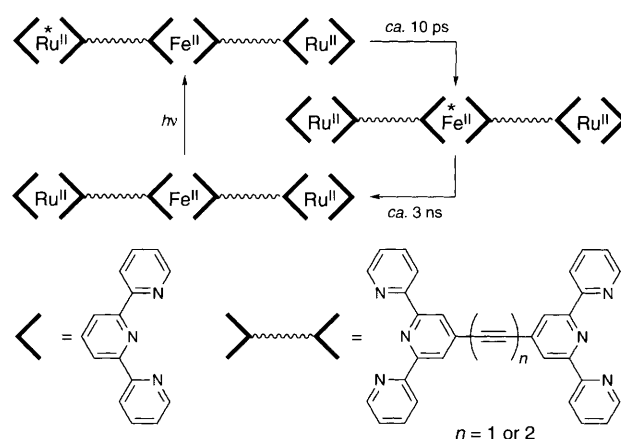
Propagation of electrons along the wire

The first intimation that alkyne substituents might provide highly beneficial, and even therapeutic, properties when used in conjunction with metal oligopyridine complexes came from our observation[25] that the triplet lifetimes (τ_T) of certain alkyne-

11 M = Os
16 M = Ru
n = 1 or 2

12 M = Os
17 M = Ru
n = 1 or 2

13 M = Os
**18** M = Ru
n = 1 or 2

19 M = Ru
20 M = Os

bridged, binuclear ruthenium(II) terpyridyl-based complexes were greatly prolonged with respect to bis(2,2':6',2''-terpyr-idyl)ruthenium(II),[Ru(terpy)₂]²⁺. In deoxygenated acetonitrile solution at 22 °C, the triplet lifetimes of 1 and 2 exceed that of [Ru(terpy)₂]²⁺, by a factor of about 3000 (Table 1). This has the effect of converting a poor photosensitizer into a viable one. The same effect is apparent in trinuclear complexes gathered around a central zinc(II) cation,[34] as in 5 and 6, in the corresponding 2,2'-bipyridyl-based complexes[35] and when the Ru[II] cation is replaced by Os[II]. It is clear that this is a general phenomenon caused by introduction of the alkynyl moiety. However, inserting a phenyl ring between terpyridyl ligand and alkyne bridge,[25] forming 3 and 4, curtails the enhancement in triplet lifetime (Table 1).

In these various complexes the alkyne substituent induces a substantial red shift in the emission maximum (λ_{EM}), indicative of a lower triplet energy (Fig. 4), and pushes the half-wave potential for one-electron reduction of the ligand (E'_{red}) to a more positive value (Table 1). The latter effect ensures that the ditopic ligand is reduced in preference to the parent ligand(s) and that the lowest-energy triplet state, being of metal-to-ligand charge transfer (MLCT) character, is formed by charge injection from metal cation to the bridging ligand. Lowering of the triplet energy inhibits mixing between the MLCT triplet and any higher-energy metal- or ligand-centred excited states.[36] This decoupling of the states is largely responsible for the observed prolongation of the triplet lifetime, especially for the terpyridyl-based complexes. At 77 K and for the lower-energy osmium(II) complexes there is a residual enhancement in triplet lifetime, when due allowance is made for the lower triplet energy,[25] corresponding to a factor of three- to five-fold, that cannot be explained in terms of decoupling of triplet states. This latter stabilization is attributed to electron delocalization over an extended π* orbital that encompasses much of the ditopic ligand.[37] Electron delocalization reduces nuclear displacement between ground and triplet states, since there are more skeletal vibrational modes to accommodate the photonic energy, and thereby decreases the electron–vibrational coupling constant that controls the rate of nonradiative deactivation of the triplet state.

A characteristic feature of these alkyne-substituted complexes is that the triplet absorption spectrum contains an intense band in the far-red region,[25,35] as illustrated in Fig. 5. It can be seen that the triplet differential absorption spectra exhibit weak absorption bands in the UV region, due to the π-radical anion of the ligand, and bleaching of the ground-state MLCT absorption band centred around 460–500 nm. In the parent complex [Ru(terpy)₂]²⁺ there is only weak, indistinct absorption across the red region of the spectrum arising from d–d transitions associated with the Ru[III] centre formed by way of MLCT. For the alkyne-substituted complexes,[25] there are additional absorption bands at longer wavelength which arise because of selective charge injection into the ditopic ligand and, therefore, are assignable to the corresponding π-radical anions.

Apart from stabilizing the triplet state, electron delocalization, by pushing electronic charge along the molecular axis, might facilitate electron- and/or hole-transfer reactions. This hypothesis was tested[38] using alkyne-bridged Ru[II]/Os[II] mixed metal complexes, 7 and 8. It was observed that triplet energy transfer from the ruthenium(II) complex to the appended
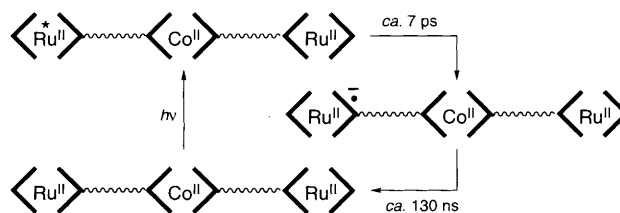
Scheme 6

osmium(II) complex was quantitative in these systems, occurring on a time scale of *ca.* 25 ps (see cover). These processes are among the fastest ever resolved for intramolecular triplet energy transfer and, because reaction must occur by way of through-bond electron exchange, they attest to the remarkable superexchange properties of the carbon bridge. It should be noted that electron exchange requires concomitant transfer of an electron and a positive hole, with the latter process taking place between the metal centres.

Comparing the rate of electron exchange (k) across one and two ethynyl groups (Table 2) allows estimation of the attenuation factor (β) for energy transfer through alkyne bridges as being of the order of 0.17 Å^{-1} [eqn. (1)]

$$k = AH_{DA}^2 \exp[-\beta R] \qquad (1)$$

Here, A is a pre-exponential factor, H_{DA} is the electronic coupling matrix element for reactants in orbital contact, and R is the length (in Å) of the bridge. This is a rather small value when compared to most other bridging media; for example, electron transfer has been monitored in alkenes ($\beta \approx 0.06$ Å^{-1}),[39] aromatic hydrocarbons ($\beta \approx 0.4$ Å^{-1}),[40] proline groups ($\beta \approx 0.7$ Å^{-1}),[41] fused alkanes ($\beta \approx 0.6$–1.0 Å^{-1}),[42] DNA ($\beta \approx 0.9$ Å^{-1}),[1] and proteins ($\beta \approx 1.7$ Å^{-1}).[43] Subsequently, the ability of alkyne spacers to facilitate electron exchange by way of a superexchange mechanism[34] was confirmed with the corresponding Ru^{II}/Fe^{II} mixed-metal systems, **9** and **10** (Scheme 5).

Intramolecular triplet energy transfer takes place[44] in the corresponding 2,2'-bipyridyl-based Ru^{II}/Os^{II} mixed-metal complexes **11–13** (Table 2). This is an interesting system because the triplet energy gap can be varied simply by changing the position at which the ethynyl group is attached to the 2,2'-bipyridine ligand. Furthermore, the reorganization energy that accompanies energy transfer is less than the triplet energy gap, such that energy transfer occurs within the Marcus 'inverted region'. Our observation that the rate of triplet energy transfer does not decrease significantly with increasing triplet energy gap is contrary to conventional Marcus theory.[45] In the linear trinuclear complexes **19** and **20** triplet energy transfer from

peripheral to central complexes is quantitative, despite the modest energy gaps.

Our understanding of electron exchange in such alkyne-bridged metal complexes[46] is that electron transfer between the terminal coordination sites of the ditopic ligand is facilitated by electron delocalization over the ditopic ligand within the triplet excited state. Hole transfer between the metal centres, which must take place *via* HOMOs localized on the ditopic ligand, might be the limiting step since this occurs over larger distances and involves interaction between d, sp^2, and sp orbitals. This viewpoint was strengthened by transient spectroscopic measurements[34] made with the Ru^{II}/Co^{II} mixed-metal systems, **14** and **15**, in which we were able to isolate the electron- and hole-transfer steps (Scheme 6). Thus, laser excitation into the Ru^{II} subunit generates the localized triplet excited state which rapidly abstracts an electron from the appended Co^{II} centre by way of a hole-transfer process (Fig. 6). The attenuation factor for this step is *ca.* 0.12 Å^{-1} and the reaction occurs on the time scale of a few ps. Charge recombination to restore the original ground-state system occurs more slowly by way of electron transfer (Fig. 6) and is characterized by a β value of only *ca.* 0.04 Å^{-1}. These studies are entirely consistent with the notion that electron transfer along the carbon wire is hardly attenuated with increasing length of the alkyne bridge. There is a larger attenuation for hole transfer but even so the derived β is rather small, presumably because the energy of HOMO states on the ditopic ligand decreases with increasing length of the alkyne bridge due to conjugation. This is a form of *positive cooperativity* and further augments the electronic properties of carbon bridges.

The occurrence of rapid triplet energy transfer, aided by electron delocalization, in these complexes raises the possibility for engineering molecular arrays capable of efficient energy migration over extended distances. Interest in such systems is stimulated by recent structural determinations of photosynthetic light-harvesting complexes[47] and by the realization that these natural antennae effectively delocalize the photon over a large number of spatially remote, chemically identical pigments. Transient depolarization measurements made with the symmet-
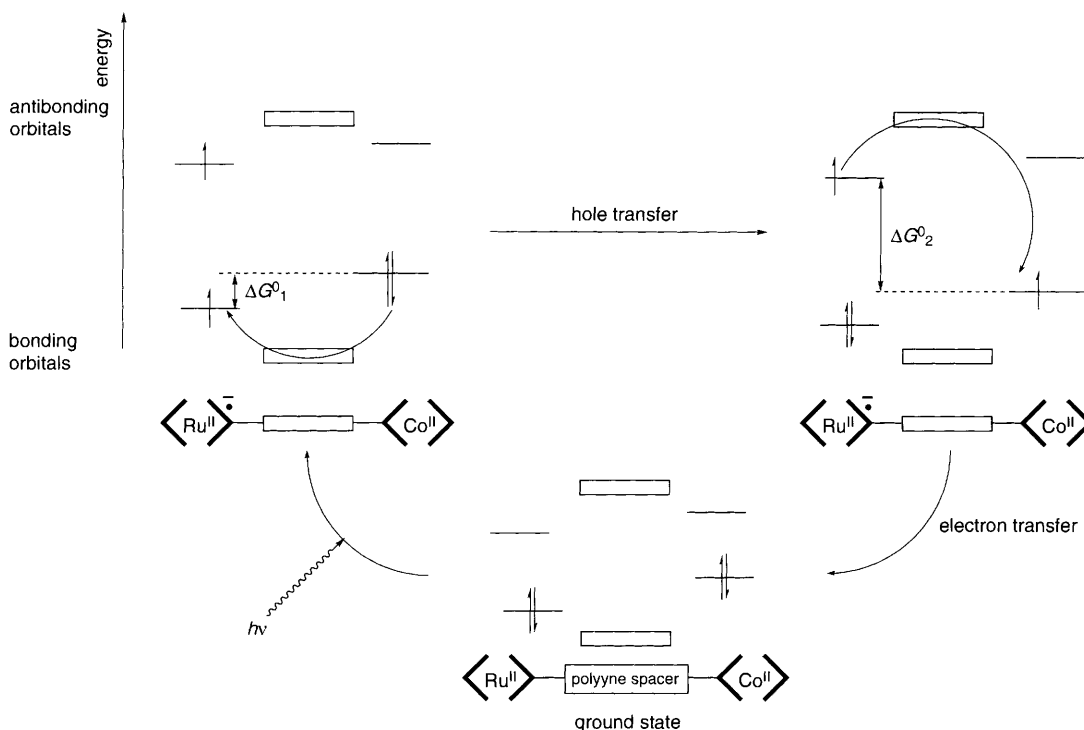

Fig. 6 Frontier molecular-orbital diagram showing light-induced hole transfer from the Co^{II} centre (through HOMOs on the bridge) to the triplet excited state of the ruthenium(II) complex followed by electron transfer from the π-radical anion of the ruthenium(II) complex (through LUMOs on the bridge) to the Co^{III} centre, thereby restoring the original ground state of the compound. $\Delta G^0_1 = -0.37$ eV and $\Delta G^0_2 = -1.75$ eV.

rical binuclear complexes **16–18** in low-temperature glassy matrices indicate that triplet energy migration occurs between the terminal metal complexes on the time scale of *ca.* 1 ns. Thus, the photon shuttles between the chromophores several thousand times within the triplet lifetime.

Interrupting electron flow

A major concern in the development of *intelligent molecular arrays* is the insertion of a bridge that can both direct electron flow and function as a switch to alternate that flow. We have
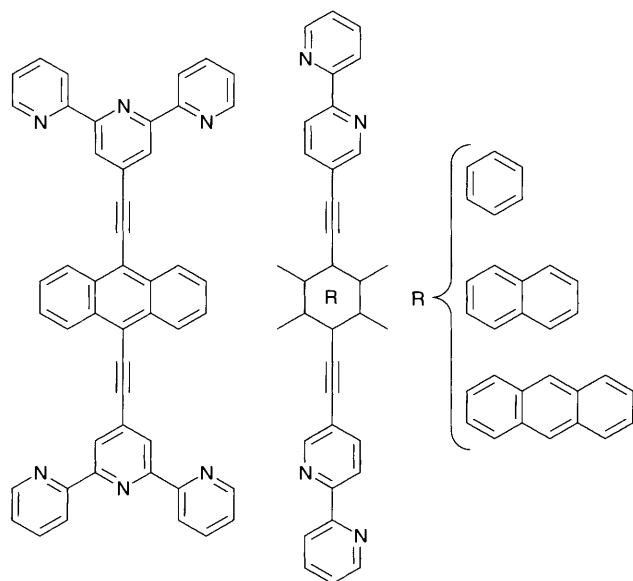

Fig. 7 Ditopic terpyridine or bipyridine ligands bridged by ethynyl-substituted phenyl, napththalene or anthracene subunits

seen[25] that the presence of a phenyl ring between ligand and bridge severs electron delocalization along the wire. This insulation may reflect restricted electronic coupling between antibonding orbitals localized on the phenyl ring and on the acetylenic function. In an effort to benefit from this electronic insulation, other aryl hydrocarbons have now been incorporated into the bridge (Fig. 7). The energy levels of such attributes are easily changed by fusing additional aryl rings to the nucleus and, therefore, it becomes possible to tune the electronics such that the central unit can operate as a relay for triplet energy transfer between terminal metal complexes. This is the case with anthracene and the 2,2′-bipyridyl-based metal complexes, where the triplet level of the relay (175 kJ mol⁻¹) lies intermediate between that of the Ruᴵᴵ donor (195 kJ mol⁻¹) and the Osᴵᴵ acceptor (160 kJ mol⁻¹). This latter system demonstrates unidirectional triplet energy transfer by way of a small cascade of individual steps, each of which is optimized with respect to matching the energy gap with the reorganization energy accompanying transfer.

A different approach to modular engineering involves the precise positioning of prefabricated units around a *metallo-synthon* formed from bis(trialkylphosphine)platinum(ii) complexes.[48] Here, σ coordination of alkyne groups to the Ptᴵᴵ core allows formation of linear **21** or 'L-shaped' **22** multicomponent structures incorporating various complexation domains. Indeed, we have used this methodology to construct binuclear, homotrinuclear, heterotrinuclear and heptanuclear complexes. It is noteworthy that the resultant complexes are kinetically stable in solution, resistant to thermal and photochemical isomerization, and photoactive. The same strategy has been used to prepare ruthenium(ii) complexes equipped with peripheral light-harvesting units comprising metalloporphyrins or aryl hydrocarbons (Scheme 7).

The central Ptᴵᴵ unit has a dramatic effect on the electronic properties of the bridge as can be seen by comparing the rates of intramolecular triplet energy transfer[49] in the linear complexes

21

22
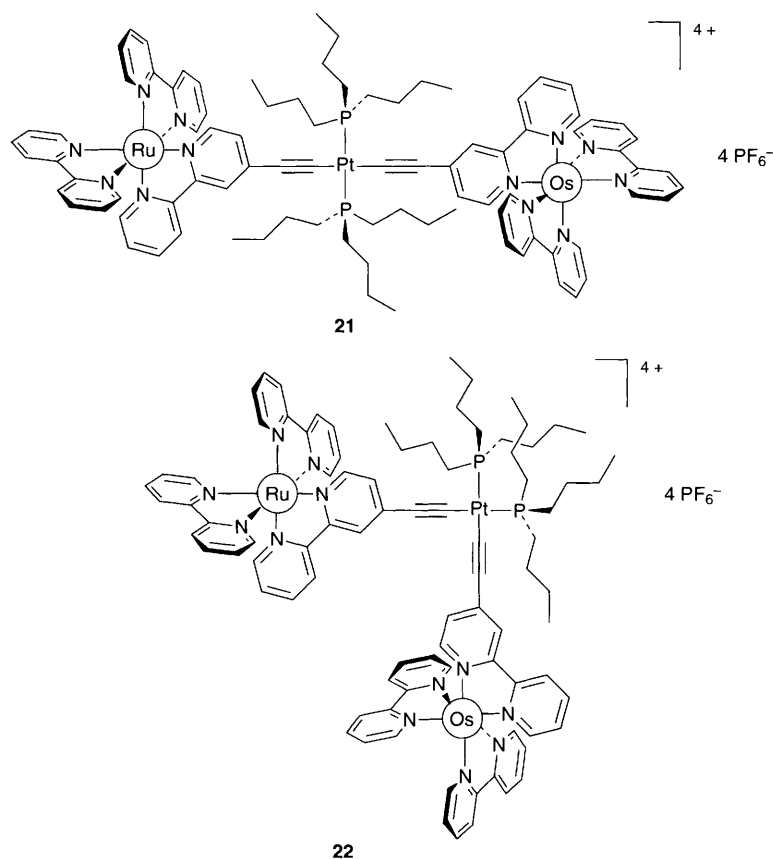
8 and 21. The metal-to-metal separation distances are comparable in the two cases but energy transfer occurs about 3000-fold faster in the absence of the Pt^{II} unit (Table 2). The rate is slightly slower for the *cis* isomer 22 than for the *trans* analogue 21, despite the shorter metal-to-metal separation. This is because through-bond electronic coupling is more pronounced in the *trans* isomer such that electron exchange contributes to the overall energy-transfer process. Such units, especially with the *cis* configuration, make effective insulators for through-bond electron-transfer processes.
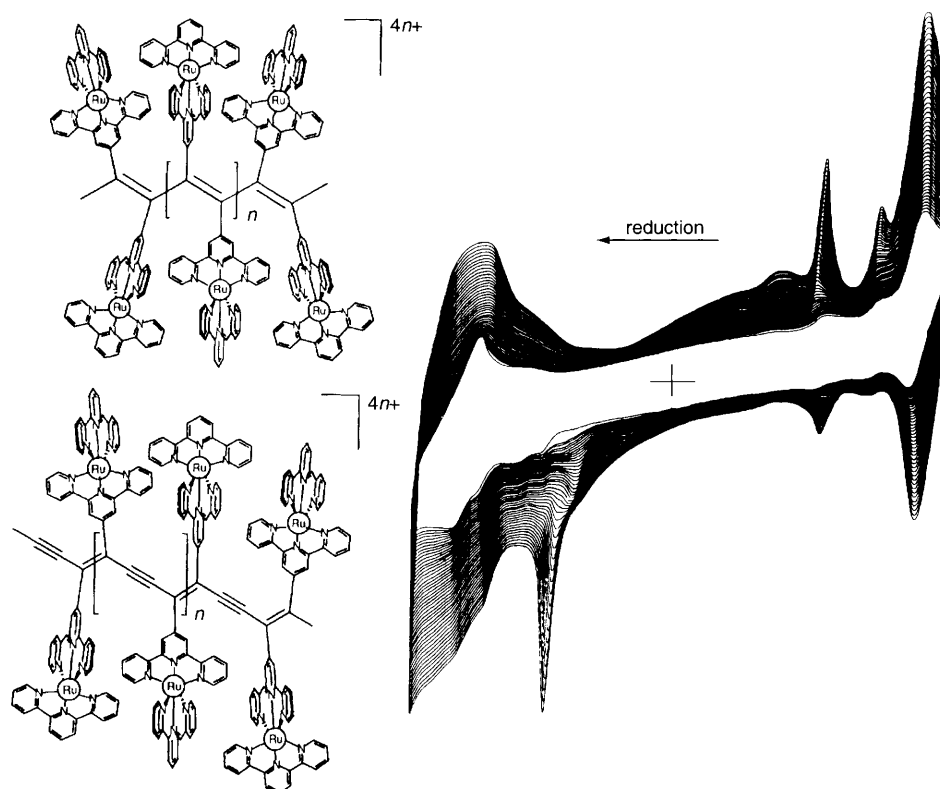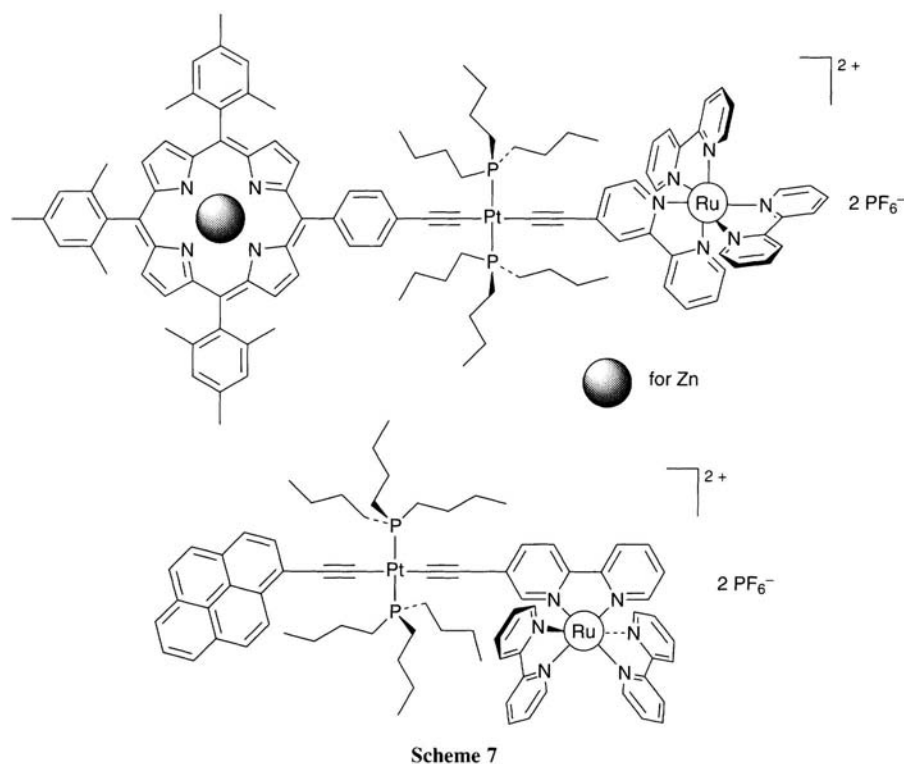

Scheme 7

Fig. 8 Cyclic voltammograms recorded in deoxygenated anhydrous acetonitrile at a scan rate of 200 mV s^{-1} at a Pt electrode showing the initial sweep and the next 45 successive scans between −1.6 and +1.7 V for complex 1. Similar electrochemistry persists after removal of the modified electrode and immersion in fresh electrolyte. Polymerization efficiency is 5% while surface coverage after 3 scans is 1 × 10^{-8} mmol cm^{-2}. Idealized structures of the polymers formed from 1 and 2 are also shown.

Electropolymerization

During reductive electrolysis of certain ethynyl-substituted mono-, bi- (*e.g.* **1**, **2**) or tri-nuclear (*e.g.* **5**, **6**, **9**, **10**, **14**, **15**) ruthenium(II) complexes in anhydrous acetonitrile the electrode surface becomes coated with a dark-red, air-stable, strongly adherent polymeric film. These films, which are highly conductive molecular arrays, are due to *in situ* electropolymerization and consist of polyacetylene or polydiacetylene polymers (Fig. 8). Polymerization occurs only if the electrode-active species contains a coordinated terpyridine moiety.[50] Thus, the 2,2'-bipyridine complexes **16**, having one or two ethynyl groups, undergo a series of reversible reductive steps, each corresponding to addition of an electron to the ligands, but do not polymerize. Complexes **1** and **2**, on the other hand, undergo facile polymerization, permitting growth of thick films. The need for a complexed terpyridine unit becomes apparent by considering the contrasting electrochemical behaviour of the mixed-ligand systems **23** and **24**. Thus, **23** does not polymerize but **24** readily forms a polymeric microstructure. The polymerization process is a further reflection of electron delocalization over an extended π* orbital in the corresponding π-radical anions. These films demonstrate no useful photoreactions because of extremely strong electronic coupling between the
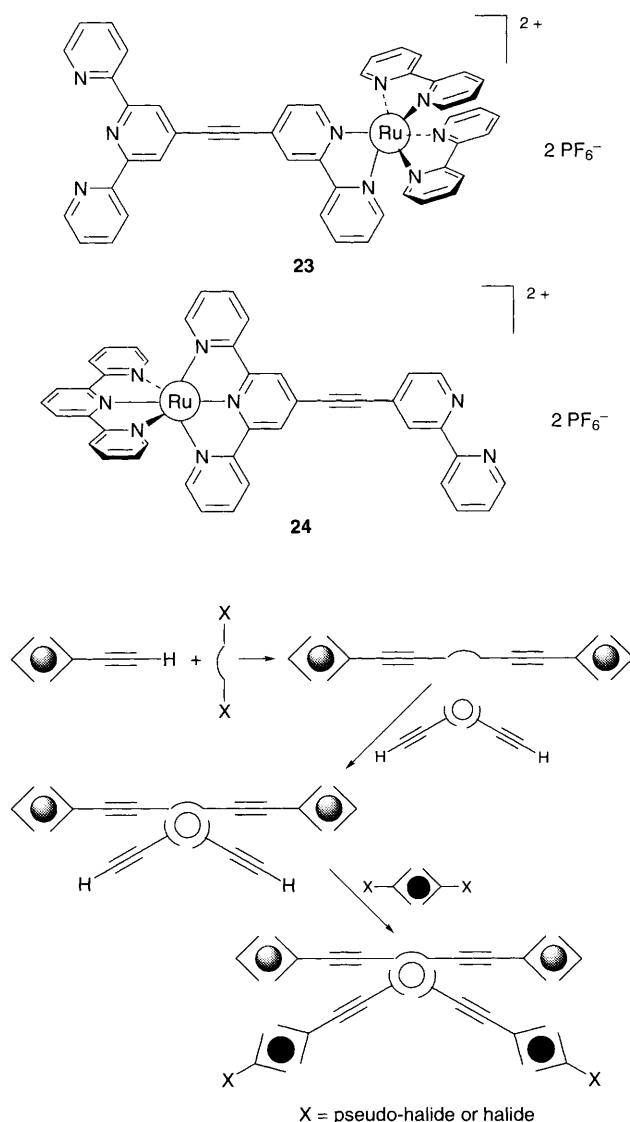

23

24

X = pseudo-halide or halide

Fig. 9 General synthetic strategy proposed for the preparation of polynuclear metal complexes

metal centres and/or severe steric crowding around the conjugated polymeric backbone.

Future trends

An essential point of our work concerns the design of photoactive molecular-scale wires possessing the highest possible H_{DA} and the lowest β, according to eqn. (1). With respect to electron transfer through LUMO levels localized on the bridge, our measured β value (β ≈ 0.04 Å^{-1}) is the lowest for any reported medium. Hole transfer is more attenuated in our particular systems, probably because of restricted coupling between d and π* orbitals. Current work intended to improve hole transfer concerns direct attachment of the carbon bridge to the metal centre,[51,52] with omission of the polypyridino ligand. The nature of the metal cation itself perturbs the degree of mixing between orbitals localized on ligand and bridge, because of its charge-transfer characteristics, and we have noted marked variations in the extent of electron delocalization for complexes formed from different transition metals. This property might be useful for designing systems having optimized rates of forward and reverse electron-transfer steps.

Molecular orbital calculations, supported by optical studies, indicate that the band gap between the HOMO and LUMO levels on polyynes capped with terminal phenyl rings decreases with increasing length of the chain. In particular, the HOMO level is very sensitive to the number of ethynyl groups in the bridge. The triplet energy shows a corresponding dependence on chain length and, relative to ruthenium(II) polypyridine complexes, becomes a definite problem when the chain comprises four or more ethynyl groups. At this point the bridge competes with terminal metal complexes for both triplet energy and oxidation equivalents. Orbital mixing between chromophore and bridge provides an excellent route for rapid non-radiative deactivation of the excited state[76] and prohibits development of a cascade of electron- or energy-transfer events along the molecular axis. Since it is highly desirable to use chromophores that absorb and emit in or around the visible region we must seek additional ways to prevent the HOMO level of the bridge from dropping too low. This can be done most easily by incorporation of other components into the bridge that tune the energetics to the required level. In turn, this sophisticated approach to molecular construction provides an opportunity to introduce unidirectional switches into the wire that promote the forward reaction but inhibit the inherent reverse process.

Preparation of advanced multicomponent materials, being both more complicated and more sophisticated than current analogues, will require the development of new synthetic strategies. In particular, a *molecular clothesline* of the type discussed here needs to be able to coordinate different metal cations at predetermined binding sites along the wire. This cannot be done, at least in an efficient manner, simply by exposing a multitopic ligand to a mixture of preformed cation-containing molecular fragments. The latter methodology is adequate for construction of ordered networks having regularly spaced entities but lacks the necessary specificity allowing the introduction of sequential redox asymmetry into the chain. Instead, the step-by-step construction of intricate, polynuclear molecular systems demands the programmed grafting of successive modules onto a carefully designed core. Thus, the use of functionalized metallo-synthons bearing one or more ethynyl or pseudohalide groups in conjunction with non-complexed oligopyridino ligands in Heck-type cross-coupling reactions provides access to novel polynuclear materials retaining vacant coordination sites. These sites can be selectively complexed with appropriate metal complexes that possess the necessary functionality to continue the synthetic sequence and/or to change the geometry. Further iteration of complexation/cross-coupling reactions provides the means by which to extend the array and to incorporate desired metallo

centres (Fig. 9) as long as the individual units are kinetically stable and the emerging chain can be properly characterized. Results from our laboratory support the contention that this programmed layering approach can be used successfully to generate logically arranged and appropriately shaped poly-nuclear complexes capable of rapid transfer of information between individual compartments.

Acknowledgements

Professor Anthony Harriman received a Ph.D. in photochemistry from the C.N.A.A. in 1974 for research conducted at Wolverhampton Polytechnic before joining the group of Lord George Porter Q.M. at the Royal Institution of Great Britain. He remained at the Royal Institution as Assistant Director of Research for 14 years before becoming Director of the Center for Fast Kinetics Research at the University of Texas at Austin. His main research interest is in the area of *artificial photosynthesis*.

Dr Raymond Ziessel gained a Ph.D. in organic chemistry from the University Louis Pasteur of Strasbourg under the supervision of Professor J.-M. Lehn and Dr J.-P. Sauvage. In 1982 he was appointed to the Centre National de la Recherche Scientifique (CNRS). After postdoctoral research at the University of California, Berkeley (with Professor R. G. Bergman), he moved in 1991 to the Engineer School of Chemistry (ECPM) in Strasbourg, where he is the Director of the Laboratoire de Recherche de Chimie, d'Electronique et de Photonique Moléculaires. His research interests cover many aspects of *molecular chemistry* and applications to *molecular electronics, molecular materials, catalysis and molecular detection*. His synthetic work concerns the design of intricate molecular architectures specific for efficacious energy transfer in transition-metal or lanthanide complexes, to exhibit ferromagnetic interactions in open-shell free radicals, to recognise and detect guest species either electrochemically or by EPR techniques. Recent interests focus on the preparation of novel *liquid crystals* and of *metallo-polyacetylenes*.

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