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Transition-metal complexes of 4′(4-anilino)-2,2′ : 6′,2″-terpyridine (and derivatives): versatile building blocks for construction of metallooligomers and macromolecules†

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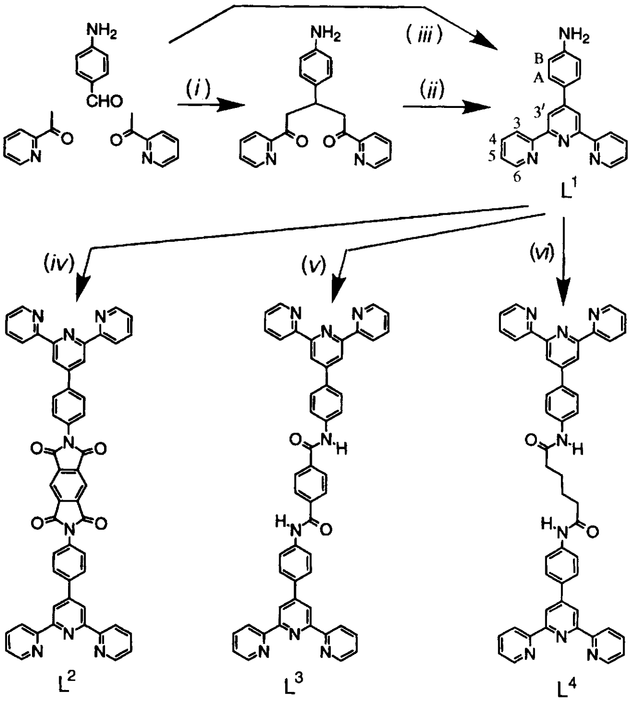
Transition-metal complexes of 4′(4-anilino)-2,2′ : 6′,2″-terpyridine have been prepared and used to construct co-ordination dimers and polymers linked by new binucleating terpyridine ligands.

There is burgeoning interest in supramolecular oligomers and polymers incorporating transition metal terpyridyl complexes as electroactive or luminescent subunits.[1-4] We report herein preliminary results demonstrating that transition-metal complexes of the new ligand 4′(4-anilino)-2,2′ : 6′,2″-terpyridine (L^1) are readily prepared, exhibit a wide variety of chromophoric, electrochemical and magnetic properties, and are excellent building blocks for the construction of metallooligomers and macromolecules.

Scheme 1 summarises the synthesis of L^1.‡ Poly(1,4-aminobenzaldehyde) could be used instead of the monomer in the direct synthesis without loss of yield. Reactions of amines have been extensively used in the construction of supramolecular systems[5] and macromolecules,[6] and, in principle, the amine functionality in L^1 should be readily elaborated using standard organic techniques and appropriate reagents (*e.g.* with organic acid chlorides to amides or with aryl diacid anhydrides to imides) making L^1 a convenient source of any number of new terpyridyl ligands, including ligands with multiple terpyridyl groups. As a test, three new binucleating ligands, L^2–L^4,§ were prepared by coupling 2 equivalents of L^1 with the appropriate difunctional reagent,[7,8] Scheme 1.

There are two routes to supramolecular oligomers based on transition-metal complexes of L^1: either (*a*) first coupling two or more L^1 with a multifunctional organic reagent to give a multinucleating ligand with two or more terpyridyl groups (*e.g.* the preparations of L^2–L^4) and then treating this ligand with metal-ion sources or (*b*) linking preformed complexes of L^1 with the same multifunctional organic reagent. To demonstrate both routes [(*a*) and (*b*)], the construction of three binuclear ruthenium(II) complexes, $[(terpy)Ru(L–L)Ru(terpy)]^{4+}$ (**1**–**3**: L–L = L^2–L^4, respectively; terpy = 2,2′ : 6′,2″-terpyridine), was investigated. Heating $[Ru(terpy)Cl_3]$ (2 equivalents) and either of L^2 or L^4 in ethane-1,2-diol or L^3 in *N*,*N*-dimethylacetamide at reflux gave complexes **1**–**3** in 44, 48 and 41% yield, respectively.§ Alternatively, complex **1** was obtained from $[Ru(terpy)L^1]^{2+}$ {from $[Ru(terpy)Cl_3]$ and L^1 in aqueous ethanol–triethylamine at reflux; 55% yield} and pyromellitic dianhydride (1*H*,3*H*-benzo[1,2-*c* : 4,5-*c*]difuran-1,3,5,7-tetrone) in dimethylacetamide at reflux, followed by pyridine–acetic anhydride (1 : 2) to effect cyclodehydration[7] in 40% yield, and complex **2** was obtained from $[Ru(terpy)L^1]^{2+}$ and terephthaloyl chloride in dimethylacetamide–pyridine at reflux[8] in 44% yield. The $[Ru(terpy)_2]^{2+}$ ion was a product in all of the above reactions. Consequently, ligand redistribution had occurred, and this and the chromatography [silica support, 20 : 2 : 1 acetonitrile–saturated KNO_3(aq)–water eluent] necessary to separate these products, combine to reduce the overall yield.

Electronic spectra of the dimers reveal a collection of high energy bands ascribable to ligand n–π* or π–π* transitions and a broad metal-to-ligand charge-transfer (m.l.c.t.) band at 485, 486 and 484 nm for complexes **1**–**3**, respectively, with absorption coefficients approximately twice that of the m.l.c.t. band at 491 nm for $[Ru(terpy)L^1]^{2+}$.[2,3,9] Fig. 1 presents representative cyclic voltammograms of complexes **1**–**3** with assignments for the redox processes. Each dimer shows a combination of the redox processes expected for two electrochemically isolated $[Ru(terpy)(X\text{-}terpy)]^{2+}$ (X-terpy = 4-substituted 2,2′ : 6′,2″-terpyridine ligand) centres (one Ru^{III}–Ru^{II} couple at *ca.* 0.8 V and two X-terpy–X-terpy$^{\bullet -}$ couples at *ca.* −1.7 and −1.9 V, all with two-electron peak currents) and for the intervening organic linkage[10] [**1**: an irreversible oxidation at 0.65 V and two reversible one-electron reductions



Scheme 1 (*i*) NaOH(aq), EtOH, 24 h; (*ii*) NH_4O_2CMe, EtOH, heat, 4 h [yield 14% overall for steps (*i*) and (*ii*)]; (*iii*) NH_4O_2CMe, acetamide, heat, 2 h; NaOH(aq), heat, 2 h; $MeCO_2H$, HBr; $NaHCO_3$, $CHCl_3$ (23%); (*iv*) pyromellitic dianhydride, dimethylacetamide, 18 h; pyridine, acetic anhydride, 1 h (91%); (*v*) terephthaloyl chloride, dimethylacetamide, pyridine, 2 h (70%); (*vi*) adipoyl chloride, dimethylacetamide, pyridine, 120 °C, 2 h (73%)

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† *Non-SI units employed:* $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}; Da ≈ 1.66×10^{-27} kg.

‡ Found: C, 77.70; H, 5.15; N, 17.00. Calc. for $C_{21}H_{16}N_4$: C, 77.80; H, 4.95; N, 17.30%). Electron-impact MS: 324 (M^+), 246 ($M^+ - C_5H_4N$). IR (Nujol mull): $\nu(NH_2)$ 3400m (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.73 (br d, *J* = 4.6, H^6), 8.69 (s, $H^{3'}$), 8.66 (d, *J* = 8.0, H^3), 7.87 (td, *J* = 7.7, 1.8, H^4), 7.78 (d, *J* = 8.5, H^A), 7.34 (ddd, *J* = 7.7, 4.7, 1.2, H^5), 6.80 (d, 2 H, *J* = 8.5 Hz, H^B), 3.90 (br s, NH_2).

§ All new compounds have been characterised by elemental analyses (C, H, N), by IR, UV/VIS, ^1H NMR and electron-impact (L^2–L^4) or electrospray (monomers and dimers) mass spectroscopies, by magnetic moment determinations both in the solid state (Gouy method) and in acetone solution (Evans method), and by cyclic and differential pulse voltammetries, and gave data in accord with their postulated structures.

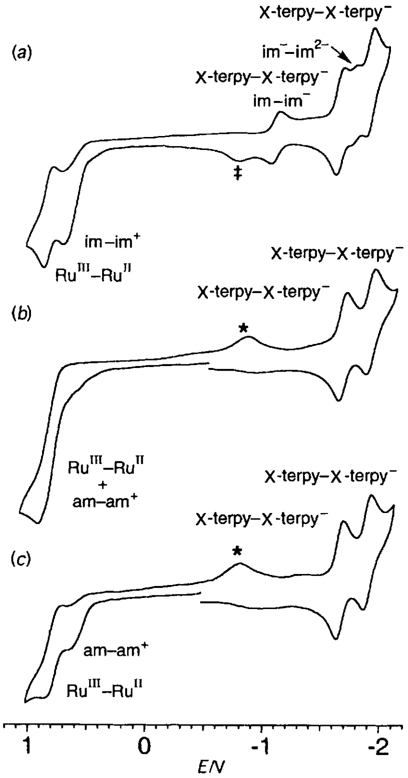

Fig. 1 Cyclic voltammograms (potentials *vs.* internal ferrocenium–ferrocene) at a platinum disc electrode of *ca.* 1 mmol dm^{-3} solutions of (*a*) [(terpy)Ru(L^2)Ru(terpy)]$^{4+}$ **1**, (*b*) [(terpy)Ru(L^3)Ru(terpy)]$^{4+}$ **2**, (*c*) [(terpy)Ru(L^4)Ru(terpy)]$^{4+}$ **3** in acetonitrile (0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate). ‡ Peak arises after the imide anion–dianion couple (im$^-$–im^{2-}) is traversed. * Peak arises after the amide oxidation (am–am$^+$) is traversed

of the imide linkage (im) at −1.13 and −1.79 V; **2**: irreversible oxidation of the amide linking group (am) at *ca.* 0.9 V (overlaps with the Ru^{III}–Ru^{II} couple); **3**: irreversible amido-centred (am) oxidation at 0.65 V]. We expect interesting photophysical properties for complexes **1**–**3**; a recent study reveals especial stabilisation for the m.l.c.t. excited state when a [Ru(X-terpy)$_2$]$^{2+}$ core is substituted at the two 4′-positions by phenyl substituents,[9] and rigid diimide spacers such as those found in **1** are electron acceptors, as the redox chemistry shows, and thus have the potential to take part in photochemical charge separation processes.[10]

Next we turned to polymers based on [ML$^1{}_2$]$^{n+}$ monomers. Homoleptic terpyridine complexes have been described for a large number of transition metals[11] and using straightforward adaptations of these syntheses we have obtained the monomers [ML$^1{}_2$]$^{n+}$ (M = Co^{II}, Cu^{II}, Fe^{II}, Mn^{II}, Ni^{II}, Rh^{III}, Ru^{II} and Zn^{II}).§ Very good yields (60–85% after recrystallisation) of the first-row transition-metal complexes were obtained. Importantly, the complexes offer a wide range of colours, magnetic, electrochemical and photophysical properties.[11] For example, the colours, the magnetic moments [μ_{eff} (300 K) Evans method] of the paramagnetic complexes, and the $E_{\frac{1}{2}}$ (*vs.* ferrocenium–ferrocene) values for the M^{III}–M^{II} couples of the complexes are: Co, deep maroon, 3.34 μ_B, −0.24 V; Cu, green, 2.36 μ_B, −0.72 V (Cu^{II}–Cu^{I} couple); Fe, deep purple, 0.69 V; Mn, yellow, 5.97 μ_B, 0.82 V; Ni, yellow-brown, 3.34 μ_B; Rh, dark orange, −1.06 V (Rh^{III}–Rh^{I} couple); Ru, red, 0.96 V; Zn, pale yellow. Emission spectra have not been recorded as yet but bis(terpyridyl) complexes of Cr, Ru, Os, Ir and Zn are expected to be luminescent.[2,3,9]

Polymerisations using either route (*a*) or (*b*) to form the homopolymers [{M(L–L)}$_n$]$^{2n+}$ (M = first-row transition metal, L–L = L^2 or L^3) should avoid the problems associated with ligand-scrambling reactions. We investigated the preparations of the iron(II) homopolymers, [{Fe(L^2)}$_n$]$^{2n+}$ **4** and [{Fe(L^3)}$_n$]$^{2n+}$ **5**. Route (*b*): [FeL$^1{}_2$]$^{2+}$ was coupled either with stoichiometric pyromellitic dianhydride in dimethylacetamide at reflux, followed by pyridine–acetic anhydride (1 : 2) to effect cyclodehydration[7] (to give crude **4**) or with terephthaloyl chloride in dimethylacetamide–pyridine at reflux[8] (to give crude **5**). Exhaustive extraction with methanol and with acetone to remove lower molecular weight oligomers, followed by fractional precipitation from dimethylformamide (dmf)–CH$_2$Cl$_2$ afforded **4** in 60–88% yield and **5** in 60% yield.§ The polymers were soluble in high boiling, polar aprotic solvents such as dimethylacetamide, dmf, dimethyl sulfoxide and 1-methyl-2-pyrrolidinone, and in anhydrous trifluoroacetic acid. Cyclic voltammograms of polymers **4** and **5** exhibited poorly reversible couples at +0.56 and +0.54 V respectively corresponding to irreversible oxidation of the organic linking groups overlapping the Fe^{III}–Fe^{II} couples. The UV/VIS spectra of both polymers display a m.l.c.t. band at 578 nm. Meaningful gel permeation chromatography (GPC) measurements of average polymer molecular weight and polydispersity could not be obtained because appropriate GPC standards are not available and the polymers were insoluble in solvents typically used for these measurements.[12] However, the polymerisation of **4** could be quenched by addition of excess acetyl chloride forming acetamide end-groups {independently, [FeL$^1{}_2$]$^{2+}$ was treated with acetyl chloride and formation of the bis(4′-phenyl acetamide) end-capped complex was shown to be quantitative within detectable limits by ^{1}H NMR spectroscopy}, thereby allowing ^{1}H NMR spectroscopic determination of the average degree of polymerisation (DP). A DP of 17.2 which corresponds to an average molecular weight of 18.2 kDa was obtained when the polymerisation was quenched after 16 h. Materials with the same electronic and NMR spectra were also obtained *via* route (*a*) by treating the binucleating ligand (L^2 or L^3) with equimolar amounts of [Fe(H$_2$O)$_6$][BF$_4$]$_2$ in methanol.

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