Bucky-ligands: fullerene-substituted oligopyridines for metallosupramolecular chemistry

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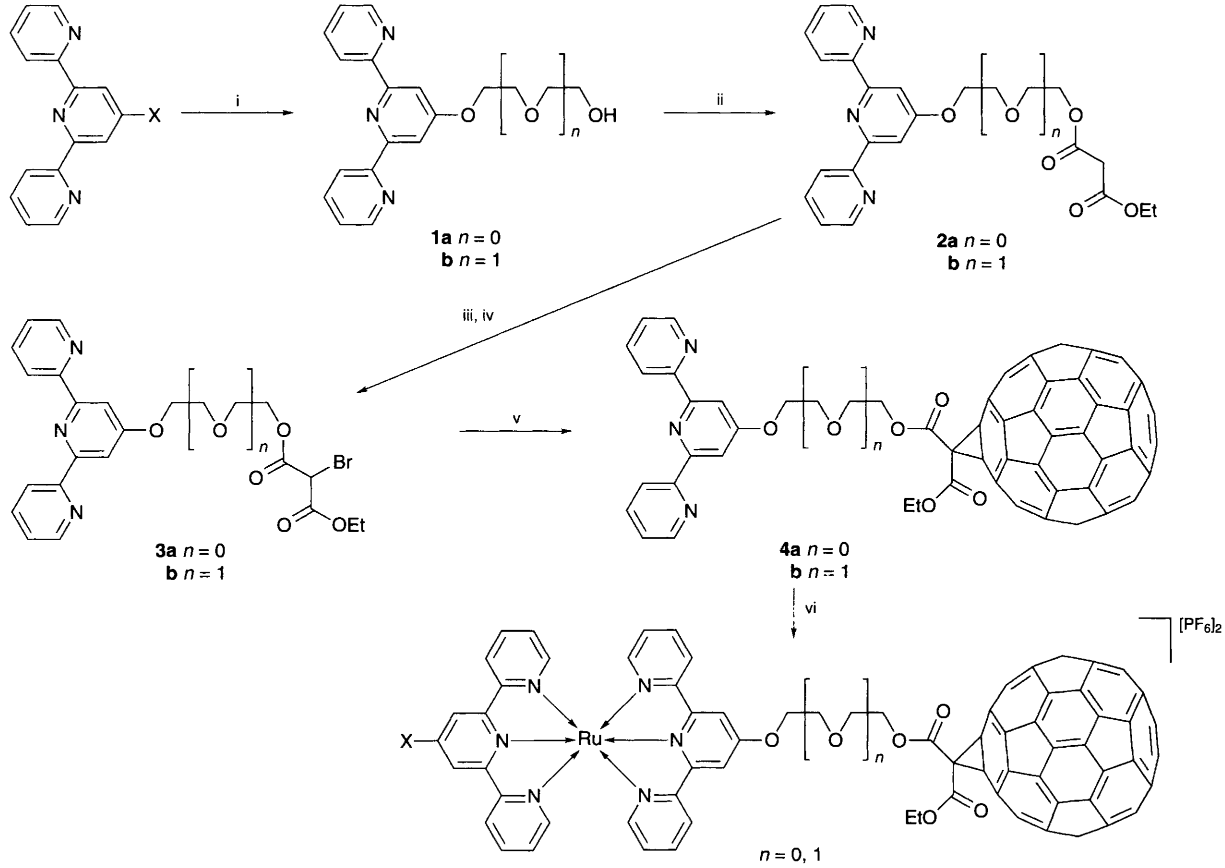
A new series of ligands are prepared in which C_{60} units are attached to 2,2′:6′,2″-terpyridines; ruthenium(II) diads and triads are prepared in which the pendant fullerene acts as an electron acceptor.

Fullerenes possess useful electronic and photochemical properties which make them natural candidates for incorporation into supramolecular photoconversion systems.[1,2] We have recently studied the synthesis and properties of cluster-functionalised 2,2′:6′,2″-terpyridines (tpy) which can undergo coordination-initiated assembly into multifunctional systems[3] and an obvious extension of this work is to fullerenes. A low-yield route to a bis(fullerene)-functionalised rotaxane[4] and a single example of a remote-functionalised ruthenium complex[5] have recently been described and preliminary results indicated significant interactions between the pendant fullerenes and metal-based photocentres. We now describe a convenient and versatile synthesis of fullerene-substituted tpy ligands and present preliminary data concerning coordination triads incorporating such electron acceptors.

We decided to incorporate polyethyleneoxy spacers between the tpy metal-binding domain and the fullerene to allow a series of compounds with variable metal–fullerene distances to be prepared. The synthetic routes leading to the two fullerene-functionalised ligands **4a** and **4b** are presented in Scheme 1. The key malonate derivatives **2a** and **2b** were prepared in 47 and 57% yield in two steps from the known compounds 4′-$MeSO_2$tpy[6] and 4′-HOtpy[7] respectively. The synthetic utility of the metal-activated nucleophilic displacement[8] reaction of 4′-$MeSO_2$tpy is of note: the facile removal of iron as hydrated oxide[9] after treatment with alkaline hydrogen peroxide leads to an extremely simple workup. Esterification of the glycol intermediates **1a** and **1b** with EtO_2CCH_2COCl gave the malonates **2a** and **2b** in 70% yield. These compounds were



Scheme 1 *Reagents and conditions:* i, $n = 0$, X = SO_2Me. (*a*) $FeCl_2$, $HOCH_2CH_2OH$, (*b*) H_2O_2, NaOH (aq); $n = 1$, X = OH, $ClCH_2CH_2OCH_2CH_2OH$, NaI, K_2CO_3, dmf; ii, $ClCOCH_2CO_2Et$, py, CH_2Cl_2, 25 °C; iii, DBU, thf, 0 °C; iv, CBr_4, thf, −78 °C; v, C_{60}, DBU, C_6H_5Me, room temp.; vi, [Ru(Xtpy)Cl_3], $AgBF_4$, Me_2CO, dmf (X = H or NMe_2)

brominated by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ane (DBU) followed by CBr_4 to give the species **3a** and **3b** as colourless oils which were used without further purification.

The fullerene incorporation was achieved by reaction of **3a** or **3b** with C_{60} in toluene in the presence of DBU.[10] After chromatographic purification, the new ligands were obtained as dark brown solids in respectable yields (**4a**, 55%; **4b**, 52%). All spectroscopic and analytical data were fully in accord with the proposed formulations.‡ In each case parent ions were observed in the FAB or MALDI TOF mass spectra of the compounds. The two new ligands exhibited fullerene-centred reductions[11] at -1.09, -1.43 and -1.86 V (*vs.* Fc–Fc^+, all potentials ±20 mV). A most interesting result is that the electrochemical behaviour of these compounds is almost independent of solvent (MeCN, thf or CH_2Cl_2) in stark contrast to C_{60} itself.[1a,11b]

In order to probe the utility of the new fullerene-functionalised ligand we have prepared ruthenium(II) diad and triad systems.[12] The complexes $[Ru(tpy)(\mathbf{4a})][PF_6]_2$ (48%) and $[Ru(tpy)(\mathbf{4b})][PF_6]_2$ (52%) were obtained as dark red microcrystalline solids from the reaction in dmf of **4a** or **4b** respectively with the solvento complex resulting from the reaction of $[Ru(tpy)Cl_3]$ with $AgBF_4$ in acetone, followed by precipitation with NH_4PF_6 and chromatographic purification of the crude salts. The mass spectrometric ($\{Ru(tpy)(\mathbf{4a})\}$ *m/z* 1460, $\{Ru(tpy)(\mathbf{4b})\}$ *m/z* 1504) together with ^1H and ^{13}C NMR spectroscopic data fully confirmed the formation of the heteroleptic complex and the latter suggested that the incorporation of the fullerene resutled in little perturbation of the tpy ligand $\{^1H$ NMR $\Delta\delta$ $[Ru(tpy)_2]^{2+}$–$[Ru(tpy)(\mathbf{4a})]^{2+} = \pm 0.05\}$. The complexes exhibit the expected MLCT absorption at 480 nm in their electronic spectra and are electrochemically active with Ru^{II}–Ru^{III} process at +0.821 V $\{[Ru(tpy)(\mathbf{4a})][PF_6]_2\}$ and +0.798 V $\{[Ru(tpy)(\mathbf{4b})][PF_6]_2\}$ {*cf.* +0.834 V for $[Ru(tpy)(EtOtpy)][PF_6]_2$, EtOtpy = 4′-ethoxy 2,2′:6′,2″-terpyridine[13]} (all potentials *vs.* Fc–Fc^+). The expected fullerene-centred reduction waves are also observed.

Finally, we constructed a triad system with a tpy ligand bearing an electron donor which might interact with the fullerene electron acceptor. The replacement of $[Ru(tpy)Cl_3]$ by $[Ru(Me_2Ntpy)Cl_3]$ (Me_2Ntpy = 4′-*N*,*N*-dimethylamino-2,2′:6′,2″-terpyridine) in the above preparations gave $[Ru(Me_2Ntpy)(\mathbf{4a})][PF_6]_2$ or $[Ru(Me_2Ntpy)(\mathbf{4b})][PF_6]_2$ in modest (22, 23% respectively) yields. Each complex exhibited mass spectrometric ($[Ru(Me_2Ntpy)(\mathbf{4a})][PF_6]_2$: *m/z* 1502, $\{Ru(Me_2Ntpy)(\mathbf{4a})\}$; 1649, $\{Ru(Me_2Ntpy)(\mathbf{4a})(PF_6)\}$) and NMR ($^1H$ and ^{13}C) spectroscopic properties fully in accord with the proposed structures. As expected,[9,13] the introduction of the electron releasing dimethylamino substituent has a dramatic effect upon the Ru^{II}–Ru^{III} redox processes for these complexes, which are shifted over 300 mV with respect to $[Ru(tpy)(\mathbf{4a})][PF_6]_2$ and are observed at +0.500 (±10) V *vs.* Fc–Fc^+. The reductions associated with the fullerene component are not shifted with respect to the parent free ligands. All of the above data suggest that we have indeed our desired donor-metal-acceptor triad system. Furthermore, these data indicate that there is no charge transfer from the amine to the fullerene in the ground state.

We are currently investigating the photochemical and photophysical properties of these and related fullerene functionalised complexes.

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Footnotes

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‡ *Data*: **4a**; ^1H NMR (300 MHz, $CDCl_3$): δ 1.45 (3 H, t, CH_3CH_2), 4.53 (2 H, q, CH_3CH_2), 4.62 (2 H, m, CH_2O), 4.93 (2 H, m, CH_2O), 7.31 (2 H, dd, H^5), 7.80 (2 H, dd, H^4), 8.02 (2 H, s, $H^{3'}$), 8.57 (2 H, d, H^3), 8.66 (2 H, m, H^6). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.22, 52.01, 63.59, 64.96, 65.66, 71.43, 107.40, 121.32, 123.91, 136.77, 138.41, 139.51, 140.81, 140.95, 141.78, 141.86, 142.14, 142.15, 142.76, 142.87, 142.90, 142.91, 142.93, 142.98, 143.73, 143.85, 144.53, 144.58, 144.60, 144.63, 144.65, 144.82, 144.90, 144.94, 145.10, 145;13, 145.20, 145.22, 145.38, 149.02, 155.80, 157.32 163.36, 163.66, 166.41. MS (FAB): *m/z* 1126 [M^+ + H]; $C_{82}H_{19}N_3O_5 \cdot 3.3\ H_2O$. Calc. C, 80.38; H, 2.47; N 3.43. Found C, 80.27; H, 2.12; N, 3.93%.

4b; ^1H NMR (300 MHz, $CDCl_3$): δ 1.45 (3 H, CH_3CH_2), 3.97 (2 H, m, CH_2O), 3.99 (2 H, m,.CH_2O), 4.37 (2 H, m, CH_2O), 4.56 (2 H, q, CH_3CH_2), 4.70 (2 H, m, CH_2O), 7.31 (2 H, dd, H^5), 7.83 (2 H, dd, H^4), 8.02 (2 H, s, $H^{3'}$), 8.59 (2 H, dd, H^3), 8.66 (2 H, m, H^6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.21, 52.13, 63.50, 66.15, 67.91, 69.13, 69.48, 71.50, 107.45, 121.34, 123.82, 136.72, 138.76, 139.24, 140.87, 141.81, 142.13, 142.14, 142.87, 142.90, 142.91, 142.96, 142.99, 143.80, 143.84, 144.53, 144.54, 144.55, 144.59, 144.60, 144.62, 144.82, 145.07, 145.09, 145.10, 145.14, 145;17, 145.19, 145.40, 145.86, 146.37, 149.01, 155.96, 157.17, 163.44, 163.68, 166.79; MS (MALDI-TOF): *m/z* 1170 [M + H^+], 1192 [M^+ + Na].

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