Convergent and divergent approaches to metallocentric metallodendrimers

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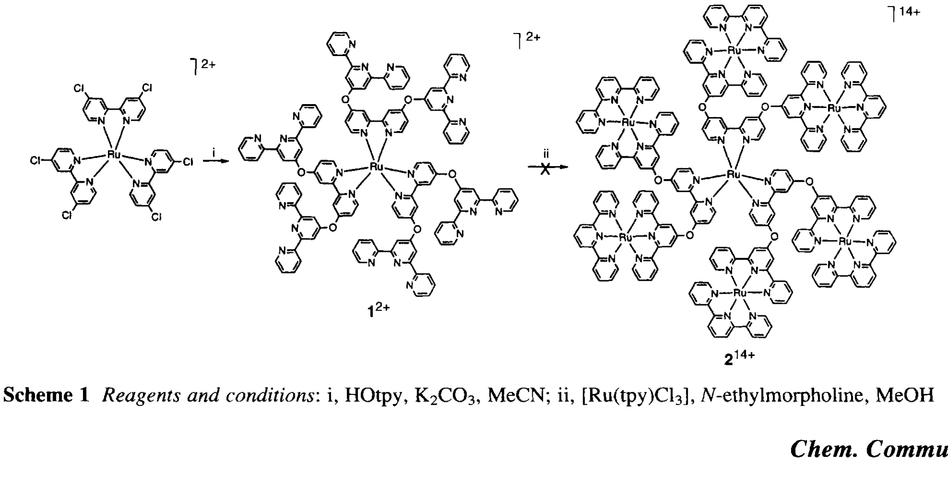
Approaches to metallodendrimers which have a metal as the central growth point are developed; although a divergent methodology was not successful a convergent approach allows the facile synthesis of species such as $\mathbf{5}^{14+}$ and $\mathbf{6}^{14+}$ in high yield.

Dendritic systems incorporating metal centres are of interest as novel magnetic, electronic or photooptical materials.[1] The commonest assembly methodology has relied upon the initial synthesis of suitable bridging ligands, which are subsequently combined with the metal components to give the desired metallodendrimers.[1,2] A consequence of this approach is a divergent or near-divergent synthetic strategy together with little control over the stereochemistry at individual metal sites.[3] We have recently shown that *in situ* ligand assembly avoids the prior preparation of bridging ligands[4] and leads to convergent syntheses.[5] In this paper we address the initiation site and show that a subtle control of topology and topography may be achieved with metallocentric dendrimers which contain a metal at the central position.

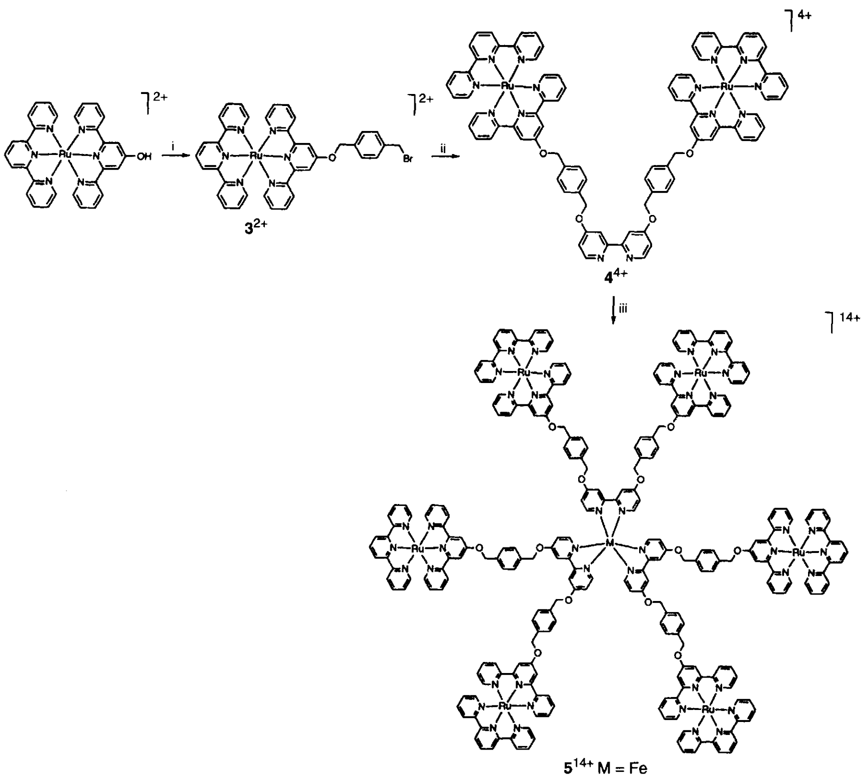
Initially we considered a *divergent* approach in which dendrimer growth commenced with reaction of a coordinated *electrophile* using the complex $[Ru(Cl_2bpy)_3]^{2+}$ (Cl_2bpy = 4,4′-dichloro-2,2′-bipyridine) as shown in Scheme 1. The Cl_2bpy ligand is activated towards displacement of halide by nucleophiles upon coordination[6] and in each Cl_2bpy ligand the two C–Cl vectors are arranged at *ca.* 80°. A model reaction of $[Ru(bpy)_2(Cl_2bpy)][PF_6]_2$ with HOtpy [HOtpy = 2,2′:6′,2″-terpyridin-4′(1′*H*)-one] in MeCN in the presence of K_2CO_3 gave a red solution from which the red complex $[Ru(bpy)_2(tpy_2bpy)][PF_6]_2$ [tpy_2bpy = 4,4′-bis(2,2′:6′,2″-terpyridinyl-4′-oxy)-2,2′-bipyridine] was precipitated in 77% yield. All NMR and spectroscopic data were fully in accord with the proposed structure. The reaction of this V-shaped species with $[Ru(tpy)Cl_3]$ in the presence of *N*-ethylmorpholine gave the trinuclear complex $[Ru(bpy)_2\{[(tpy)Ru]_2tpy_2bpy\}][PF_6]_6$. Encouraged by this observation we investigated the reaction of $[Ru(Cl_2bpy)_3][PF_6]_2$ with HOtpy; the reaction proved to be extremely sensitive to traces of moisture, but when conducted in super-dry MeCN with oven-dried K_2CO_3 the complex $\mathbf{1}[PF_6]_2$ was obtained in good yield. Traces of $[Ru(tpy_2bpy)_2(tpyXbpy)]^{2+}$ [tpyXbpy = 4-(2,2′:6′,2″-terpyridinyl-4′-oxy)-4′-X-2,2′-bipyridine; X = Cl, OH *etc.*] may be removed by repeated chromatography and recrystallisation. The ^{1}H NMR spectrum of $[Ru(tpy_2bpy)_3][PF_6]_2$ is extremely simple and exhibits only eight resonances; three from the 2,2′-bipyridine rings and five from the tpy groups. Unfortunately, the growth reaction of $[Ru(tpy_2bpy)_3][PF_6]_2$ with $[Ru(tpy)Cl_3]$ under a wide range of reaction conditions was unsuccessful and always gave mixtures of compounds with varying numbers of terminator {Ru(tpy)} groups in the surface generation. Modelling suggested that the desired heptanuclear complex $\mathbf{2}^{14+}$ would be extremely sterically crowded.

Accordingly we made a strategy change and adopted a *convergent* route in which a spacer relieved these steric interactions. The complex $[(tpy)Ru(HOtpy)][PF_6]_2$[4,5] was treated with 1,4-bis(bromomethyl)benzene in MeCN in the presence of K_2CO_3 to give, after work-up, $\mathbf{3}[PF_6]_2$ in 74% yield. This key intermediate was fully characterised (TOF MS: *m*/*z* 767 {**3**}, ^{1}H NMR as expected, $E_{1/2}$ Ru^{II}–Ru^{III} +0.82 V *vs.* Fc–Fc$^+$) and is a metal complex which also bears a pendant, remote, electrophilic reactive benzyl halide. Our chosen reaction partner was 2,2′-bipyridine-4(1*H*),4′(1′*H*)-dione (HO_2bpy)[7] which was prepared by the reaction of 4,4′-diamino-2,2′-bipyridine with $NaNO_2$ in concentrated sulfuric acid in 63% yield. The reaction of $\mathbf{3}[PF_6]_2$ with HO_2bpy in refluxing acetonitrile in the presence of K_2CO_3 for 6 h gave a deep red solution from which $\mathbf{4}[PF_6]_4$ was precipitated as an orange solid upon treatment with aqueous $[NH_4][PF_6]$. After chromatographic purification, $\mathbf{4}[PF_6]_4$ was isolated in 47% yield (TOF MS *m*/*z* 1994 {$\mathbf{4}(PF_6)_3$}, 1853 {$\mathbf{4}(PF_6)_2$}, ^{1}H NMR as expected, $E_{1/2}$ Ru^{II}–Ru^{III} +0.82 V *vs.* Fc–Fc$^+$). The electrochemical data indicate that the ruthenium centre is not sensitive to the reaction which has occurred at the benzylic site.

The compound $\mathbf{4}[PF_6]_4$ is the building block for the heptanuclear species $\mathbf{5}^{14+}$ and $\mathbf{6}^{14+}$ as it is a dinuclear *complex* which also contains a vacant didentate metal-binding domain. In contrast to our previous studies of systems containing vacant tpy metal-binding domains,[4,5] reaction with an octahedral metal centre is likely to lead to the assembly of three of species **2**. Furthermore, the use of labile first-row transition-metal centres allows a convergent spontaneous self assembly.[3] In practice, the



Scheme 1 *Reagents and conditions*: i, HOtpy, K_2CO_3, MeCN; ii, $[Ru(tpy)Cl_3]$, *N*-ethylmorpholine, MeOH



Scheme 2 *Reagents and conditions*: i, 1,4-bis(bromomethyl)benzene, K_2CO_3, MeCN; ii, HO_2bpy, K_2CO_3, MeCN; iii, $[NH_4]_2Fe[SO_4]_2{\cdot}6H_2O$ or $Co(O_2CMe)_2$, MeCN, H_2O

reactions could not be simpler. The reaction of **4**$[PF_6]_4$ with $[NH_4]_2Fe[SO_4]_2{\cdot}6H_2O$ in aqueous acetonitrile gave an orange solution from which a brown solid was precipitated upon treatment with aqueous $[NH_4][PF_6]$. This brown solid was recrystallised to give the heptanuclear species **5**$[PF_6]_{14}$ as a brown solid. The MALDI TOF spectrum exhibited a highest mass peak at *m*/*z* 6330 {**5**$(PF_6)_{11}$.} The Ru^{II}–Ru^{III} redox process is observed as a fully reversible process at +0.81 V *vs*. Fc–Fc^+ although the Fe^{II}–Fe^{III} process is not observable. The ^1H NMR spectrum exhibits the expected two CH_2 environments (δ 5.45, 5.67), with essentially no alteration in the positions of the resonances assigned to the tpy domains and the phenylene spacers with respect to **4**$[PF_6]_4$. However the resonances assigned to the bpy ring in **5**$[PF_6]_{14}$ (δ 8.54, H^6; δ 8.13, H^3; δ 7.11, H^5) are extremely broad and shifted, suggesting that a high-spin complex has been obtained. We are currently further investigating the behaviour of this compound.

A similar heptanuclear species **6**$[PF_6]_{14}$ is obtained in 77% yield from the reaction of **4**$[PF_6]_4$ with $Co(O_2CMe)_2{\cdot}4H_2O$ in aqueous acetonitrile. Once again, the MALDI TOF mass spectrum provided convincing support for the formulation of the product and exhibited intense ions corresponding to {**6**$(PF_6)_n$} (*n* = 12–10). The electrochemistry also resembles that of the iron analogue, and a fully reversible Ru^{II}–Ru^{III} redox process is observed at +0.82 V *vs*. Fc–Fc^+ with no detectable Co^{II}–Co^{III} process. This complex is paramagnetic: the resonances assigned to the tpy domains are essentially unshifted compared to **4**$[PF_6]_4$ but the three resonances of the bpy domain are observed as relatively sharp peaks at δ 95, 78 and 41. These reactions are summarised in Scheme 2.

In conclusion, we have demonstrated a new and facile convergent method for assembly of metallocentric metallodendrimers. We are currently extending these studies to higher generations by the use of functionalised Xtpy ligands in the outer generations and also investigating the electrochemical behaviour of such systems.

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