ChemComm

A rigid 1,3,5-phenylene-based metallodendrimer containing a ruthenium(II) bis(terpyridyl) complex

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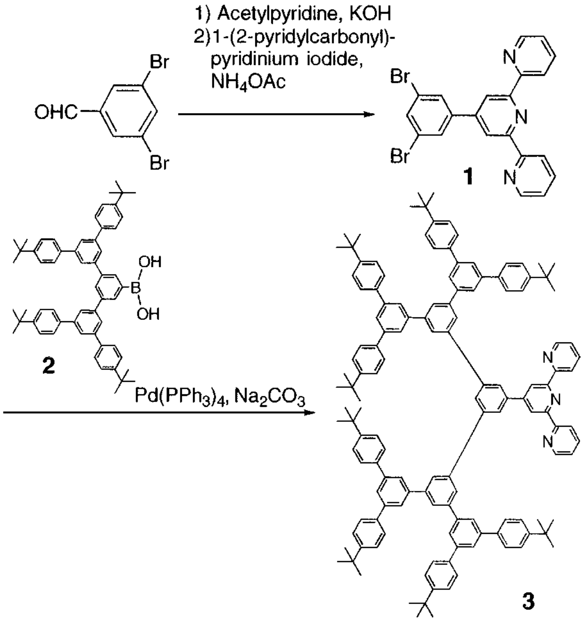
Received (in Cambridge, UK) 26th October 1999, Accepted Accepted 18th November 1999

A new 1,3,5-phenylene-based metallodendrimer containing a ruthenium bis(terpyridyl) complex was prepared and characterized; the rigid dendritic branches are found to affect the electrochemical properties of the redox-active core.

Dendrimers are well defined, highly branched macromolecules constructed from an interior core with a regular array of branch units.[1] To investigate the influence of dendritic structures on electrochemical, photochemical and catalytic properties, dendrimers containing functional units have been designed and synthesized.[2] The dendritic structures influence the micro-environment around the cores and modify their properties.[3] Polypyridyl ruthenium(II) complexes ($[Ru(bpy)_3]^{2+}$ and $[Ru(tpy)_2]^{2+}$) are widely used for the construction of dendrimers because of their unique electrochemical and photochemical properties.[4] However, these dendrimers have been prepared by attaching flexible dendron units around metal complexes. Rigid dendrimers have been prepared using phenylene, phenylacetylene and phenylenevinylene units as repeating units in the dendritic structures.[5] The construction of a well defined rigid dendritic structure around a redox-active metal complex unit may result in interesting electrochemical and optical changes.

Herein, we report the first rigid metallodendrimer containing $[Ru(tpy)_2]^{2+}$ in the interior core. The synthesis of the new 1,3,5-phenylene-based dendritic ligand **3** was performed using the methodology developed by Miller *et al.* (Scheme 1).[6] The terpyridyl core **1** was obtained from 3,5-dibromobenzaldehyde and 1-(2-pyridylcarbonylmethyl)pyridinium iodide according to the literature.[7] The dendron **2** was prepared in a stepwise manner through a Suzuki coupling reaction between an arylboronic acid and 3,5-dibromo-1-(trimethylsilyl)benzene.[8] Finally, the coupling of **2** to **1** using $Pd(PPh_3)_4$ as a catalyst proceeded smoothly to give the dendritic ligand **3** in 70% yield. This new dendritic ligand was characterized by ^1H NMR and matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometric techniques. MALDI-TOF mass spectra of **3** gave the correct molecular peak ($[M + H^+]$ m/z = 1823). Fig. 1 shows the ^1H NMR spectrum of **3** in $CDCl_3$ which provides structural information. The ^1H NMR spectrum in the aromatic region of **3** is very simple and readily assignable and indicates the successive generation of a highly symmetric layered structure.



Scheme 1

Treatment of **3** with $RuCl_3{\cdot}3H_2O$ generated the desired metallodendrimer $[Ru(\mathbf{3})_2]^{2+}$ (Scheme 2) which was purified by column chromatography after anion exchange with hexafluorophosphate ion. The presence of *tert*-butyl groups at the exterior positions of the dendrimer completely encapsulates the $Ru(tpy)_2$ core and enhances the hydrophobicity with metallodendrimer $[Ru(\mathbf{3})_2]^{2+}$ being highly soluble in a variety of organic solvents such as alkanes, but not in polar solvents such as acetonitrile and alcohols. By contrast, the low molecular weight complex bis(4′-(*p*-tolyl)-2,2′:6′,2″-terpyridyl)ruthenium(II) complex ($[Ru(tpy\text{-}phMe)_2]^{2+}$) only showed solubility in polar solvents. The Homogeneity of $[Ru(\mathbf{3})_2]^{2+}$ was demonstrated by GPC analyses and MALDI-TOF mass spectrometry. Examination by GPC analysis showed that $[Ru(\mathbf{3})_2]^{2+}$ has a sharp and symmetrical elution peak with a polydispersity (M_w/M_n) of < 1.01. The MALDI-TOF mass spectrum of $[Ru(\mathbf{3})_2]^{2+}$ gave the correct mass at m/z 3891 for the $[M - PF_6]$ peak. Fig. 2 shows the absorption spectra of **3** and $[Ru(\mathbf{3})_2]^{2+}$, with absorption maxima (λ_{max}) and molar absorption coefficients (ε) collected in Table 1. The spectrum of $[Ru(\mathbf{3})_2]^{2+}$ in the visible region showed a characteristic MLCT transition at 490 nm, indicating the formation of a $[Ru(tpy)_2]^{2+}$ core.[10] The molecular coefficient for the MLCT band of $[Ru(\mathbf{3})_2]^{2+}$ was almost the same as that of $[Ru(tpy\text{-}phMe)_2]^{2+}$. Moreover, the absorbance at 260 nm of $[Ru(\mathbf{3})_2]^{2+}$ was approximately double that of the dendritic ligand **3**. As revealed by a computer generated ball-and-stick model, the dendritic ligand **3** is a hemispherical structure with a radius of *ca.* 1.5 nm (Scheme 2). The metallodendrimer $[Ru(\mathbf{3})_2]^{2+}$ is thus formed by metal-mediated

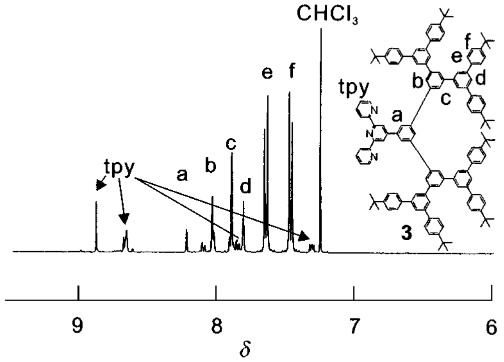
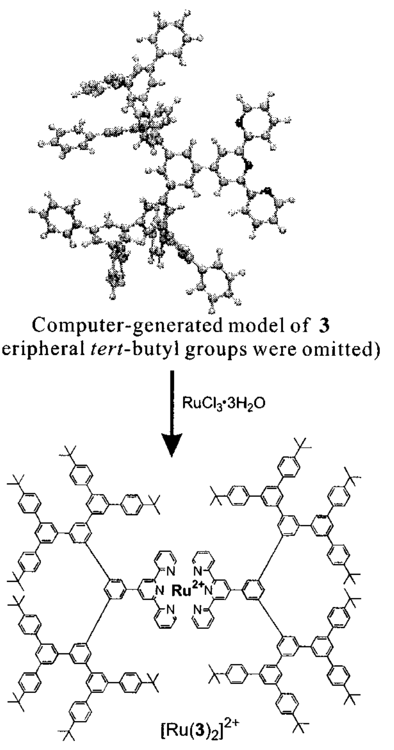


Fig. 1 ^1H NMR spectrum of **3** in $CDCl_3$.



Scheme 2

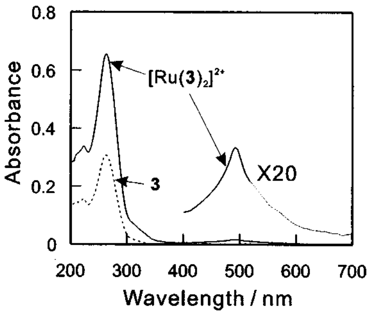


Fig. 2 UV–VIS absorption spectra of **3** and $[Ru(\mathbf{3})_2]^{2+}$ in CH_2Cl_2. ([**3**], $[Ru(\mathbf{3})_2]^{2+}$ = 1.0 μM).

assembly through the formation of a metal complex between two ligands possessing well defined hemispherical dendritic structures and one Ru^{2+} ion.

The influence of the rigid dendritic branches on the redox properties of the redox-active $[Ru(tpy)_2]^{2+}$ core was studied by cyclic voltammetry in CH_2Cl_2 using Bu_4NPF_6 (0.1 M) as supporting electrolyte (Table 1). The metallodendrimer $[Ru(\mathbf{3})_2]^{2+}$ exhibited one oxidation ($E_{1/2}$ = +1.25 V *vs.* SCE) and two reduction processes ($E_{1/2}$ = −1.28 and −1.43 V *vs.* SCE). The average peak potentials ($E_{1/2}$) for these processes were almost the same as those of the non-dendiritic [Ru(tpy-phMe)$_2$]$^{2+}$ complex.[4a,9] However, $[Ru(\mathbf{3})_2]^{2+}$ showed a large voltage difference between the current maxima of the reduction and return oxidation wave (ΔE), indicative of slower electron transfer than for the non-dendritic complex. This observation was similar to the electrochemical results of a flexible metallodendrimer containing redox-active core subunits.[3,4] The rigid dendritic branches around the $[Ru(tpy)_2]^{2+}$ core lead to a distance of 1.5 nm between the core and the electrode surface. The remoteness of the redox-active core from the electrode surface was found to hinder the electron transfer processes.

Table 1 Structural, spectroscopic and electrochemical data for $[Ru(\mathbf{3})_2]^{2+}$

	m/z^a	Absorption^b λ_{max}/nm (ε/M^{-1} cm^{-1})	$E_{1/2}{}^c$/V *vs.* SCE	ΔE^c/ mV
$[Ru(\mathbf{3})_2]^{2+}$	3891	490 (25000)	+1.25	180
	[M − PF_6^-]	260 (653000)	−1.28	120
			−1.43	125
[Ru(tpy-phMe)$_2$]$^{2+}$		490 (28900)	+1.20	76
			−1.24	71
			−1.46	83

^{a} *m/z* Value determined by MALDI-TOF experiments. ^{b} CH_2Cl_2 solution. ^{c} From cyclic voltammetry in CH_2Cl_2 solution, 100 mV s^{-1} scan rate, Bu_4NPF_6 supporting electrolyte, Pt electrode, Ag/AgCl reference. $E_{1/2}$ is defined as the average of the two voltages at the current maximum/ minimum of the redox waves. ΔE is defined as the difference of the peak voltages for the reduction and return oxidation waves.

In summary, we have reported the construction of a new rigid metallodendrimer, in which the metal complex is encapsulated in a precise position within the rigid dendritic macromolecule. Further photochemical investigations of the rigid metallodendrimer are currently in progress.

This research was supported in part by a Grant-in-Aid for COE Research ‘Advanced Fiber/Textile Science and Technology’ (#10CE2003) and Scientific Research (#11450366) from the Ministry of Education, Science, Sports and Culture of Japan.

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Communication a908500i