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A Convergent Approach for the Generation of Dendrimers Containing the $[Ru_3O(CH_3COO)_6]$ Electroactive Core

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We report on a convergent approach for the generation of dendrimers containing the $[Ru_3O(ac)_6]$ electroactive core, of great interest as multielectron transfer catalysts. The proposed strategy is based on the generation of the trimeric complex $[\{Ru_3O(ac)_6(4\text{-pic})_2(pz)\}_2\text{-}\mu_2\text{-}Ru_3O(ac)_6(CH_3OH)]^{3+}$ (ac = acetate, 4-pic = 4-methylpyridine, pz = pyrazine). In this complex, the labile CH_3OH ligand can be displaced by the bridging pyrazine ligand of $[Ru_3O(ac)_6(pz)_3]^0$, leading to the self-assembly of the $[\{[Ru_3O(ac)_6(4\text{-pic})_2(pz)]_2\text{-}\mu_2\text{-}Ru_3O(ac)_6(pz)\}_3\text{-}\mu_3\text{-}Ru_3O(ac)_6]^{n+}$ dendrimer containing 30 ruthenium atoms.

Introduction

Dendrimers are defined as hyperbranched structures obtained from organic, inorganic or both kinds of building blocks.[1–5] Firstly, the interest in this kind of macromolecules arose from the aesthetic appeal and from the challenge to synthesize nanometer-sized species in a controlled fashion, following a "bottom-up" approach. Rapidly, this class of compounds attracted attention because of their ability to mimic biological systems or to feature valuable functions, as catalysts and drug delivery agents. Several dendrimeric polynuclear (polypyridine)Ru^{2+} and -Os^{2+} systems have already been reported in the literature.[6–10] From the electrochemical point of view, along with those examples, $[Ru_3O(ac)_6(L)_3]^{n+}$ complexes (L = solvent or N-heterocyclic ligand) constitute appealing building blocks, since each triangular $[Ru_3O]$ unit displays at least four reversible redox processes in the range from –1.5 V to 2.5 V (vs. SHE). The $E_{1/2}$ values associated with each process are highly dependent on the ligand L in such a way that the choice of terminal and bridging ligands provides a suitable manner to modulate the $[Ru_3O]$ electrochemical properties.[11–14] However, the synthesis of such dendrimeric clusters remains rather challenging, requiring new strategies to overcome the formation of random coordination polymers. In this work we report on a convergent approach for the generation of dendrimers containing the $[Ru_3O(CH_3COO)_6]$ electroactive core, as illustrated in Figure 1.

The proposed scheme in Figure 1 involves the generation of the trimeric carbonyl complex $[\{Ru_3O(ac)_6(4\text{-pic})_2(pz)\}_2\text{-}\mu_2\text{-}Ru_3O(ac)_6(CO)]^{2+}$ by treating $[Ru_3O(ac)_6(CO)(CH_3OH)_2]^0$ with the $[Ru_3O(ac)_6(4\text{-pic})_2(pz)]^+$ species. In the $[Ru_3O(ac)_6(CO)(CH_3OH)_2]^0$ complex, the labile CH_3OH can be displaced by the pyrazine ligand, while the carbonyl ligand remains attached to the cluster moiety. After this, the carbonyl species can be converted into $[\{Ru_3O(ac)_6(4\text{-pic})_2(pz)\}_2][Ru_3O(ac)_6(CH_3OH)]^{3+}$ by treatment with bromine. In this complex, the presence of a labile methanol group is strategic for allowing its binding to the $[Ru_3O(ac)_6(pz)_3]^0$ core, in order to yield the $[\{[Ru_3O(ac)_6(4\text{-pic})_2(pz)]_2\text{-}\mu\text{-}Ru_3O(ac)_6(pz)\}_3\text{-}\mu_3\text{-}Ru_3O(ac)_6]^{n+}$ dendrimer.

Results and Discussion

The synthesis of the trimeric complex $[\{Ru_3O(ac)_6(4\text{-pic})_2(pz)\}_2][Ru_3O(ac)_6(CH_3OH)]^{3+}$ was considered the key point for the generation of the coordination dendrimer proposed in Figure 1. This species was isolated in pure form, and characterized based on analytical and ^1H NMR spectroscopy, exhibiting a good solubility in organic solvents. However, a characteristic of this type of polymeric clusters[15–18] is their facility to undergo autoxidation and redox reactions, yielding multiple oxidation states in solution. For this reason, as a general procedure, the electronic spectra were obtained under controlled applied potentials, by means of spectroelectrochemical techniques.

The cyclic voltammograms of the monomeric $[Ru_3O(ac)_6L_3]$ species exhibit a characteristic sequence of 4 or 5 reversible waves in the –2 to +2 V region.[11–13] Two waves, corresponding to the $Ru^{III,III,III/III,III,II}$ and $Ru^{IV,III,III/III,III,III}$

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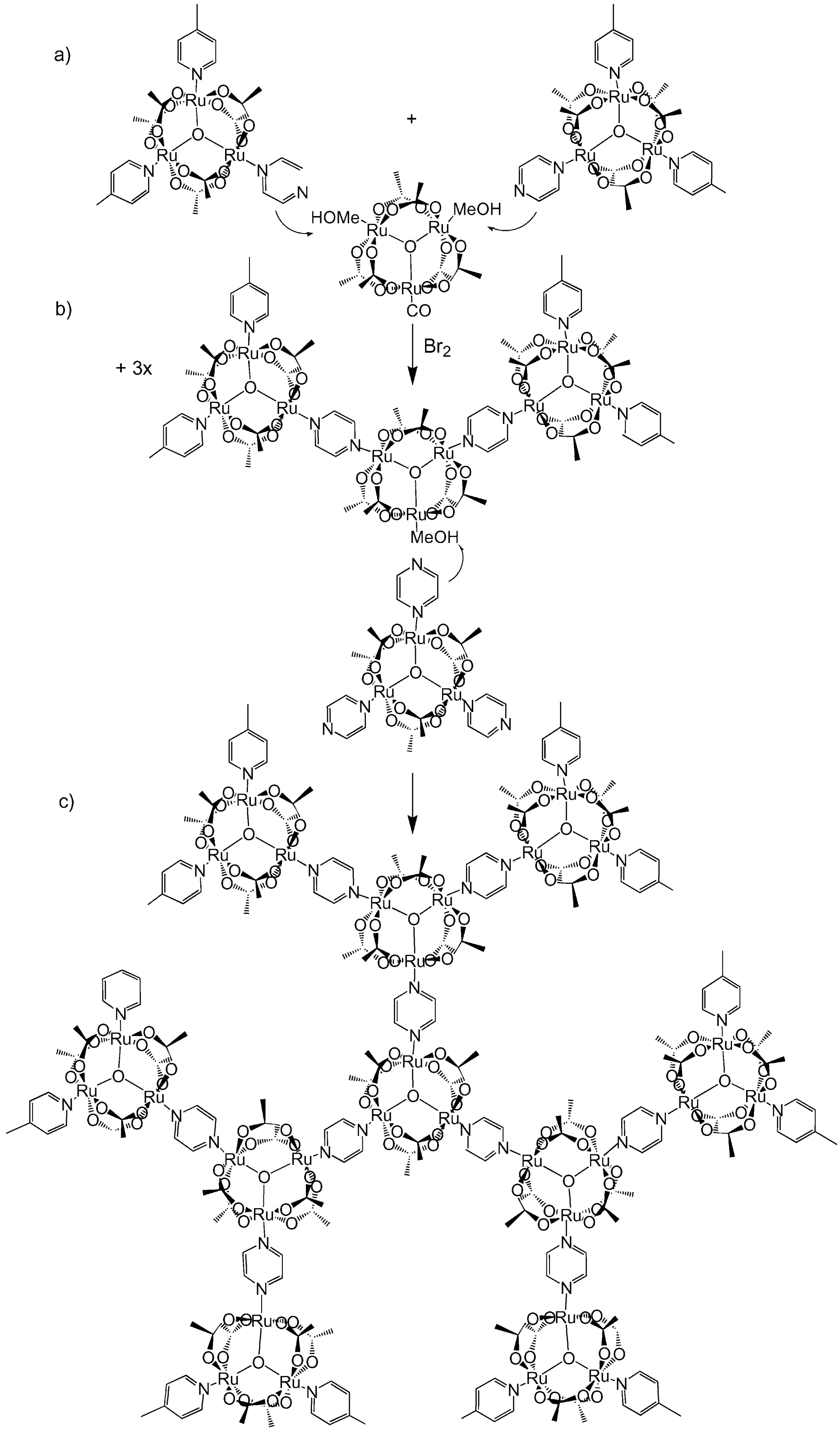

Figure 1. A convergent synthetic approach, starting from two suitable molecular building blocks (a), yielding a trimeric species (b) which exhibits a strategic labile site, capable of promoting the dendrimer self-assembly (c) in the presence of a bridging triangular core complex.

processes are usually observed around 0 and 1 V, respectively. In the case of the trimeric cluster, as shown in the cyclic voltammogram of Figure 2A, it is observed that two pairs of broad, quasi-reversible waves, split into two components at 0.24, 0.43 V and 1.28, 1.41 V, respectively, which is in accordance with the molecular structure, corresponding to the peripheral and central moieties. Similar results have been obtained by differential pulsed voltammetry, confirming the ratio 1:2 for the number of electrons (Supporting Information).

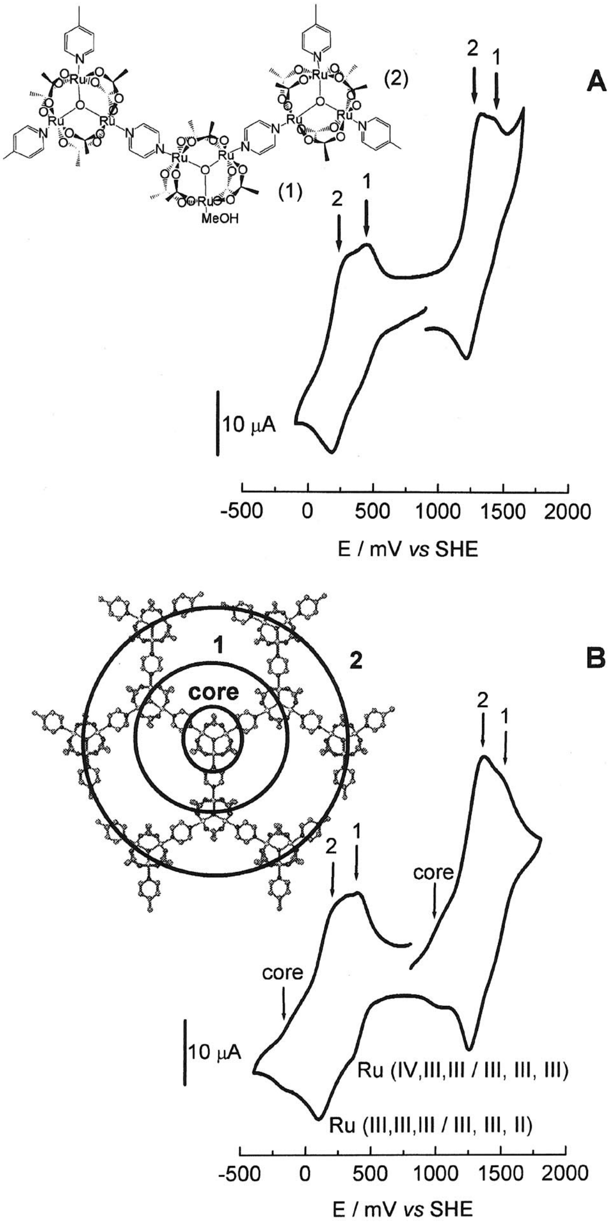

Figure 2. Cyclic voltammograms of the trimer (A) in acetonitrile, and dendrimer (B) in dichloroethane, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate = 50 mV s–1.

The spectroelectrochemical behavior of the trinuclear species is rather similar to the (μ-oxido)ruthenium trinuclear compounds previously described in the literature.[11–13] At the starting potential (at 0.47 V in Figure 3), the system corresponds to the $Ru^{III,III,III}$ oxidation state, exhibiting the characteristic internal electronic transitions (IC = intracluster) of the Ru_3O centre at 703 nm (ε = 2.19×10^4 mol dm^3 cm^{-1}) and the cluster-to-ligand charge-transfer band (CLCT) at 419 ($\varepsilon = 2.52\times10^4$ mol dm^3 cm^{-1}). The reduction process at 0.29 V leads to the decay of these two bands associated with the central moiety, accompanied by the rise of two new IC and CLCT bands at 976 and 531 nm, respectively, exhibiting three characteristic isosbestic points (Figure 3).

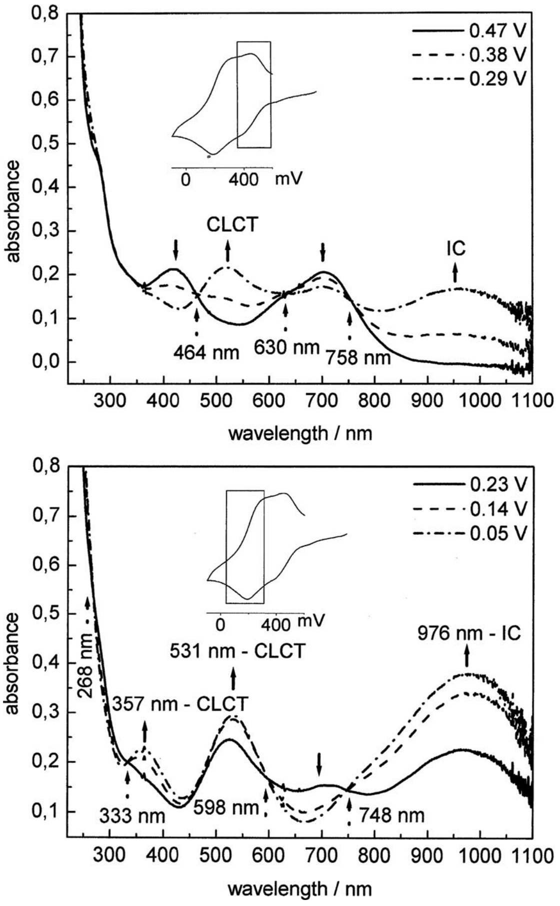

Figure 3. Spectroelectrochemical behaviour associated with the $[Ru_3O]^{1+/0}$ redox processes for the $[\{Ru_3O(ac)_6(4\text{-pic})_2(pz)\}_2]$-$[Ru_3O(ac)_6(CH_3OH)]^{3+}$ trimer in a 3×10^{-3} M acetonitrile solution.

Further reduction, localized at the peripheral moieties, at 0.05 V, leads to the complete decay of the intracluster band at 703 nm, and enhancement of the new intracluster band at 976 nm. Two bands are discernible at 357 and 531 nm, corresponding to the cluster-to-pyridine and cluster-to-pyrazine charge-transfer bands, respectively, associated with the reduced peripheral clusters. The new set of isosbestic points corroborates the assignment of such a consecutive reduction process, corresponding to the peripheral sites.

In a convergent approach, the trimeric species were treated with the $[Ru_3O(ac)_6(pz)_3]^0$ complex in CH_2Cl_2 in a molar ratio of 3:1 at room temperature during 5 d. Our confidence on this route is based on the fact that the methanol substitution reaction is the most probable event, leading to the dendrimer self-assembly under the conditions of this work. As a matter of fact, the reaction can be monitored spectrophotometrically, from the spectral changes associated with the $Ru^{III,III,III}$ and $Ru^{II,III,III}$ centres, easily identified by their characteristic bands at 715 and 997 nm, respectively, which are bathochromically shifted from those of the starting compounds (703, 930 nm). In an attempt to isolate the product, the final solution was concentrated to dryness and eluted on a neutral alumina column with a mixture of 20% CH_3CN/80% CH_2Cl_2 (v/v). Unfortunately, the purification procedure was complicated by the observed tendency of the product to exhibit many oxidation states in solution, under the influence of the air, water and trace contaminants. This is a very difficult problem, which could not yet be solved, particularly under the dynamic conditions of column chromatography. For this reason, the best attempt, carried out under carefully controlled conditions, led to only 6% yield of the product.

In contrast to the precursor complexes, the dendrimer is less soluble in ordinary solvents like CH_3CN, reflecting its high nuclearity. Unfortunately, this aspect, in association with the occurrence of a mixture of oxidation states, complicates its characterization using the conventional analytical techniques. ESI-MS has also been attempted, but with little success, even by using low cone voltages (e.g. 5–10 eV). As a matter of fact, as we have recently reported,[19] extensive cluster dissociation reactions take place in the gas phase involving the ruthenium–pyrazine, ruthenium–pyridine and related bonds, generating a rather complex distribution of low molecular mass cluster fragments. Similar studies are being planned for polymeric clusters, with their identification based on the corresponding fragmentation patterns.

In the case of dendrimeric clusters, electrochemical and spectroelectrochemical techniques are much more convenient for characterization purposes, because of the possibility of controlling the oxidation states. In addition, the detection and assignment of the many successive redox processes can be taken as real fingerprints for the dendrimeric species, especially when compared with the characteristic data of the precursor complexes.

In fact, as one can see in Figure 3, the cyclic voltammetry is consistent with the expected dendrimeric structure, exhibiting electrochemical signals corresponding to the three types of clusters at the theoretical 1:3:6 ratio for core, 1st and 2nd generations, respectively. Such assignment is corroborated by the detection of three successive spectroelectrochemical processes, as illustrated in Figure 4. It has been observed that the isolated product spontaneously changes its colour from green to violet, both in solution and the solid state. The violet fraction is strongly retained on the chromatographic column, thus explaining the difficulties found in the purification process. Based on the spectroelectrochemical results (Figure 4), these two fractions were identified as the dendrimer in oxidised and reduced forms.

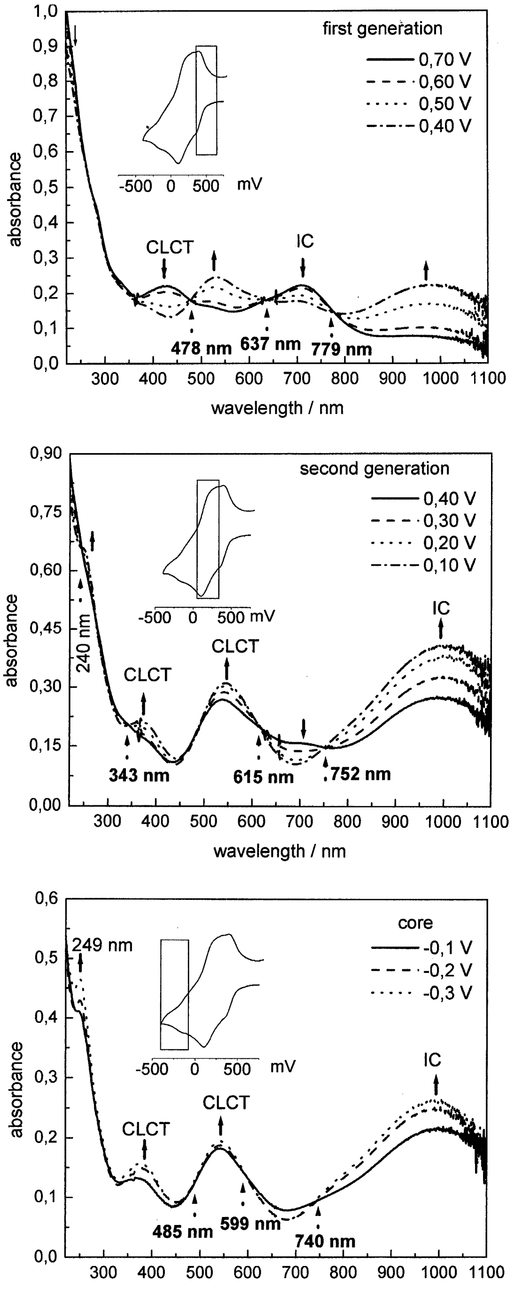

Figure 4. Spectroelectrochemical behaviour associated with the $[Ru_3O]^{1+/0}$ redox processes for the $[\{[Ru_3O(ac)_6(4\text{-pic})_2(pz)]_2\text{-}\mu_2\text{-}Ru_3O(ac)_6(pz)\}_3\text{-}\mu_3\text{-}Ru_3O(ac)_6]^{n+}$ dendrimer in a 4×10^{-4} M dichloroethane solution.

Taking into account that the 4-methylpyridine terminal ligand is a stronger electron donor than pyrazine, the $E_{1/2}$ values of the redox processes for the first generation of clusters should be higher than for the second generation, as shown in Figure 2. In addition, due to the electron-withdrawing nature of the pyrazine connector, one can expect that the Ru_3O^+ core would be the easiest centre to reduce. However, contrary to this argument, the core was actually the fragment easiest to oxidise, reflecting an increase in its electronic density. Therefore, one can conclude that there is a pronounced backdonation promoting a removal of electron density from the boundaries of the oligomer to the centre through the pyrazine bridging ligand. This behaviour and the well-known[15,16] dependence of the $[Ru_3O]$ properties on ligands parameters such as pK_a and E_L can provide the basis to plan, by the appropriate choice of ligands, dendrimeric structures having a gradient of electrochemical potential. This is particularly relevant for catalytic purposes[20,21] or for mimicking biologic systems such as the mitochondrial or photosynthetic electron-transport chain.[1–5]

Conclusion

A convergent synthetic approach for the generation of a dendrimeric cluster encompassing 30 ruthenium atoms has been successfully demonstrated on the basis of the self-assembly of trimeric species displaying strategic labile sites to allow their binding to a bridging core complex.

Experimental Section

Materials and Methods: UV/Vis spectra were recorded with a Hewlett Packard model 8453 diode array spectrophotometer. ^{1}H NMR spectra were recorded with a Varian 300 MHz spectrometer, model INOVA 1, and the assignments were carried out as previously reported.[21,22] Cyclic voltammetric measurements were carried out with a Princeton Applied Research model 283 potentiostat. A platinum disk electrode was employed for the measurements, using the conventional Luggin capillary arrangement with an Ag/AgNO$_3$ (0.010 M) reference electrode in CH$_3$CN containing 0.100 M tetraethylammonium perchlorate (TEAClO$_4$). A platinum wire was used as the auxiliary electrode. All the $E_{1/2}$ values presented here were converted to SHE by adding 0.503 V to the observed values. In the case of dendrimer ClCH$_2$CH$_2$Cl was used as solvent and tetrabutylamonium hexafluorophosphate (TBAPF$_6$) as electrolyte. For spectroelectrochemical measurements, a three-electrode system was used, arranged in a rectangular quartz cell of 0.025 cm internal optical path length. A gold minigrid was used as transparent working electrode, in the presence of the above-mentioned solutions, auxiliary and reference electrodes. The synthesis of compounds [Ru$_3$O(ac)$_6$(4-pic)$_2$(pz)]PF$_6$, [Ru$_3$O(ac)$_6$(4-pic)$_2$(H$_2$O)]PF$_6$, [Ru$_3$O-(ac)(4-pic)$_3$]PF$_6$, [Ru$_3$O(ac)(4-pic)$_2$(CO)], and [Ru$_3$O(ac)$_6$(CO)-(CH$_3$OH)$_2$]·H$_2$O were carried out according to literature procedures.[23,24] $C_{28}H_{36}F_6N_4O_{13}PRu_3$ (1084.8): calcd. C 31.0, H 3.3, N 5.2; found C 31.1, H 3.5, N 5.6. $C_{24}H_{34}F_6N_2O_{14}PRu_3$ (1022.7): calcd. C 28.2, H 3.4, N 2.7; found C 27.0, H 3.3, N 2.6. $C_{30}H_{39}F_6N_3O_{13}PRu_3$ (1097.8): calcd. C 32.8, H 3.6, N 3.8; found C 33.8, H 3.8, N 4.0. $Ru_3C_{25}O_{14}H_{32}N_2$ (887.7): calcd. C 33.8, H 3.6, N 3.1; C 33.3, H 3.5, N 2.9. $C_{15}H_{28}O_{17}Ru_3$ (783.6): calcd. C 23.0, H 3.6; found C 21.7, H 3.5.

[{Ru$_3$O(ac)$_6$(4-pic)$_2$(pz)}$_2$][Ru$_3$O(ac)$_6$(CO)](PF$_6$)$_2$: [Ru$_3$O(ac)$_6$(CO)-(CH$_3$OH)$_2$] (67 mg, 0.085 mmol) and [Ru$_3$O(ac)$_6$(4-pic)$_2$(pz)]PF$_6$ (185 mg, 0.170 mmol) were dissolved in a mixture of CH$_3$OH (10 mL) and CH$_2$Cl$_2$ (70 mL) and allowed to react during 5 d, protected from direct light. The resulting solution was concentrated to dryness, dissolved in a minimum volume of CH$_2$Cl$_2$ and purified on a neutral alumina column. The main fraction was eluted with a mixture of 10% CH$_3$CN/CH$_2$Cl$_2$ (v/v), concentrated to dryness, dissolved in a minimum volume of CH$_2$Cl$_2$ and filtered into stirring diethyl ether. This procedure led to a green solid which was dried under vacuum (75 mg, 30%). $C_{69}H_{90}F_{12}N_8O_{40}P_2Ru_9$ (2871): calcd. C 28.9, H 3.2, N 3.9; found C 29.2, H 3.2, N 4.0. ^{1}H NMR (CDCl$_3$): δ = –0.17 (8 H, H$_\alpha$ 4-pic), 0.53 (4 H, H$_\alpha$ pz), 1.73 [12 H, CH$_3$ ac (d)], 1.76 [6 H, CH$_3$ ac (c)], 2.36 (12 H, CH$_3$ 4-pic), 4.80 [24 H, CH$_3$ ac (b)], 5.43 (8 H, H$_\beta$ 4-pic), 5.50 [12 H, CH$_3$ ac (a)], 6.10 (4 H, H$_\beta$ pz) ppm.

[{Ru$_3$O(ac)$_6$(4-pic)$_2$(pz)}$_2$][Ru$_3$O(ac)$_6$(CH$_3$OH)](PF$_6$)$_3$: [Ru$_3$O(ac)$_6$-(CO)(CH$_3$OH)$_2$] (54 mg, 0.0685 mmol) and [Ru$_3$O(ac)$_6$(4-pic)$_2$(pz)]-PF$_6$ (148 mg, 0.137 mmol) were dissolved in a mixture of CH$_3$OH (5 mL) and CH$_2$Cl$_2$ (10 mL) and allowed to react during 5 d, protected from direct light. Then a 0.15 M solution of Br$_2$ in CH$_2$Cl$_2$ was added in order to oxidise[23] the central fragment [Ru$_3$O(ac)$_6$-(pz)(CO)]; the addition was finished when the absorption spectrum of the reaction mixture did not show any significant change. The resulting solution was concentrated to dryness, the crude material was dissolved in CH$_3$OH containing NaPF$_6$, and this solution was left in the refrigerator. After 2 d, a green solid was isolated by filtration, dissolved in a minimum volume of CH$_2$Cl$_2$ and purified on a neutral alumina column. The main fraction was eluted in CH$_3$CN, concentrated to dryness, dissolved in a minimum volume of CH$_2$Cl$_2$ and filtered into stirring diethyl ether. This procedure yielded a green solid which was dried under vacuum (105 mg, 48%). $C_{69}H_{94}F_{18}N_8O_{40}P_3Ru_9$ (3020): calcd. C 27.5, H 3.1, N 3.7; found C 28.1, H 3.2, N 3.5. ^{1}H NMR ([D$_6$]DMSO): δ = –1.05 (4 H, H$_\beta$ pz), –0.88 (4 H, H$_\alpha$ pz), –0.84 (8 H, H$_\alpha$ 4-pic), 2.64 (12 H, CH$_3$ 4-pic), 3.97 [24 H, CH$_3$ ac (b)], 4.07 [12 H, CH$_3$ ac (d)], 4.98 [12 H, CH$_3$ ac (a)], 5.24 [6 H, CH$_3$ ac (c)], 5.62 (8 H, H$_\beta$ 4-pic). More details are provided as Supporting Information.

[{[Ru$_3$O(ac)$_6$(4-pic)$_2$(pz)]$_2$-μ$_2$-Ru$_3$O(ac)$_6$(pz)}$_3$-μ$_3$-Ru$_3$O(ac)$_6$](PF$_6$)$_{10}$: The reaction of [{Ru$_3$O(ac)$_6$(4-pic)$_2$(pz)}$_2$][Ru$_3$O(ac)$_6$(CH$_3$OH)]-(PF$_6$)$_3$ (160 mg, 0.052 mmol) with [Ru$_3$O(ac)$_6$(pz)$_3$]PF$_6$[13] was carried out in CH$_2$Cl$_2$, in a molar ratio of 3:1, at room temperature during 5 d. The solution was concentrated to dryness and the crude material purified on a neutral alumina column, using a mixture of 20% CH$_3$CN/CH$_2$Cl$_2$ (v/v). This procedure led to 10 mg (6%) of the dendrimer.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR, cyclic voltammetry and differential-pulse voltammetry data.

Acknowledgments

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