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# Synthesis and characterization of polyamidoamine dendrimers surface-functionalized with bromotricarbonylpyridyliminerhenium(I) units

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**Abstract**

A novel type of rhenium-containing dendrimers has been prepared and characterized. A series of Schiff base-terminated PAMAM dendrimers were prepared by condensing the terminal amine groups of PAMAM dendrimers with pyridine-2-carboxaldehyde. Complete condensation of the terminal amines was confirmed by $^1$H NMR spectroscopy. Bromotricarbonylrhenium(I) moieties were introduced onto the surface of these modified PAMAM derivatives by refluxing with bromopentacarbonylrhenium(I). These complexes had been characterized by a variety of analytical and spectroscopic techniques and their IR, NMR, and mass spectra discussed. The crystal structure of the model compound $[(CH_3CONHCH_2CH_2N{=}CH{-}Py)ReBr(CO)_3]$ confirms a facial configuration of the three carbonyl ligands. UV–Vis absorption spectroscopy suggests that the $\{Re(CO)_3\}$ moieties are quite far apart even in the second generation PAMAM dendrimers and do not interact with one another. In fact, the intensity of the metal-to-ligand ($d\pi$–$p\pi^*$) charge-transfer is a linear function of the number of $\{Re(CO)_3\}$ chromophores.


*Keywords:* Poly(amidoamine); Metallodendrimer; Rhenium carbonyl

## 1. Introduction

Polymers are known to form effective drug delivery systems for treatment of localized cancer and some of them have been very successful, especially polymeric micelles made of block copolymers of PEG and amino acid cores [1]. These polymeric drug conjugates are supposed to enhance the bioavailability of the drug and to provide a site-specific controlled release mechanism towards cancer cells, in order to accumulate the drug at the intended site of action [2,3]. Among the countless polymers that have been prepared, there are only few candidates which will satisfy all the desirable features [4–6]. Dendrimers, highly branched, well defined, globular macromolecules, represent a promising system which can be considered for such applications [7–9]. Their near monodisperse molecular weight can be modified such that drugs can be either covalently attached to a large number of peripheral binding-sites or physically entrapped in cavities of the dendritic backbone [10,11]. Owing to their well-defined skeleton, non-toxicity, lack of immunogenicity, and biodegradability, the polyamidoamine dendrimers (PAMAM), are suitable carriers for drug delivery applications [12–15].

Complexes containing the $\{M(CO)_3\}^+$ ($M = {}^{188/186}Re$, $^{99m}Tc$) core have attracted much attention in nuclear medicine for diagnostic and therapeutic purposes [16–18]. *N*-heterocycles are known to form strong bonds to Re(I) metal centers [19–24]. Comparatively, there are few reports of rhenium containing dendrimers. One type of adamantine-terminated dendrimers having a Re(V) core is solubilized by introducing β-cyclodextrin groups at the peripherals [25]. However, this is at the expense of reduced number of radiofunctional sites. Vessières and Coworkers

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[1] described the synthesis of a metal-containing hyperbranched dendrimer based on a chlorotricarbonylrhenium(I) 2,2′-bipyridine complex. The instability of this compound, however, hinders its application as a radiotherapeutical agent. We now report a stable PAMAM analogue functionalized at the periphery with {$ReBr(CO)_3$} moieties.

The surface of PAMAM dendrimers was initially modified by reacting pyridine-2-carboxyaldehyde with the primary amine end groups of G0, G1 and G2 PAMAM dendrimers to afford the corresponding terminally modified PAMAM Schiff bases. These surface modified iminopyridyl dendrimers were further reacted with [$ReBr(CO)_5$] to give [*fac*-($MeCONHCH_2CH_2N{=}CH{-}Py$)$ReBr(CO)_3$] (**1C**), and the different generation complexes [G0(PAMAM)-$Py_4${$ReBr(CO)_3$}$_4$] (**4C**), [G1(PAMAM)$Py_8${$ReBr(CO)_3$}$_8$] (**8C**), and [G2(PAMAM)$Py_{16}${$ReBr(CO)_3$}$_{16}$] (**16C**). The products were characterized by $^1H$, $^{13}C$ NMR, UV–Vis, fluorescence and IR spectroscopy, CHN analysis, and MALDI-TOF mass spectrometry. Compound **1C** was also characterized by single crystal X-ray diffraction.

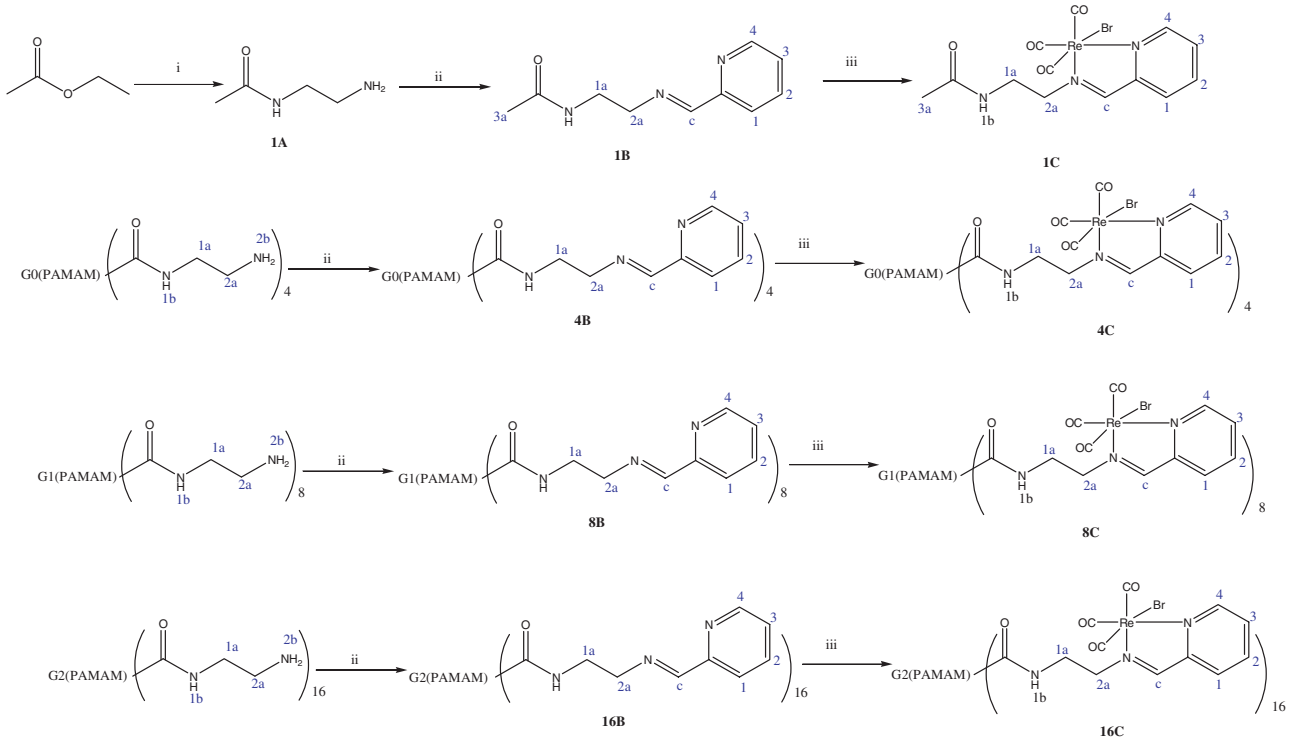
## 2. Result and discussions

### 2.1. Synthesis

The synthesis of the new rhenium carbonyl metallodendrimers is summarized in Scheme 1. The pyridylimine PAMAM dendrimer ligands were precipitated as light yellow solids by dropwise addition of a methanolic solution of ligands into diethyl ether. These samples turned oily when exposed to air, probably due to the absorption of moisture. The metallodendrimers were synthesized by complexation reactions between dendrimer ligands and [$ReBr(CO)_5$]. The Schiff-base [$MeCONHCH_2CH_2N{=}CH{-}Py$] (**1B**) reacts over a period of 2 h with [$ReBr(CO)_5$] in methanol to give the [*fac*-($MeCONHCH_2CH_2N{=}CH{-}Py$)$ReBr(CO)_3$] (**1C**). The different generation rhenium containing dendrimers [G0(PAMAM)$Py_4${$ReBr(CO)_3$}$_4$] (**4C**), [G1(PAMAM)$Py_8${$ReBr(CO)_3$}$_8$] (**8C**), [G2(PAMAM)$Py_{16}${$ReBr(CO)_3$}$_{16}$] (**16C**) were synthesized in the same way using surface-modified PAMAM Schiff bases with [$ReBr(CO)_5$] in a mixture of methanol and chloroform. Generally, the higher the generation of the dendrimers, the poorer the solubility of their rhenium derivatives in common organic solvents. All the complexes were found to be very soluble in DMF and DMSO.

### 2.2. Crystal structure of [*fac*-[$MeCONHCH_2CH_2N{=}CHPy$]$ReBr(CO)_3$] (**1C**)

The rhenium atom of **1C** is coordinated octahedrally by three facial CO ligands, a bromide ligand and a bidentate pyridylimino group (Fig. 1). The short N(2)—C(6) length of 1.25(2) Å is consistent with a C=N double bond. The N(3)—C(9) bond of the amide group [1.33(2) Å] is intermediate in length between a C=N double bond (see above) and a C—N single bond [C(8)—N(3) 1.43(2) Å], consistent




Scheme 1. (i) ethylenediamine, 100 °C, 36 h; (ii) pyridine-2-carboxaldehyde, anhydrous sodium sulfate (the higher the generation, the longer the reaction time); (iii) [$ReBr(CO)_5$], 60 °C (the higher the generation, the longer the reaction time). The numbers refer to the assignment of $^1H$ NMR signals of the compounds (see Fig. 2).

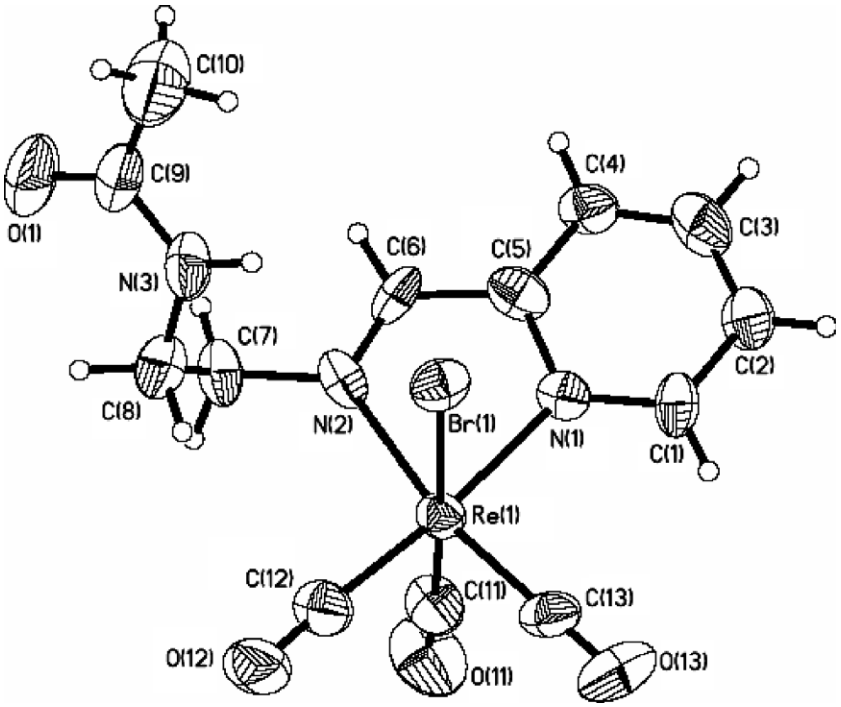



Fig. 1. Molecular structure of **1C**(40% thermal ellipsoids).

with the conjugation of the nitrogen lone pair with the C═O bond. This conjugation is further confirmed by the virtual coplanarity of the atoms C(8), N(3), C(9), O(1) and C(10) [maximum deviation 0.03 Å, for N(3)]. The Re(1)—N(1) distance [2.17(1) Å] is equal to the Re(1)—N(2) distance [2.18(1) Å] within experimental error, reflecting the imino nature of both nitrogen atoms; the basicity of the two N towards Re(I) center are quite similar. However, the CO *trans* to N(2) is more bent away from linearity (169°) than the CO *trans* to N(1) (174°). This may be due to the constrained N(1)—Re—N(2) angle of the ligand. The chelate ring is also virtually planar, with a maximum deviation of 0.06 Å [for N(1)].

### 2.3. Spectroscopic characterization

All the rhenium complexes are deep orange, and show strong characteristic absorption IR bands at 2016, 1914, and 1902 $cm^{-1}$. The band at 2016 $cm^{-1}$ may be assigned to the A vibrational mode and the 1914, 1902 $cm^{-1}$ doublet to the E vibrational mode of the $\{Re(CO)_3\}$ group with approximate $C_{3v}$ site symmetry. The removal of degeneracy of the E mode is due to the reduced symmetry of the molecule. The $\nu$(C═N) stretching absorption observed for the uncomplexed dendrimers at 1567 $cm^{-1}$ shifts to lower frequency [26] at 1551 $cm^{-1}$. This is a result of reduced polarity of the C═N bonds upon coordination of the $\{ReBr(CO)_3\}$ moiety.

Evidence for the condensation reactions is provided by proton NMR spectroscopy (Fig. 2); the proton resonances of the terminal amines at 1.5–1.8 ppm disappear and those of the $CH_2$ protons adjacent to the imine moiety shifted downfield upon condensation. The downfield shift of the pyridyl protons upon coordination with the rhenium carbonyl groups suggests that coordination of the pyridyl nitrogen to the metal has a deshielding effect on the ring protons. The protons (1a) and (2a) (Scheme 1) are also shifted to lower fields on coordination, which may be attributed to the anisotropic effect of the carbonyl ligands as well as the electron-withdrawing effect of the metal.

The MALDI-TOF mass spectra (Fig. 3) showed ion peaks that correlated well with the calculated monoisotopic molecular masses. The pyridylimine dendrimer $[G0(PAMAM)Py_4]$ gave a peak at $m/z$ 873.29, which corresponds with $[G0(PAMAM)Py_4]^+$ (873.0). No attempts were made to interpret the subsequent fragmentations. Reliable molecular weight determinations can not be obtained for the higher generation dendrimer ligands because of the broad distributions of the peaks observed [27]. An interesting feature observed, common to the rhenium complexes under these spectral conditions, is that the C═N bond of each branch of the PAMAM complexes tends to be hydrogenated under the spectrometer conditions used. For instance, compound **1C** was observed as $[(MeCONHCH_2CH_2NHCH_2Py)Re(CO)_3]-Br]^+$ at $m/z$ 463.9 (calcd. 463.5) and compound **4C** was observed as $[G0(PAMAM)(NHCH_2)_4Py_4\{ReBr(CO)_3\}_4-Br]^+$ at $m/z$ 2201.7 (calcd. 2201.1). The highest peak of compound **8C** is observed at $m/z$ 4401.5 (calcd. 4402.8), which corresponds to the successive loss of 7Br, giving $[G1-(PAMAM)(NHCH_2)_8Py_8\{ReBr(CO)_3\}_8-7Br]^+$.

The UV–Vis absorption and emission spectra of complexes **1C**, **4C**, **8C** and **16C** are shown in Fig. 4. The reference compound **1C**, which contains a single rhenium

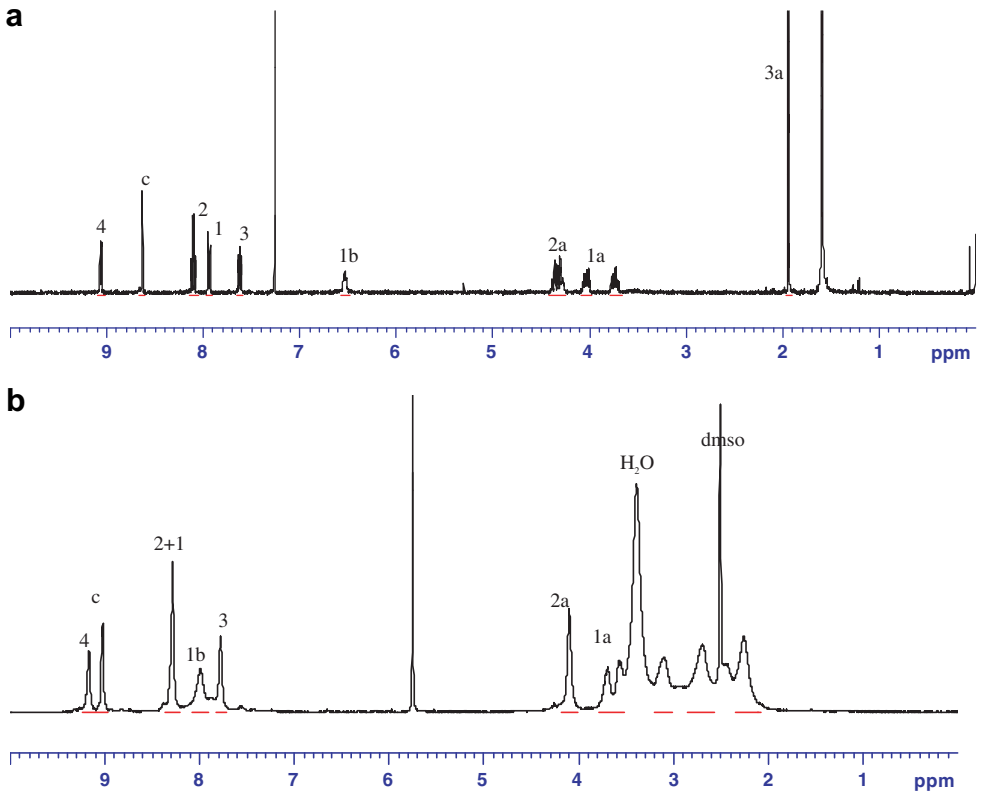



Fig. 2. $^{1}$H NMR spectra: (a) [ReBr(**1B**)(CO)$_3$] (**1C**) in $CDCl_3$; (b) [G2(PAMAM)Py$_{16}${ReBr(CO)$_3$}$_{16}$] (**16C**) in [$(CD_3)_2SO$]. Peaks are labeled according to the protons they are assigned to (see Scheme 1).

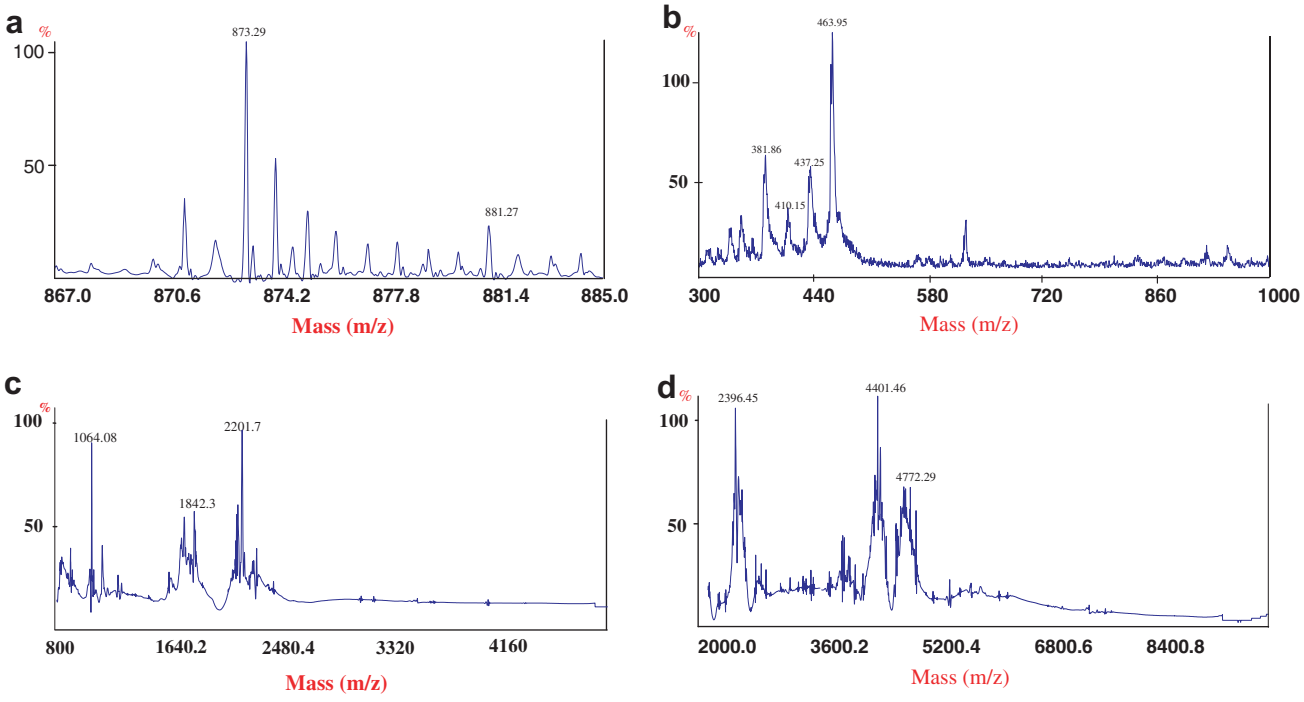



Fig. 3. MALDI-TOF mass spectra of: (a) [G0—Py$_4$]; (b) [(MeCONHCH$_2$CH$_2$N=CH—Py)ReBr(CO)$_3$] (**1C**); (c) [G0(PAMAM)Py$_4${ReBr(CO)$_3$}$_4$] (**4C**); (d) [G1(PAMAM)Py$_8${ReBr(CO)$_3$}$_8$] (**8C**).

carbonyl group, shows a comparatively weak absorption band at about 400 nm attributed to the d$\pi$–p$\pi^*$ metal-to-ligand (diimine) charge-transfer (MLCT). The intensity of this absorption increases as the number of chromophores increases. The molar extinction coefficient is linearly related to the number of chromophores present. This

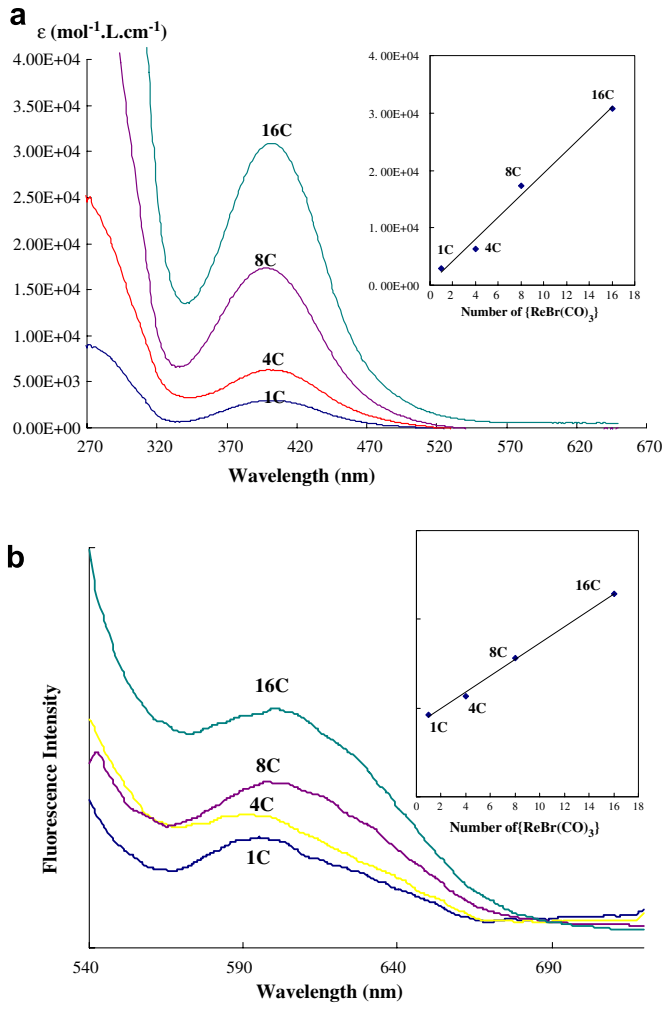



Fig. 4. (a) UV–Vis absorption spectra in DMF solution; (inset) linear relationship of the value of $\varepsilon$ ($mol^{-1}$ L $cm^{-1}$) at 400 nm with the number of {$ReBr(CO)_3$} groups; (b) emission spectra ($\lambda_{exc} = 400$ nm) of **1C**, **4C**, **8C**, and **16C** in DMF solution; (inset) linear relationship of fluorescence intensity at 610 nm with the number of {$ReBr(CO)_3$} groups; (all solutions were of equal molar concentration $2 \times 10^{-5}$ M).

suggests that the rhenium carbonyl bromide moieties are quite independent of one another and has little or no metal–metal interactions up to the second generation.

Excitation of the rhenium containing dendrimer complexes at 400 nm gives a weak single emission at room temperature, with a maximum at around 610 nm. All complexes exhibit very similar spectroscopic features, except for a small bathochromic shift for **8C** and **16C**. The intensity of emission increases as the number of {$Re(CO)_3$} groups increases.

## 3. Conclusions

A series of terminally functionalized bromotricarbonylpyridyliminerhenium PAMAM dendrimers (generations 0–2) having four, eight, and 16 {$ReBr(CO)_3$} moieties have been synthesized. Unlike other polymeric carriers, they are more structurally defined and capable of carrying a much higher 'payload' of Re(I) derivatives at the terminals. The improved solubility in polar solvents such as alcohols also increases the potential of these rhenium(I) complexes to be used in the biomedical and radiopharmaceutical fields.

## 4. Experimental

### 4.1. Materials and apparatus

All experiments were carried out in an atmosphere of purified nitrogen or argon, employing standard Schlenk techniques. All reagents purchased from commercial sources were used without further purification unless otherwise indicated. Solvents were dried and distilled under nitrogen before use. Generation 0, 1, and 2 PAMAM dendrimers, and acetylethylenediamine (**1A**) were prepared according to published methods [28,29].

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker CRX400 400 MHz spectrometer at 25 °C in $CDCl_3$ or $(CD_3)_2SO$. Elemental analyses were carried out using a Euro EA 3011 Elemental Analyzer. The IR spectra were recorded on a Perkin–Elmer 1725X FTIR spectrometer. UV–Vis absorption spectra were recorded on a Cary-WINUV 50Bio UV–Vis spectrophotometer. Luminescence spectra were recorded on a Perkin–Elemer LS 50B Luminescence spectrometer.

Mass spectra were recorded on Voyager STR (Applied Biosystems) matrix-assisted laser desorption ionization time-of-flight (MALDI/TOF) mass spectrometer. Data were acquired in the linear mode to produce average $m/z$ data with optimum accuracy and sensitivity. The molecular weights of the compounds were recorded using a mixture of 2 μl of DMF and 5 μl of methanol as the solvent for the complexes. The matrix used was a saturated solution of sinapinic acid in a 0.1% (v/v) solution of trifluoroacetic acid in acetonitrile/water (1:1 v/v) mixture. In the analysis, 0.5 μl of the sample solution was mixed with an equal volume of the matrix solution and spotted on the target plate.

Single crystal of **1C** was obtained by layering a $CH_2Cl_2$ solution of the complex with hexane. Single crystal X-ray diffraction data was collected using a Siemens P4 diffractometer in the $\theta$–$2\theta$ mode, with graphite-monochromated Mo $K\alpha$ radiation (0.71073 Å) at 298 K. The data was corrected for absorption effects using ψ-scan data. The crystal structure was solved by direct methods and refined on $F^2$ by the full matrix least-squares method using the SHELXTL PLUS software package [30]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions and allowed to ride on their carrier atoms. The absolute structure was determined by the method of Flack [31]. Crystallographic and geometric parameters are listed in Tables 1 and 2, respectively.

#### 4.1.1. Synthesis of pyridylimine ligands

*4.1.1.1. Preparation of [$MeCONHCH_2CH_2N{=}CHPy$] (**1B**).* About 1.0 g (9.8 mmol) of acetylethylenediamine dissolved in 8 ml methanol was added into 1.1 g (1.0 mmol)

of pyridine-2-carboxaldehyde dissolved in methanol in the presence of a large excess of anhydrous sodium sulfate at 0 °C. The mixture was allowed to stir at room temperature for 2 h. This was filtered and dried under vacuum. The crude yellow oil obtained was dissolved in dichloromethane, and hexane added slowly whereupon yellow oil (**1B**) separated (1.3 g, 70% yield). $^1$H NMR ($CDCl_3$): $\delta = 2.00$ (s, 3H, *Me*CO), 3.63 (m, 2H, NH*CH*$_2$), 3.78–3.80 (t, 2H, *CH*$_2$N=), 7.80–8.70 (Py, and *NH*), 8.42 (s, 1H, *CH*=N). $^{13}$C NMR ($CDCl_3$, $\delta$): 170.54, 163.91, 154.43, 150.07, 137.07, 126.26, 122.12, 60.80, 40.55, and 23.73.

*4.1.1.2. Preparation of [G0—Py$_4$] (**4B**), [G1—Py$_8$] (**8B**), [G2—Py$_{16}$] (**16B**).* The synthetic method was similar to that used for the synthesis of [MeCONHCH$_2$CH$_2$N=CHPy] (**1B**), except for varying mole ratios; G0 PAMAM (1.6 g, 3.1 mmol) and pyridine-2-carboxaldehyde (2.9 g, 27.1 mmol); G1 (3.0 g, 2.1 mmol) and pyridine-2-carboxaldehyde (3.6 g, 33.6 mmol); G2 (2.0 g, 0.6 mmol) and pyridine-2-carboxaldehyde (2.0 g 18.7 mmol). Reactions were carried out at room temperature. The crude products obtained were usually dark yellow oils. They were purified by dropwise addition of the compound in methanolic solution to diethyl ether to give light yellow solids. These samples turned oily when allowed standing in air, probably due to the absorption of moisture.

*4.1.1.3. Spectral data.* [G0—Py$_4$] (**4B**), $^1$H NMR: ($CDCl_3$): $\delta = 1.99$, (8H, *CH*$_2$CO), 2.08, (4H, *CH*$_2$N), 2.31, (8H, *CH*$_2$CH$_2$CO), 3.31, (m, 8H, NH*CH*$_2$CH$_2$N=), 3.45, (t, 8H, NHCH$_2$*CH*$_2$N=), 7.01–8.33, (Py), 8.08, (s, 4H, CH=N). $^{13}$C NMR ($CDCl_3$, $\delta$): 173.18, 163.72, 158.87, 137.21, 125.43, 122.30, 66.26, 60.68, 50.66, 40.36, and 34.45.

[G1—Py$_8$] (**8B**), $^1$H NMR ($CDCl_3$), $\delta = 2.30$, (24H, C*H*$_2$CO); 2.40–2.68, (36H, C*H*$_2$N); 3.20, (16H, NH*CH*$_2$CH$_2$N); 3.56, (m, 16H, NH*CH*$_2$CH$_2$N=); 3.76 (t, 16H, NHCH$_2$*CH*$_2$N=); 7.29–8.62 (Py); 8.36, (s, 8H, CH=N); $^{13}$C NMR [$(CD_3)_2SO$, $\delta$]: 172.58, 163.79, 154.69, 150.17, 137.74, 126.02, 121.71, 60.36, 55.78, 50.44, 37.8, 33.99.

[G2—Py$_{16}$] (**16B**), $^1$H NMR ($CDCl_3$), $\delta = 2.01$, (48H, C*H*$_2$CO); 2.18–2.67, (72H, C*H*$_2$N); 3.18, (32H, NH*CH*$_2$CH$_2$N); 3.51–3.54, (m, 32H, NH*CH*$_2$CH$_2$N=); 3.75 (t, 32H, NHCH$_2$*CH*$_2$N=). 7.30–8.59 (Py), 8.35, (s, 8H, C*H*=N).

*4.1.2. Synthesis of metallodendrimers*

*4.1.2.1. Preparation of [ReBr(1B)(CO)$_3$] (**1C**).* To a suspension of [ReBr(CO)$_5$] [32] (0.2 g, 0.5 mmol) in a mixture containing methanol and chloroform (3:1, v:v), was added a solution of [MeCONHCH$_2$CH$_2$N=CHPy] (**1B**) (0.1 g, 0.5 mmol) at 50 °C. The mixture was refluxed for 2 h. The solvent was removed under vacuum and the orange solid residue recrystallized from dichloromethane/hexane giving 0.09 g orange-red needles (**1C**) (33%). Anal. Calc. for $C_{13}H_{13}BrN_3O_4Re$: C, 28.84; H, 2.42; N, 7.76. Found: C, 28.32; H, 2.56; N, 7.51%. $^1$H NMR: ($CDCl_3$, $\delta$): (see Fig. 2.) $\delta = 1.94$, (s, 3H, MeCO); 3.75–3.96 (m, 2H, NH*CH*$_2$); 4.30–4.36 (m, 2H, *CH*$_2$N=); 6.53 (s, 1H, *NH*); 7.60–9.07 (Py); 8.62 (s, 1H, *CH*=N). $^{13}$C NMR ($CDCl_3$, $\delta$): 196.30, 196.00, 185.95, 171.15, 168.3, 155.05, 153.83, 139.71, 129.11, 128.48, 62.53, 39.66, and 23.64.

*4.1.2.2. Preparation of [G0—Py$_4$—{ReBr(CO)$_3$}$_4$] (**4C**), [G1—Py$_8$—{ReBr(CO)$_3$}$_8$] (**8C**), [G2—Py$_{16}$—{ReBr(CO)$_3$}$_{16}$] (**16C**).* The syntheses were similar to that for [ReBr(**1B**)(CO)$_3$] (**1C**) except that [ReBr(CO)$_5$] (0.10 g, 0.25 mmol) and [G0—Py$_4$] (0.05 g, 0.06 mmol), [ReBr(CO)$_5$] (0.17 g, 0.42 mmol) and [G1+Py$_8$] (**8B**) (0.10 g, 0.05 mmol), [ReBr(CO)$_5$] (0.35 g, 0.85 mmol) and [G2+Py$_{16}$] (0.20 g, 0.04 mmol) were used, and the reactions were carried out under reflux. The solvent was removed and the orange solid residue recrystallized from DMF/ether.

*4.1.2.3. Spectral data.* [G0—Py$_4$—{ReBr(CO)$_3$}$_4$] (**4C**). Anal. Calc. for $C_{58}H_{60}N_{14}O_{16}Br_4Re_4$: C, 30.48; H, 3.18; N, 8.58. Found: C, 30.31; H, 3.50; N, 8.65%. $^1$H NMR

Table 1
Selected crystallographic data for **1C**

| | |
|---|---|
| Empirical formula | $C_{13}H_{13}BrN_3O_4Re$ |
| Formula weight | 541.37 |
| Color, habit | Yellow, needle |
| Crystal system | Orthorhombic |
| Space group | *Pna*2(1) |
| $a$ (Å) | 6.9931(9) |
| $b$ (Å) | 20.048(3) |
| $c$ (Å) | 12.378(4) |
| $V$ (Å$^3$) | 1735.3 (6) |
| $Z$ | 4 |
| Crystal size (mm$^3$) | $0.1 \times 0.2 \times 0.3$ |
| $\Theta$ Range (°) | 1.93–24.99 |
| Maximum and minimum transmission | 0.7283, 0.3019 |
| $\mu$ (mm$^{-1}$) | 9.323 |
| Reflections collected | 2063 |
| Independent reflections | 1690 |
| $R_{(int)}$ | 0.0305 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0327, 0.0769 |

Table 2
Selected bond lengths (Å) and bond angles (°) of **1C**

| | | | |
|---|---|---|---|
| Re(1)—C(11) | 1.93(2) | C(13)—Re(1)—N(2) | 168.8(5) |
| Re(1)—C(12) | 1.91(2) | N(1)—Re(1)—N(2) | 74.1(4) |
| Re(1)—C(13) | 1.93(2) | C(11)—Re(1)—Br(1) | 176.3(5) |
| Re(1)—N(1) | 2.17(1) | C(12)—Re(1)—Br(1) | 92.1(4) |
| Re(1)—N(2) | 2.18(1) | C(13)—Re(1)—Br(1) | 90.5(4) |
| Re(1)—Br(1) | 2.627(2) | N(1)—Re(1)—Br(1) | 84.3(3) |
| C(12)—Re(1)—C(11) | 88.0(6) | N(2)—Re(1)—Br(1) | 83.9(3) |
| C(12)—Re(1)—C(13) | 88.9(6) | C(1)—N(1)—Re(1) | 127.0(9) |
| C(11)—Re(1)—C(13) | 93.2(6) | C(5)—N(1)—Re(1) | 115.3(9) |
| C(11)—Re(1)—N(1) | 95.2(6) | C(6)—N(2)—Re(1) | 117.0(9) |
| C(12)—Re(1)—N(1) | 174.2(5) | C(7)—N(2)—Re(1) | 127.0(9) |
| C(13)—Re(1)—N(1) | 95.7(5) | O(11)—C(11)—Re(1) | 178(2) |
| C(11)—Re(1)—N(2) | 92.4(6) | O(12)—C(12)—Re(1) | 176(2) |
| C(12)—Re(1)—N(2) | 101.0(6) | O(13)—C(13)—Re(1) | 178(1) |

[$(CD_3)_2SO$, $\delta$]: $\delta = 2.12$, (8H, $CH_2CO$), 2.21–2.33, (4H, $CH_2N$), 2.77 (8H, $CH_2CH_2CO$), 3.57–3.68, (8H, $NHCH_2CH_2N$=), 4.09, (8H, $NHCH_2CH_2N$=), 7.77–9.13, (Py), 9.03, (s, 4H, CH=N).

$^{13}C$ NMR [$(CD_3)_2SO$, $\delta$]: 197.68, 197.35, 187.53, 172.91, 171.28, 155.54, 154.00, 141.24, 130.07, 64.28, 52.14, 50.13, 39.18, and 33.59.

[G1—$Py_8$—{$ReBr(CO)_3$}$_8$] (**8C**), Anal. Calc. for $C_{134}H_{158}N_{34}O_{36}Br_8Re_8$: C, 32.48; H, 3.22; N, 9.62. Found: C, 32.43; H, 3.59; N, 9.33%. $^1H$ NMR [$(CD_3)_2SO$, $\delta$]: $\delta = 2.23$, (24H, $CH_2CO$), 2.40–2.67, (36H, $CH_2N$); 3.07, (16H, $NHCH_2CH_2N$); 3.44–3.78, (16H, $NHCH_2CH_2N$=); 4.09 (16H, $NHCH_2CH_2N$=); 7.78–9.15 (Py); 9.04, (s, 8H, CH=N); $^{13}C$ NMR [$(CD_3)_2SO$, $\delta$]: 197.99, 197.45, 187.68, 172.66, 171.37, 155.65, 154.03, 141.26, 130.07, 64.38, 52.94, 50.11, 39.23, 33.69.

[G2—$Py_{16}$—{$ReBr(CO)_3$}$_{16}$] (**16C**). Anal. Calc. for $C_{186}H_{336}N_{74}O_{76}Br_{16}Re_{16}$: C, 33.40; H, 3.29; N, 10.08. Found: C, 32.00; H, 4.29; N, 9.20%. $^{13}C$ NMR [$(CD_3)_2SO$, $\delta$]: 197.57, 197.14, 187.37, 173.11, 171.16, 155.22, 153.80, 141.18, 129.99, 63.98, 52.84, 49.96, 36.80, and 32.69.

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structure of **1C** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 612878. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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