Amphiphilic Dendrimers with Heteroleptic Bis([2,2′:6′,2″]terpyridine)-Ruthenium(II) Cores

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A new series of dendrimers was assembled through formation of homo- and heteroleptic Ru^{II} complexes with [2,2′:6′,2″]terpyridine ligands bearing hydrophilic and hydrophobic dendrons, with the aim to develop amphiphilic vectors for potential use in gene delivery (*Scheme 1*). The synthesis started with the preparation of the 4′-(3,5-dihalo-4-methoxyphenyl)-[2,2′:6′,2″]terpyridine ligands **1a**,**b** *via* the *Kröhnke* pyridine synthesis (*Scheme 2*), followed by attachment of dendrons **10a**–**10f** (*Fig. 2*) by *Sonogashira* cross-coupling to give the dendritic ligands **11**–**16** (*Schemes 3* and *4*). Ligands were subsequently introduced into the coordination sphere of Ru^{III} to give the stable intermediates [Ru(**11**)Cl$_3$] (**24**; *Scheme 7*) and [Ru(**14**)Cl$_3$] (**27**; *Scheme 8*). These were transformed under reductive conditions into the heteroleptic complexes [Ru(**11**)(**13**)](PF$_6$)$_2$ (**25**) and [Ru(**13**)(**14**)](PF$_6$)$_2$ (**29**). Removal of the (*tert*-butoxy)carbonyl (Boc) protecting groups in **25** and **29** then gave the desired amphiphilic dendrimers **26** (*Scheme 7*) and **30** (*Scheme 8*) with branchings of generations 0 and 1. Complex formation was analyzed by high-resolution matrix-assisted laser-desorption-ionization *Fourier*-transform ion-cyclotron-resonance mass spectrometry (HR-MALDI-FT-ICR-MS), which provided spectra featuring unique fragment-ion series and perfectly resolved isotope distribution patterns (*Figs. 4* and *5*). The preparation of homo- and heteroleptic complexes with terpyridine ligands bearing generation-2 dendrons failed due to steric hindrance by the bulky wedges.

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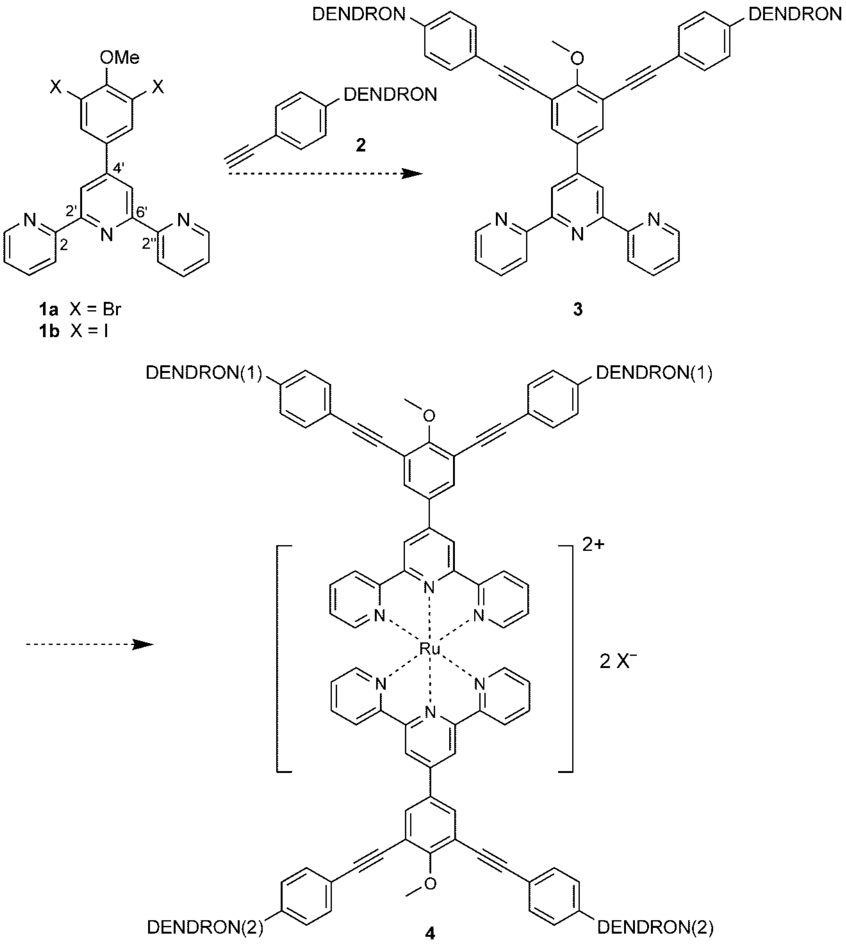
1. Introduction. – Dendrimers are well-known carriers of structure and function in a wide variety of applications (for recent monographs and reviews, see [1]). Dendrons have been shown to create specific microenvironments and to tune in a unique way binding and reactivity properties of functional cores in dendritic enzyme mimics [2][3]. Self-assembly properties [4] are particularly enhanced in amphiphilic dendrimers that are characterized by rich structural diversity including unimolecular micelles [5], dendritic block copolymers [6], globular amphiphiles with fullerene cores [7], and mesophase-forming tapered dendrons [8]. Dendritic self-assembly has recently been used to generate novel vectors for gene transfection [9][10].

Another efficient route towards large supramolecular assemblies is based on transition-metal complexation; this approach has been successfully applied to the construction of a rich variety of metallodendrimers [11]. In our program, targeting novel dendritic amphiphiles for potential application as gene transfection agents [10], we decided to use transition metal complexation as a versatile way to assemble lipophilic and cationic dendritic wedges. Here, we report the synthesis and characterization of a series of homo- and heteroleptic complexes of Ru^{II} with dendritic [2,2′;6′,2″]terpyridine ligands. For the preparation of the bisterpyridine Ru^{II} complexes, we intended to apply the versatile protocols reported by *Constable et al.* [12] and *Sauvage* and co-workers [13].

2. Results and Discussion. – A modular approach was selected for the synthesis of the targeted amphiphilic dendrimers, consisting in *i*) preparation of halogenated [2,2′;6′,2″]terpyridine ligands **1a** and **1b**, *ii*) *Sonogashira* cross-coupling [14] with dendron-functionalized arylacetylenes **2** to give the dendron-substituted terpyridines **3**, and *iii*) formation of the heteroleptic Ru^{II} complexes **4** (*Scheme 1*). The synthesis of terpyridine ligands with different substitution patterns is well-documented [15]. Substitution at C(4′) (for conventional numbering, see *Scheme 1*) is a particularly convenient process [16]. Both Pd-catalyzed *Sonogashira* [17] and *Suzuki* cross-couplings [18][19] have been used to introduce halogenated terpyridine moieties into dendritic structures, without any problems arising from complexation of Pd^{II} to the ligands [20].

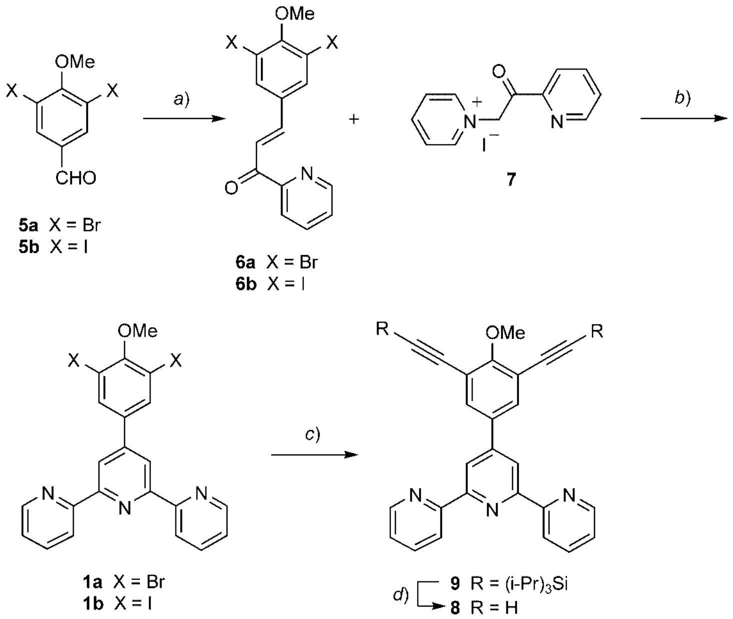
Scheme 1. *Synthetic Strategy Towards Amphiphilic Dendrimers with a Bisterpyridine Ru^{II} Core*



2.1. *Synthesis of the Halogenated Terpyridine Ligands.* The preparation of terpyridine derivatives **1a** and **1b** started from the 3,5-dihalogenated anisaldehydes

5a and **5b**, respectively [21] (*Scheme 2*). The desired ligands were subsequently obtained by the *Kröhnke* pyridine synthesis [22] (for other protocols for terpyridine syntheses that were less successful in this work, see [15][23]). Carefully controlled aldol condensation [15][24] of **5a** or **5b** with 2-acetylpyridine in EtOH provided enones **6a** and **6b**, respectively, in high yields. Maintaining the reaction temperature below 5° and with KOH as base proved critical for the success of the condensation [25]. The one-pot conversion of **6a** and **6b** with pyridinium iodide **7** [26] provided the desired ligands **1a** and **1b**, respectively, without formation of any constitutionally isomeric [17c][27] terpyridine side products.

Scheme 2. *Synthesis of Dihalogenated and Diethynylated Terpyridine Ligands*



a) 2-Acetylpyridine, KOH, EtOH, −10° → 20°, 18 h; 83% (**6a**), 86% (**6b**). *b*) NH_4OAc, AcOH, 120–160°, 16–24 h; 29% (**1a**), 64% (**1b**). *c*) From **1a**, $(i\text{-}Pr)_3Si{-}C{\equiv}CH$, $[Pd(PPh_3)_2Cl_2]$, CuI, Bu_4NBr, $(i\text{-}Pr)_2NH$, THF, 60°, 16 h; 90%. *d*) Bu_4NF, wet THF, 20°, 30 min; 90%.

The diiodo derivative **1b** was recrystallized from MeCN to yield crystals suitable for X-ray structure analysis (*Fig. 1*). The compound crystallizes in colorless prisms (triclinic unit cell; space group: $P\bar{1}$; two pairs of conformationally isomeric molecules per unit cell). The three rings of the terpyridine moiety adopt a nearly planar alignment, where N-atoms in adjacent rings are antiperiplanar with respect to each other. Looking along the *b*-axis, the crystal packing revealed that neighboring stacks of **1b** interlock in a herringbone pattern.

As an alternative to the route depicted in *Scheme 1*, we also explored an 'inverted' *Sonogashira* cross-coupling protocol starting from diethynylated terpyridine **8** and the corresponding haloarylated dendrons. Under optimized conditions, cross-coupling of poorly soluble **1a** with $(i\text{-}Pr)_3Si{-}C{\equiv}CH$ gave a good yield of dialkynylated **9**, which

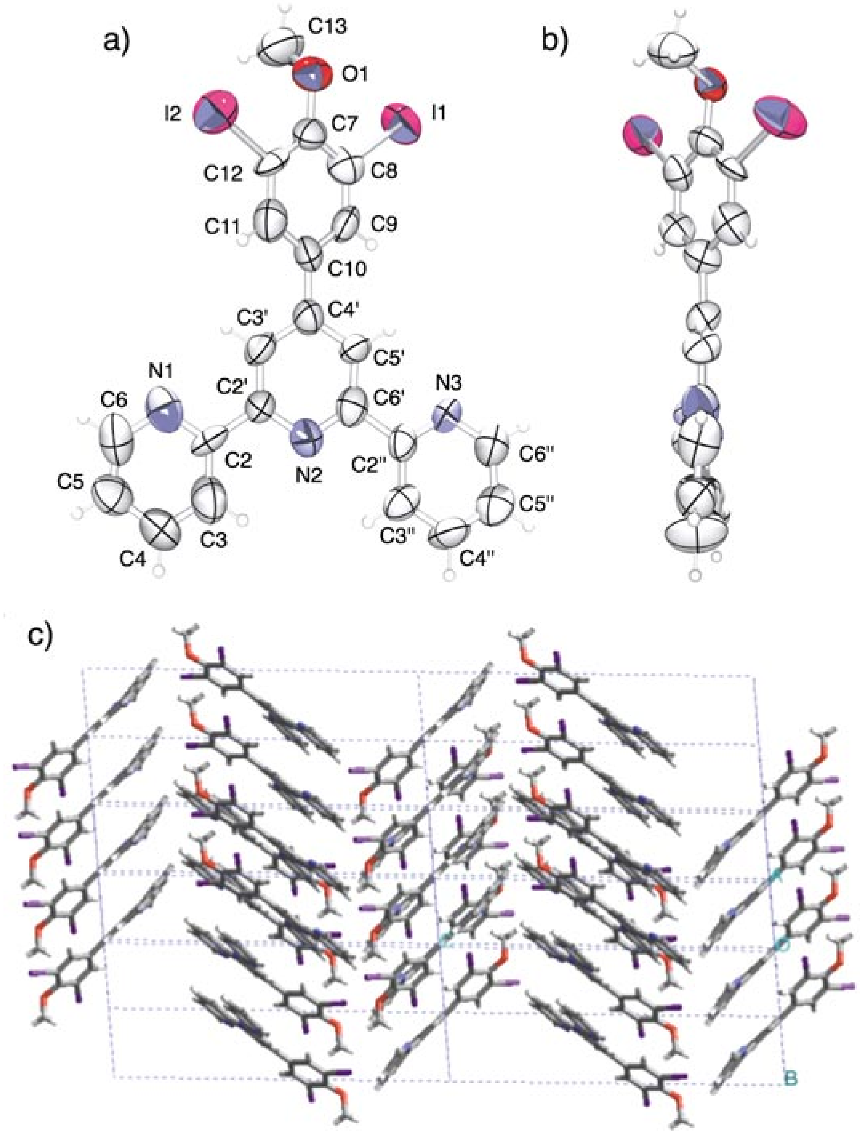


Fig. 1. a), b) *ORTEP Plots:* a*) front and* b*) side views of* **1b**. Arbitrary numbering. Atomic displacement parameters obtained at 293 K are drawn at the 75% probability level. Shown is one of the two conformers of **1b**, with the dihedral angle C(3′)–C(4′)–C(10)–C(11) = 39.2°. In the second conformer (not shown), this dihedral angle is 28.4°. *c*) *Crystal packing of* **1b**. The view along the *b*-axis shows the herringbone pattern of interlocking stacks.

was readily deprotected to give **8** (*Scheme 1*). Although the coupling of iodoaryl-substituted dendrons to **8** was successful, the reduced stability of the diethynyl derivative and its propensity for oxidative *Hay*-type polymerizations led us to abandon this approach.

2.2. *Attachment of the Dendrons to the Terpyridine Ligand.* The synthesis of dendrons **10a** – **10f** (*Fig. 2*) has been reported in [10]. The *Sonogashira* cross-couplings of diiodoterpyridine **1b** (which was found to be far more reactive and more soluble than the corresponding dibromo derivative **1a**) with the smaller phenylethynylated, zeroth-generation (G0) and first-generation (G1) dendrons **10a** – **10d** went smoothly to provide the dendritic ligands **11** – **14**, respectively, in high yields (*Scheme 3*). In the case of **13** and **14**, GPC (gel-permeation chromatography) purification (*Bio-Beads S-X1*; CH_2Cl_2) was required to remove small amounts of mono-coupled product. The high-resolution matrix-assisted laser-desorption-ionization *Fourier*-transform ion-cyclotron-resonance mass spectrum (HR-MALDI-FT-ICR, matrix: 2,5-dihydroxybenzoic acid (DHB)) of **13** displayed a series of characteristic fragment ions, which contrasts the lack of fragmentation in the spectrum of the ester analog **12**. While the sodium adduct of the molecular ion of **13** appeared as a weak signal only (1534.7987 ($[M+Na]^+$, $C_{84}H_{109}N_{11}NaO_{15}^+$; calc. 1534.8002)), successive loss of $C_5H_8O_2$ ('Boc') fragments gave rise to increasingly strong peaks separated by $\Delta m/z = 100$.

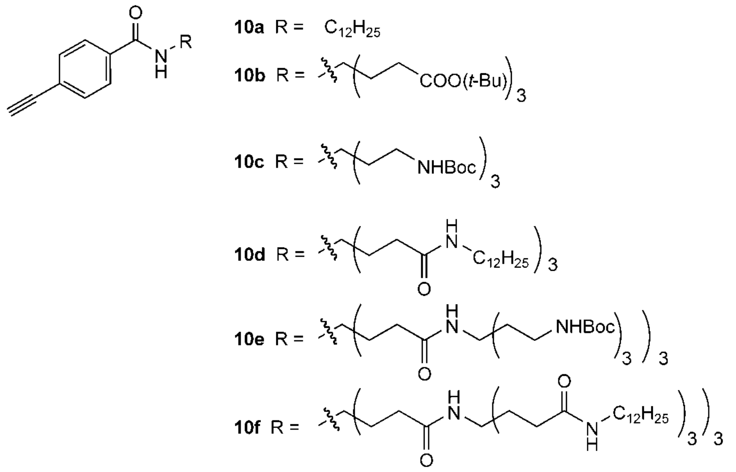
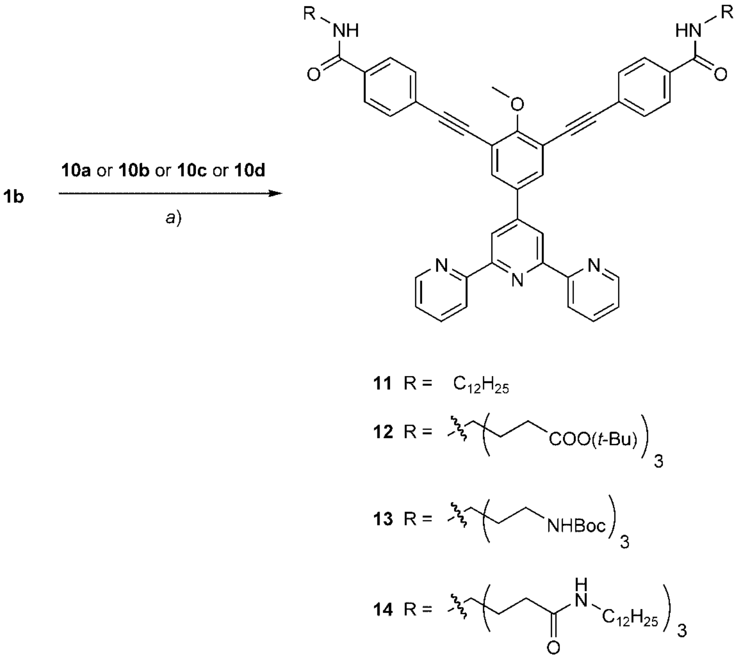


Fig. 2. *G1 and G2 dendrons* **10a** – **10f** *with phenylacetylene termini* [10]. Boc = *tert*-butyloxycarbonyl.

The preparation and purification of the terpyridine ligands **15** and **16** (*Scheme 4*), obtained by coupling the G2 dendrons **10e** and **10f** to **1b**, proved to be a greater challenge. While analytical GPC (THF) of **15** did not indicate any contamination after preparative GPC purification (CH_2Cl_2), HR-MALDI-MS (DHB matrix) revealed the presence of traces of homo-coupled product **17** ($[M+Na]^+$: m/z 3425). Further purification was postponed since a reasonable difference in hydrodynamic radii between **15** and **17** could only be expected after assembly to the metal complexes. As with G1 ligand **13**, the mass spectrum of **15** (3762.2500 ($[M+Na]^+$, $C_{192}H_{307}N_{29}NaO_{45}^+$; calc. 3762.2524)) displayed a series of characteristic fragment peaks resulting from successive loss of all eighteen Boc groups, with the $[M - 18\,Boc]^+$ ion becoming the base peak. Similar fragmentation was also observed for homo-coupled **17**. The cross-

Scheme 3. *Attachment of G1 Dendrons to the Terpyridine Ligand*

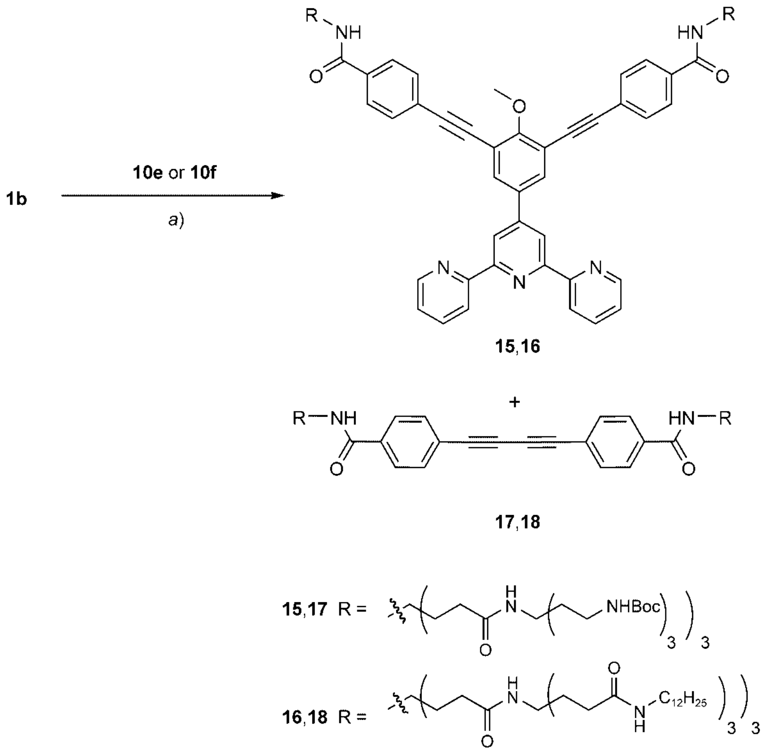


a) $[Pd(PPh_3)_2Cl_2]$, CuI, Bu_4NBr, $(i\text{-}Pr)_2NH$, THF, 20°, 16 h; 63% (**11**); 84% (**12**); 72% (**13**); 54% (**14**).

coupling between **1b** and the bulky dendron **10f** to give **16** never went to completion, even when using the more reactive $[Pd(PPh_3)_4]$ as catalyst, and considerable amounts of homo-coupled **18** ($[M+Na]^+$: m/z 5158 (100%)) were found in the product mixture. Again, separation of **16** and **18** by GPC was not successful; only one sharp GPC peak was recorded (THF). On the other hand, formation of the dendritic ligand **16** was unambiguously demonstrated by MALDI-MS (matrix: DHB), which depicted the sodium complex of the molecular ion $[M+Na]^+$ as the second-most-intense peak at m/z 5497 (58%). As for the corresponding G1 derivative **14**, only very little fragmentation was observed in the spectrum of **16**.

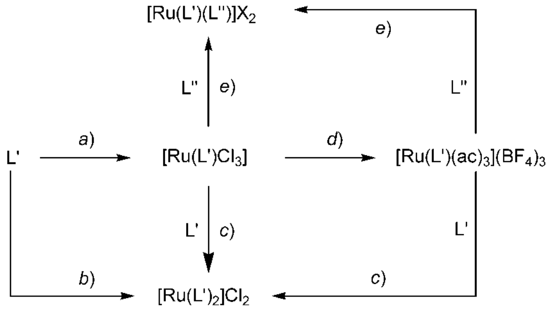
2.3. *Synthesis of the Homo- and Heteroleptic Ru^{II} Complexes.* We have chosen homo- and heteroleptic terpyridine complexes of Ru^{II} [12][13] to assemble the dendrons for a variety of reasons. The 4′-substituted [2,2′:6′,2″]terpyridine ligands do not give rise to chiral complexes as substituted 1,10-phenanthroline (phen) [28] and 3,3′-bipyridine (bipy) [29] ligands do, and the corresponding Ru^{II} (d^6) complexes are low-spin and thus diamagnetic. Heteroleptic Ru^{II} bisterpyridine complexes can be prepared in two steps *via* intermediate Ru^{III} complexes [12], while the conversion leading to homoleptic complexes can be suppressed (*Scheme 5*). This is possible because *i*) ligand exchange on Ru^{III} is roughly 10^4 times slower than on Ru^{II} [30], *ii*) in many cases the initially formed complex $[Ru(L')Cl_3]$ (L = ligand) is insoluble in the solvents used for its preparation (MeOH, EtOH) and thus precipitates from the reaction mixture, and *iii*) an excess of $RuCl_3 \cdot H_2O$ can be used as starting material in

Scheme 4. *Attachment of G2 Dendrons to the Terpyridine Ligand*



a) [Pd(PPh$_3$)$_2$Cl$_2$], CuI, Nu$_4$NBr, (*i*-Pr)$_2$NH, THF, 20°, 16 h; 35% (**15** and traces of **17**); 35% (**16** and **18**).

Scheme 5. *General Scheme for the Synthesis of Homoleptic and Heteroleptic Complexes of Ru^{II}*



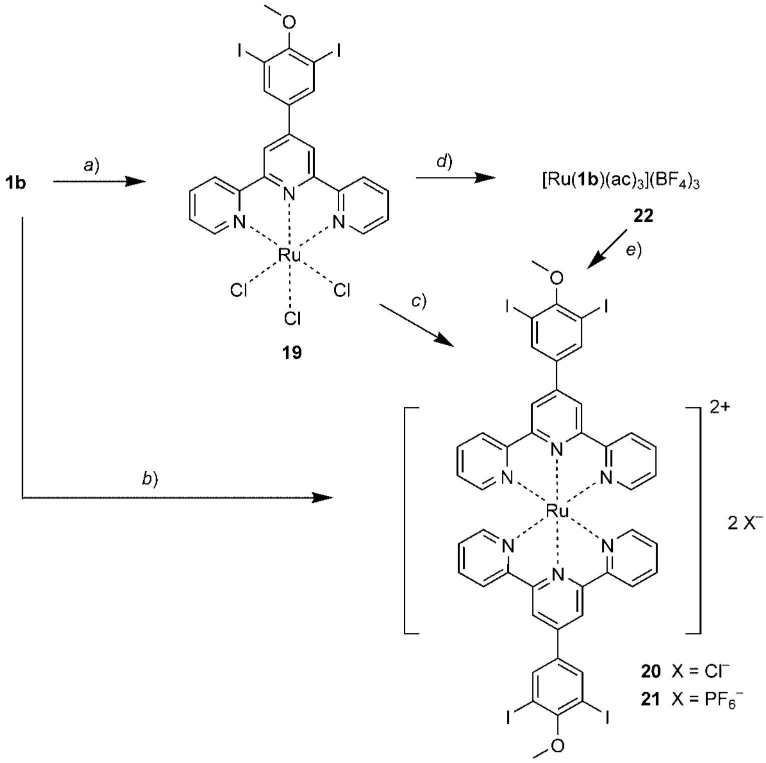
a) RuCl$_3$·H$_2$O (excess), EtOH, Δ. *b*) RuCl$_3$·H$_2$O (0.5 equiv.), *N*-ethylmorpholine, EtOH, Δ. *c*) L′, *N*-ethylmorpholine, EtOH, Δ. *d*) AgBF$_4$, EtOH, acetone, Δ. *e*) L″, EtOH, Δ. X = Cl$^-$, PF$_6^-$; ac = acetone.

the first step. Ru Complexes are also much more stable than the corresponding Fe complexes. Exchange rates in homoleptic hexaqua complexes (which are closely related to the exchange rates of other ligands) of Fe^{II}/Fe^{III} are 10^8 times higher than those of the corresponding Ru^{II}/Ru^{III} complexes [31]; thus homoleptic and heteroleptic complexes will not equilibrate on relevant time scales.

When **1b** was reacted with a ten-fold excess of $RuCl_3 \cdot H_2O$, the monoterpyridine derivative $[Ru(\mathbf{1b})Cl_3]$ (**19**) was obtained in 95% yield, besides small amounts of the homoleptic complex $[Ru(\mathbf{1b})_2]Cl_2$ (**20**) (*Scheme 6*). The latter was readily detected by its intense red color and characteristic peaks in the mass spectra. Crystals of $[Ru(\mathbf{1b})Cl_3]$, suitable for X-ray crystallography, were obtained when the crude mixture was taken up in MeCN (*Fig. 3*). The brown prisms exhibited a monoclinic unit cell of space group *P*2(1)/*n*. Two sets of four molecules in the unit cell adopt two different conformations, differing primarily in the dihedral angle (1.7° and 38.9°) between the central terpyridine ring and the aryl ring attached to C(4′).

With 0.5 equiv. of $RuCl_3 \cdot H_2O$ in the presence of *N*-ethylmorpholine as reducing agent, homoleptic $[Ru(\mathbf{1b})_2]Cl_2$ (**20**) was formed in one step in 51% yield. Prolonged heating to reflux led to some degradation, although the starting material never disappeared completely. This is probably due to inaccuracies in the weighing of

Scheme 6. *Synthesis of Homoleptic Complexes* **20** *and* **21**



a) $RuCl_3 \cdot H_2O$ (excess), EtOH, Δ, 3 h; 95%. *b*) $RuCl_3 \cdot H_2O$ (0.5 equiv.), *N*-ethylmorpholine, EtOH, Δ, 12 h; 51% (**20**). *c*) **1b**, *N*-ethylmorpholine, EtOH, Δ, 12 h (yield of **20** not determined). *d*) $AgBF_4$, EtOH, acetone, 75°, 6 h. *e*) **1b**, EtOH, Δ, 6 h; 88% (**21**, from **19**).

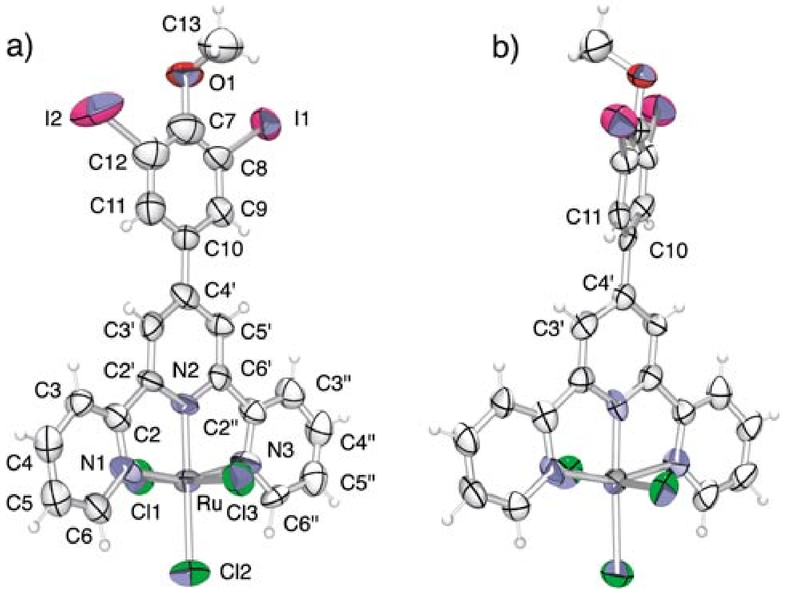


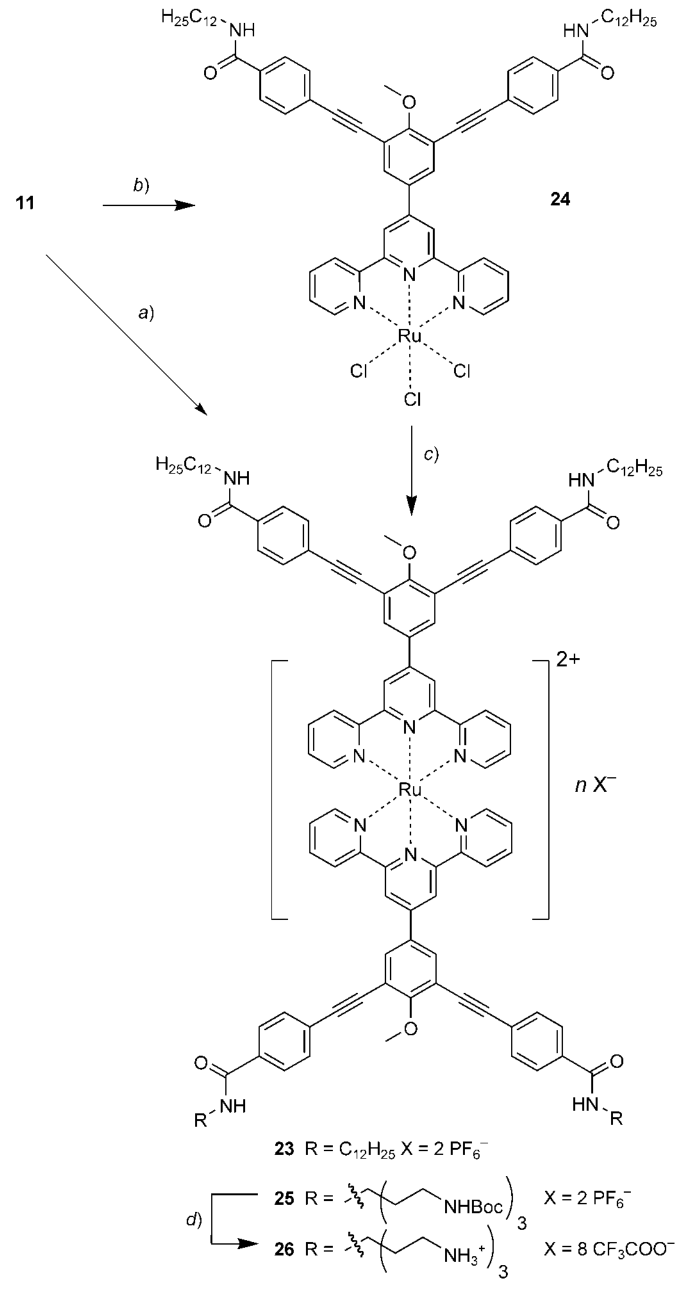
Fig. 3. *ORTEP plot of [Ru(***1b***)$_2$Cl$_3$]* (**19**). Arbitrary numbering; atomic displacement parameters obtained at 293 K are drawn at the 50% probability level. The two conformers in the unit cell differ primarily in the dihedral angle between the central terpyridine ring and the aryl ring attached to C(4′), which adopts a value of 1.7° in conformer 1 (*a*) and 38.9° in conformer 2 (*b*).

hygroscopic $RuCl_3 \cdot H_2O$. The complex was conveniently isolated as [Ru(**1b**)$_2$](PF$_6$)$_2$ (**21**) upon precipitation from a saturated aqueous solution of KPF_6.

The formation of bis-terpyridine complex **21** was best carried out in two steps. Addition of 1 equiv. of **1b** and *N*-ethylmorpholine (as reducing agent) to monoterpyridine derivative **19** and heating the EtOH solution for 12 h to reflux provided cleanly [Ru(**1b**)$_2$]Cl$_2$ (**20**). To accelerate the ligand exchange, [Ru(**1b**)Cl$_3$] was treated with $AgBF_4$ in acetone/EtOH mixtures to give [Ru(**1b**)(ac)$_3$](BF$_4$)$_3$ (**22**) [13]. MALDI Mass spectra (matrix: 2-{(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidine}malononitrile (DCTB)) revealed that the coordination of the acetone ligands was not stable enough to be detected. After filtration over *Celite*, **1b** was added to the solution of **22**, and the conversion to the homoleptic complex **21**, obtained after counterion exchange ($BF_4^- \rightarrow PF_6^-$), went smoothly and cleanly (88% yield from **19**). In the HR-MALDI mass spectrum (DCTB) of **21**, the [Ru(**1b**)$_2$]$^+$ ion appears as the parent ion (1282.764 ($[M - 2\ PF_6]^+$, $C_{44}H_{30}I_4N_6O_2Ru^+$; calc. 1282.7569)) besides strong peaks for [Ru(**1b**)$_2$(PF$_6$)]$^+$ (45%) and [Ru(**1b**)$_2$Cl]$^+$ (62%). The latter peak is visible even after repeated precipitation from aqueous KPF_6 solution; therefore, we conclude that the Cl^- ion is picked up from the matrix. A second group of weaker peaks at half the *m*/*z* values originates from the same, but doubly charged species.

The homoleptic complex [Ru(**11**)$_2$](PF$_6$)$_2$ (**23**) was readily prepared in 80% yield and excellent purity by reacting terpyridine ligand **11** with 0.5 equiv. of $RuCl_3 \cdot H_2O$ in the presence of *N*-ethylmorpholine, followed by counterion exchange through precipitation from a saturated aqueous solution of KPF_6 (*Scheme 7*). The HR-MALDI

Scheme 7. *Synthesis of Homoleptic and Heteroleptic Complexes* **23**, **25**, *and* **26**



a) $RuCl_3 \cdot H_2O$ (0.5 equiv.), *N*-ethylmorpholine, EtOH, Δ, 6 h; 80% (**23**). *b*) $RuCl_3 \cdot H_2O$ (excess), EtOH, Δ, 6 h; 99%. *c*) **13**, *N*-Ethylmorpholine, EtOH, Δ, 6 h; 66% (**25**). *d*) CF_3COOH, CH_2Cl_2, 20°, 2 h; 95%.

mass spectra displayed essentially only the $[Ru(\mathbf{11})_2]^+$ ion (2025.0827 ($[M - 2\,PF_6]^+$, $C_{128}H_{150}N_{10}O_6Ru^+$; calc. 2025.0897) with the expected isotopic pattern and without any visible fragmentation.

For the formation of heteroleptic complexes, the dendritic terpyridine ligand **11** was reacted with an excess of $RuCl_3 \cdot H_2O$ as described above (*Scheme 6*). Monoterpyridine derivative $[Ru(\mathbf{11})Cl_3]$ (**24**) precipitated from the reaction mixture and was isolated by filtration. Traces of the homoleptic complex were removed by washing with small amounts of EtOH. However, even after heating for 6 h to reflux, remaining free ligand **11** was detected in the product mixture by MALDI-MS (DCTB). In addition to the prominent ions $[Ru(\mathbf{11})Cl_3]^+$ (*m/z* 1170), $[Ru(\mathbf{11})Cl_2]^+$ (*m/z* 1134, 100%), and $[Ru(\mathbf{11})Cl]^+$ (*m/z* 1098), the spectra revealed the presence of a peak at *m/z* 1056 (46%), which we tentatively assign to the Ni^{II} complex ion $[Ni(\mathbf{11})Cl]^+$. The source of the metal presumably is the spatula used in handling complex **24**. Due to overlapping isotope patterns of the Ni complex and $[Ru(\mathbf{11})]^+$ at *m/z* 1062, it was not possible to unambiguously identify the metal, however.

The amphiphilic heteroleptic complex $[Ru(\mathbf{11})(\mathbf{13})](PF_6)_2$ (**25**) was obtained in 66% yield by treating **24** with 1 equiv. of dendritic ligand **13** in the presence of *N*-ethylmorpholine. Similar to the free ligand **13**, the complete series of fragment ions corresponding to the successive loss of all six Boc groups was observed in the HR-MALDI mass spectra (DCTB, *Fig. 4*). The dominant peak in the spectrum corresponds to the $[Ru(\mathbf{11})(\mathbf{13})]^+$ ion (2575.2999 ($[M - 2\,PF_6]^+$, $C_{148}H_{184}N_{16}O_{18}Ru^+$; calc. 2575.3054)). Gratifyingly, none of the alleged Ni impurity seen in the mass spectrum of **24** could be detected.

Deprotection of **25** with CF_3COOH in CH_2Cl_2 gave the final amphiphile **26** as the trifluoroacetate salt (*Scheme 7*). The complex remained stable even under the strongly acidic conditions, and no equilibration with the corresponding homoleptic compounds occurred. The HR-MALDI mass spectra (DHB) depicted the hexa(primary amine) ion obtained after loss of eight CF_3COOH, as a strong peak at *m/z* 1974.9863 (48%, $[M - 8\,CF_3COOH]^+$, $C_{118}H_{136}N_{16}O_6Ru^+$; calc. 1974.991) besides two prominent fragment ions presumably originating from β-elimination of one (*m/z* 1958, 100%) and two (*m/z* 1941, 63%) NH_3 groups from the hydrophilic dendrons. These fragment ions were also seen in the electrospray-ionization (ESI) MS in MeOH, which displayed strong peaks with corresponding isotope patterns for $[MH - 8\,CF_3COOH]^+$, $[M + 3\,H - 8\,CF_3COOH]^{3+}$, and $[M + 4\,H - 8\,CF_3COOH]^{4+}$. However, ^{1}H- and ^{13}C-NMR spectra of **26** ($(CD_3)_2SO$) did not show any side products, which supports our assumption that the fragmentation occurs during the transfer of the complex from the state of a salt into the gas-phase ion. Similarly, the ^{19}F-NMR spectra ($(CD_3)_2SO$) displayed only a single resonance assigned to the CF_3 group of the counterions. No residual PF_6^- counterions were detected.

When attempting the synthesis of the monoterpyridine complex $[Ru(\mathbf{14})Cl_3]$ (**27**; *Scheme 8*) under the conditions outlined above, namely by refluxing **14** in EtOH or MeOH with 10 equiv. of $RuCl_3 \cdot H_2O$, complex reaction mixtures resulted. Not even trace amounts of the desired compound were formed, as judged by mass spectrometry. This is presumably due to the insolubility of **14** in the solvents. $RuCl_3 \cdot H_2O$ is not soluble in CH_2Cl_2, $CHCl_3$, or THF, which are all good solvents for the ligand, and the ligand is not soluble in alcohols up to BuOH, or MeCN and H_2O. In an attempt to solve

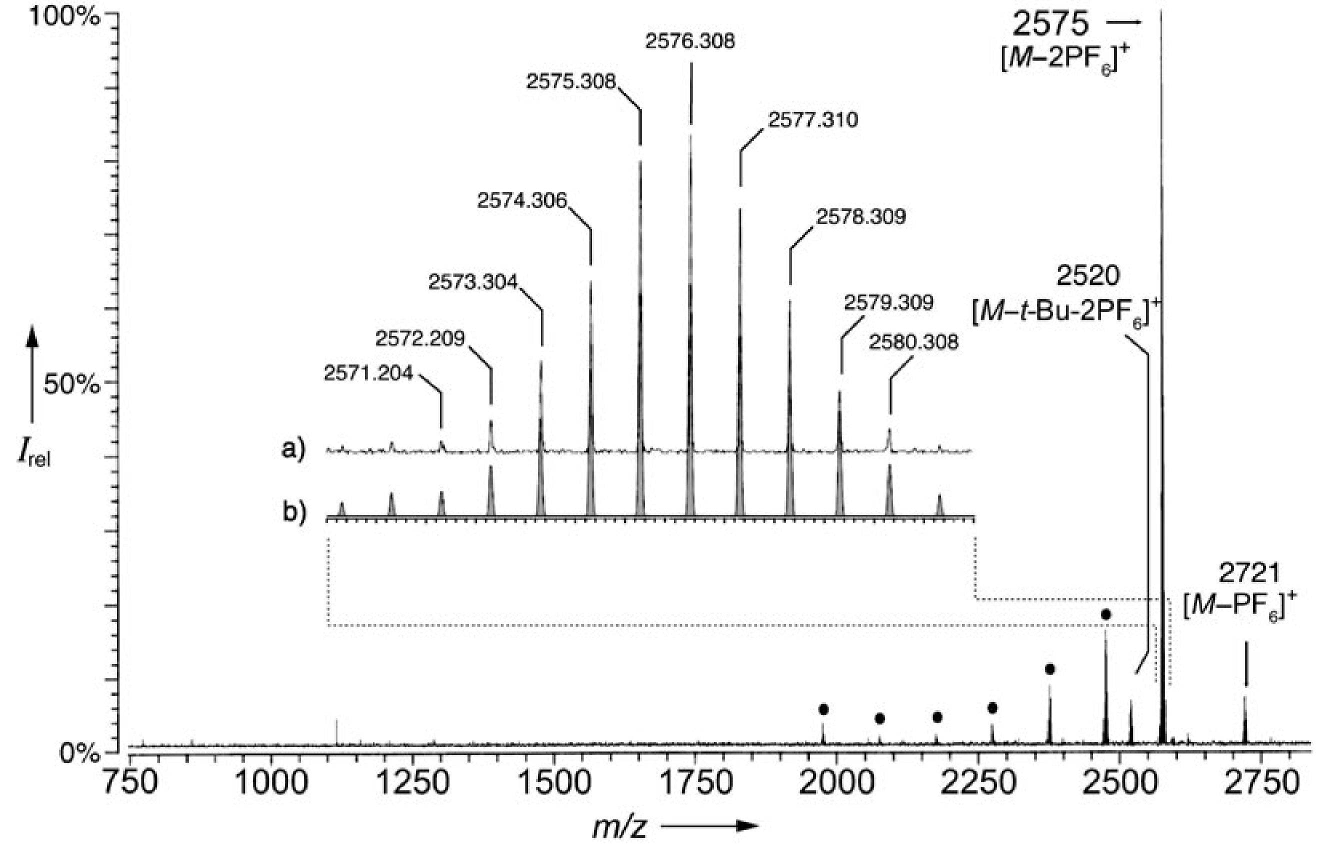
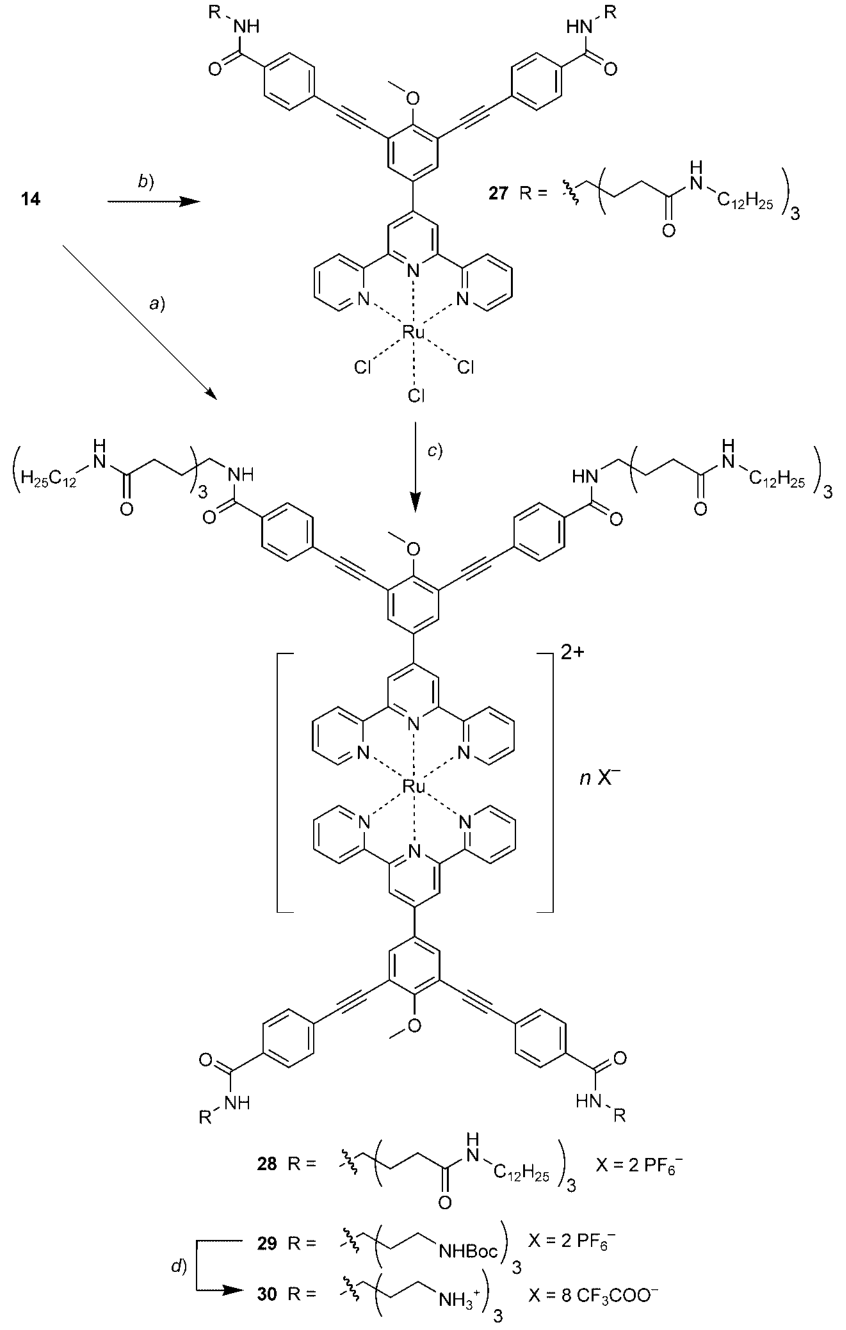


Fig. 4. *HR-MALDI FT-ICR MS* (matrix: DCTB) *of [Ru*(**11**)(**13**)*]*$(PF_6)_2$ (**25**). The experimental isotope pattern (*a*) for the base peak, corresponding to [Ru(**11**)(**13**)]$^+$ is depicted in the inset. Calculated values (*b*) closely match the distribution. The marked peaks (●) correspond to fragment ions resulting from successive loss of one or more Boc groups.

Scheme 8. *Synthesis of Homoleptic and Heteroleptic Complexes* **28**–**30**



a) $RuCl_3 \cdot H_2O$ (0.5 equiv.), *N*-ethylmorpholine, $MeOCH_2CH_2OH$, Δ, 6 h; 61% (**28**). *b*) $RuCl_3 \cdot H_2O$ (excess), $MeOCH_2CH_2OH$, Δ, 6 h; 91%. *c*) **13**, *N*-Ethylmorpholine, $MeOCH_2CH_2OH$, Δ, 6 h; 52% (**29**). *d*) CF_3COOH, CH_2Cl_2, 20°, 2 h; 99%.

this problem (similar solubility problems have been reported in the literature; see [13][17d,f]), we turned to solvent mixtures. Mixtures of chlorinated solvents and MeOH or ethyleneglycol, however, did not led to improvement, and, therefore, we turned in a next attempt to high-boiling solvents. Eventually, 2-methoxyethanol (b.p. 124–125°) was found to solubilize both ligand and metal salt, which subsequently enabled the synthesis of **27**. However, separation and purification of the monoterpyridine complex was now more complicated, since it could no longer be selectively precipitated as was the case for the reactions in EtOH or MeOH. Purification by GPC (*Bio-Beads S-X1*; CH_2Cl_2) was necessary to attain good purity. The HR-MALDI mass spectra (DCTB) demonstrated the high purity of the complex, with expected peaks appearing at *m/z* 2320 (22%, $[Ru(\mathbf{14})Cl_3 + Na]^+$), 2261 (100%, $[Ru(\mathbf{14})Cl_2]^+$), and 2226 (52%, $[Ru(\mathbf{14})Cl]^+$). There is hardly any fragmentation detected, but an unexpected peak at *m/z* 2081, 93 mass units above the value expected for the free ligand **14**, was observed. As in the case of $[Ru(\mathbf{11})Cl_3]$ (**24**), this peak was tentatively assigned to a Ni species ($[Ni(\mathbf{14})Cl]^+$).

The direct formation of the homoleptic complex by reacting **14** with 0.5 equiv. of $RuCl_3 \cdot H_2O$ in the presence of *N*-ethylmorpholine proceeded smoothly in 2-methoxyethanol. Counterion exchange by precipitation from a concentrated aqueous solution of KPF_6, followed by GPC purification (*Bio-Beads S-X1*; CH_2Cl_2), gave $[Ru(\mathbf{14})_2](PF_6)_2$ (**28**) in 61% yield. In the HR-MALDI mass spectra (DCTB), the $[Ru(\mathbf{14})_2]^+$ ion with the expected isotopic pattern appeared as the base peak at *m/z* 4279 (48%, $[M - 2\,PF_6]^+$, $C_{264}H_{410}N_{22}O_{18}Ru^+$; calc. 4279.0882). A single contaminant ion at *m/z* 4238 (65%) was identified, which we tentatively assign to a $[Ni(\mathbf{14})_2]^+$ ion.

Preparation of the protected amphiphile **29** from **27** and **13** in the presence of reducing agent proceeded cleanly in 2-methoxyethanol (*Scheme 8*). Above all, the alleged Ni impurity did not carry through to this step. Accordingly, the MALDI mass spectra (DCTB) after ion exchange ($Cl^- \rightarrow PF_6^-$) depicted a pure compound, showing the $[Ru(\mathbf{13})(\mathbf{14})]^+$ ion as the base peak at *m/z* 3704 (HR-MALDI-MS: 3702.3000 ($[M - 2\,PF_6^-]^+$, $C_{216}H_{314}N_{22}O_{24}Ru^+$; calc. 3702.3064)). The characteristic successive loss of the six Boc groups ($\Delta m/z = -100$) accounts for all significant fragment ions (*Fig. 5*). Cleavage of the Boc protecting groups with CF_3COOH in CH_2Cl_2 then gave the targeted amphiphile **30** with hydrophilic and hydrophobic branching of generation-1 (*Scheme 8*). The HR-MALDI mass spectra (in DHB or DCTB) showed the $[MH - 8\,CF_3COOH]^+$ ion as the base peak at *m/z* 3102.9990 ($C_{186}H_{267}N_{22}O_{12}Ru^+$; calc. 3102.9997), but only with very low intensity. The poor signal-to-noise ratio was also not improved upon changing to ESI-MS.

Attempts to prepare the amphiphilic heteroleptic complex $[Ru(\mathbf{15})(\mathbf{16})](PF_6)_2$ with two G2 dendrons were less successful. Already the synthesis of the monoterpyridine complex $[Ru(\mathbf{16})Cl_3]$ from $RuCl_3 \cdot H_2O$ and **16** in 2-methoxyethanol, in which the ligand is only poorly soluble, or in the better solvent triethyleneglycol monomethyl ether failed (MALDI-MS). Note that impure **16** was used, with a major amount of homo-coupled **18** present in the sample. This was, however, not expected to influence the reactivity of the terpyridine ligand. Rather, it is the steric bulk of the dendritic wedge that dramatically reduces the reactivity of **16**.

We then tried to directly prepare the homoleptic complex $[Ru(\mathbf{16})_2]Cl_2$ by heating to reflux a solution of **16**, 0.5 equiv. of $RuCl_3 \cdot H_2O$, and reducing agent. Again, MALDI

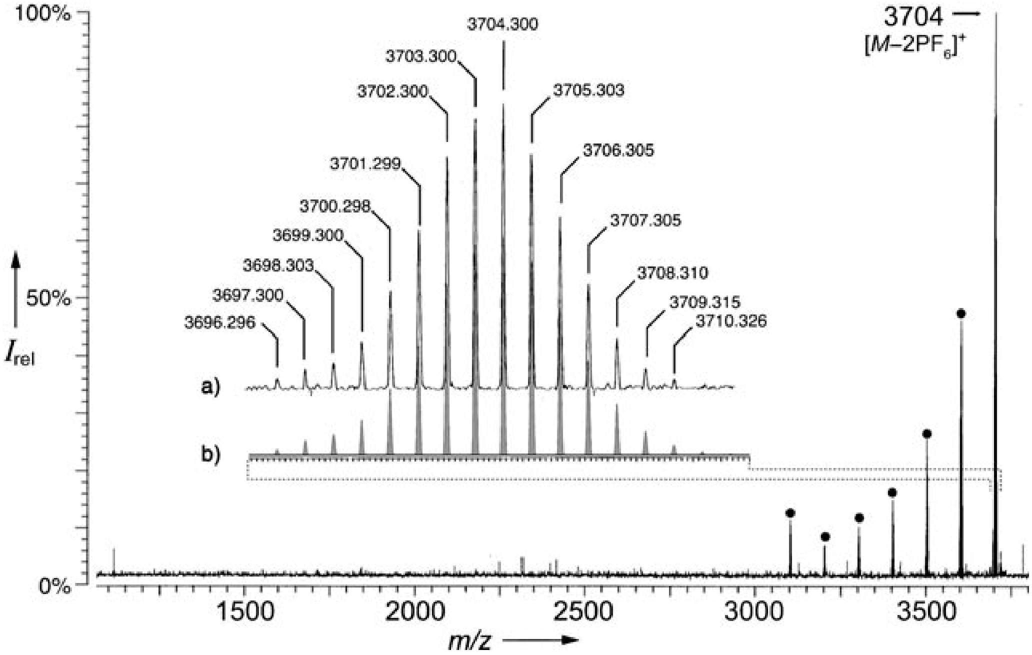


Fig. 5. *HR-MALDI FT-ICR MS (DTCB) of [Ru*(**13**)(**14**)*](PF$_6$)$_2$* (**29**). The experimental isotope pattern (*a*) for the base peak, corresponding to [Ru(**13**)(**14**)]$^+$ closely matches the calculated distribution (*b*). Marked peaks (●) correspond to fragment ions resulting from successive loss of one or more Boc groups.

mass spectra did not indicate formation of any desired product. [Ru(Me$_2$SO)$_4$]Cl$_2$ is a more reactive Ru^{II} source than RuCl$_3 \cdot$ H$_2$O because of the faster ligand exchange on Ru^{II} and the more-labile Me$_2$SO ligands [32]. Homoleptic complexes are usually assembled quickly, as the reduction step is eliminated. However, this more reactive starting material was also not effective in the preparation of [Ru(**16**)$_2$]Cl$_2$.

Similarly, the more-soluble G2 carbamate dendron **15** could not be transformed into the corresponding complexes [Ru(**15**)Cl$_3$] and [Ru(**15**)$_2$]Cl$_2$ by any one of the methods described above. Apparently, the G2 dendrons are shielding the terpyridine binding site efficiently. This could be due to collapse of the dendritic wedges onto the terpyridine core or by simple aggregation. The complexes may possibly also be destabilized by the steric bulk of the G2 dendrons. Alternatively, the many amide functions in the dendrons may sequester the Ru ions, although the formation of higher-molecular-weight complexes could not be detected by MALDI-MS.

In a final experiment, the highly soluble complex [Ru(**1b**)(ac)$_3$](BF$_4$)$_3$ (**22**; *Scheme 6*) was reacted with G2 dendron **16** in CH$_2$Cl$_2$ in the presence of reducing agent, with the intention to introduce the carbamate wedges **10e** by *Sonogashira* cross-coupling later, after heteroleptic complex formation. However, this attempt to circumvent the solubility problems associated with **15** also failed. At this point, the synthesis of higher-generation dendrimers based on the heteroleptic Ru^{II} bis-terpyridine core was abandoned.

3. Conclusions. – In an approach to prepare novel amphiphilic dendrimers as potential vectors for gene transfection, lipophilic and hydrophilic dendrons of generations G0, G1, and G2 were attached by *Sonogashira* cross-coupling to a novel diiodinated terpyridine core. The assembly of stable homoleptic and heteroleptic Ru^{II} complexes with terpyridine ligands carrying two G0 and G1 dendrons was successful, whereas the assembly of such complexes from terpyridines functionalized with G2 dendrons failed. The G2 dendrons apparently are shielding the terpyridine binding site efficiently, thereby preventing it from undergoing ligand displacement; possibly, they may also be destabilizing the complexes with their steric bulk. Steric hindrance could result from collapse of the dendritic wedges onto the terpyridine core and/or from aggregation.

In light of the many reported syntheses of dendritic homo- and heteroleptic Ru^{II} complexes of considerable size, it is hard to accept that this approach failed already at the stage of the G2 dendrons. However, our systems differ substantially from those previously described. In contrast to **15** and **16**, most of the known ligand systems are soluble in short-chain alcohols, which greatly facilitates complexation. When ligand solubility was poor, soluble Ru complexes with one ligand already in place were used in the assembly of homo- and heteroleptic complexes. The dendritic systems described by *Newkome et al.* [17a, b] and *Chow et al.* [17c, d] differ by bearing long, flexible spacers between the terpyridine unit and *single* dendrons. Only one other terpyridine ligand with double dendron substitution for the formation of homoleptic Ru^{II} complexes has been reported by *Shirai* and co-workers [25].

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Experimental Part

General. Reagent-grade solvents (*Fluka*, *J. T. Baker*, or *Riedel-de Haën*) and chemicals (*Aldrich*, *Acros*, *Fluka*, *Lancaster*, *Sigma*, *ABCR*, or *STREM*) were used without further purification, except where stated otherwise. Syntheses of compounds **5a** and **5b** [21], **7** [26], and **10a** – **10f** [10] are reported in the literature cited. THF was freshly distilled from sodium benzophenone ketyl under N_2. CH_2Cl_2 was freshly distilled from CaH_2. Solvents for chromatography were of technical quality and were distilled once prior to use. Evaporation *in vacuo* was carried out at water aspirator pressure, drying at 10^{-2} Torr. Solvents and reagents for *Sonogashira* cross-couplings were degassed by freeze-pump-thaw cycles for batches smaller than 10 ml. For reactions carried out at larger scale, degassing was done by bubbling through a gentle stream of Ar, while sonicating, for 30 min. TLC: SiO_2 *60 F_{254}* from *Merck*, visualization by UV light ($\lambda = 254$ or 366 nm) or by staining with ninhydrin. Column chromatography (CC): SiO_2 *60* (230 – 400 mesh, 40 – 63 μm) from *Fluka*, 0 – 0.4 Torr pressure. Gel-permeation chromatography (GPC): anal. GPC: *Shodex SEC* columns with a *Merck-Hitachi L-7360* column oven (40°), *L-7100* pump (1 ml min^{-1} fixed flow rate), *L-7400* variable wavelength UV detector (fixed at $\lambda = 290$ nm), and *D-2500* chromato-integrator or *L-7500* autosampler; prep. GPC: *Bio-Beads S-X1* (200 – 400 mesh) from *Bio-Rad*, gravity-flow conditions, flow rate < 1 drop s^{-1}. M.p.: *Büchi Smp 20* melting-point apparatus; uncorrected. IR [cm^{-1}]: *Perkin-Elmer FT-IR 1600* spectrometer; the intensity of the bands is described as strong (*s*), medium (*m*), or weak (*w*). NMR (^1H, ^{13}C, ^{19}F): *Varian Gemini 300* or *Bruker AMX-500* instruments; spectra were recorded at 298 K with solvent signal or TMS as reference. Mass spectrometry (MS): EI-MS: *VG-TRIBRID* spectrometer at 70 eV; MALDI-TOF-MS: *Bruker REFLEX* spectrometer, DHB as matrix; HR-MALDI-FT-ICR-MS: *Ion Spec Ultima FT-ICR* mass spectrometer, 2,5-dihydroxybenzoic acid (DHB) or 2-{(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidine}malononitrile (DCTB) as matrix. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie at ETH Zürich on a *LECO CHN/900* instrument.

*(2*E*)-3-(3,5-Dibromo-4-methoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one* (**6a**). A mixture of **5a** (2.31 g, 7.86 mmol) and 10% aq. KOH soln. (460 μl, 10 mol-%) in EtOH (100 ml) was sonicated under a stream of Ar for

30 min. The mixture was cooled to 0°, and a soln. of 2-acetylpyridine (881 µl, 952 mg, 7.86 mmol) in abs. EtOH (20 ml) was added in four portions over 4 h while stirring under Ar. After 6 h, a yellowish microcrystalline precipitate was collected by filtration. The mixture was stored at – 10° without stirring for 12 h. The precipitate formed was collected by filtration, and the filtrate was concentrated *in vacuo* at 5° to one third of its volume. A third crop of precipitate was collected by filtration and combined with the other precipitates to afford crude **6a** (2.57 g, 83%). Yellowish microcrystals. M.p. 156°. IR (KBr): 1673*s*, 1611*s*, 1582*m*, 1532*m*, 1474*m*, 1426*m*, 1394*m*, 1329*m*, 1264*m*, 1218*m*, 1032*m*, 994*s*, 796*m*, 740*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.75 (*ddd*, *J* = 5.0, 1.7, 0.8, 1 H); 8.21, 7.72 (*AB*, *J* = 16.2, 2 H); 8.18 (*ddd*, *J* = 7.8, 1.3, 1.2, 1 H); 7.88 (*ddd*, *J* = 7.9, 7.7, 1.7, 1 H); 7.85 (*s*, 2 H); 7.51 (*ddd*, *J* = 7.7, 5.0, 1.3, 1 H); 3.92 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 189.221; 155.93; 154.10; 149.20; 141.14; 137.37; 134.15; 132.87; 127.39; 123.25; 122.68; 118.91; 60.93. HR-MALDI-MS (DHB): 395.9220 (MH^+, $C_{15}H_{12}{}^{79}Br_2NO_2^+$; calc. 395.9235).

*(2*E*)-3-(3,5-Diiodo-4-methoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one* (**6b**). A mixture of **5b** (7.98 g, 20.58 mmol) and 10% aq. KOH soln. (1.15 ml, 2.06 mmol) in EtOH (160 ml) was sonicated under a stream of Ar for 30 min. The mixture was cooled to 0°, and a soln. of 2-acetylpyridine (2.31 ml, 2.49 g, 20.58 mmol) in abs. EtOH (40 ml) was added in four portions over 4 h while stirring under Ar. After 6 h, a yellowish microcrystalline precipitate was collected by filtration. The mixture was allowed to warm to 20°, and stirring was continued for 12 h. The formed precipitate was collected by filtration, and the filtrate was concentrated *in vacuo* at 5° to one third of its volume. A third crop of precipitate was collected by filtration, and the precipitates were combined to afford crude **6b** (8.96 g, 86%). Yellowish microcrystals. M.p. 168° (dec.). IR (KBr): 1671*s*, 1605*s*, 1582*m*, 1560*m*, 1522*m*, 1464*m*, 1419*m*, 1390*m*, 1324*m*, 1255*m*, 1217*m*, 1029*m*, 994*m*, 791*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.76 (*ddd*, *J* = 4.8, 1.5, 0.9, 1 H); 8.21 (*m*, 1 H); 8.20, 7.70 (*AB*, *J* = 16.2, 2 H); 8.11 (*s*, 2 H); 7.90 (*ddd*, *J* = 7.8, 7.8, 1.8, 1 H); 7.52 (*ddd*, *J* = 7.5, 4.7, 1.3, 1 H); 3.89 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 188.87; 160.39; 153.82; 148.94; 140.56; 139.83; 137.86; 135.09; 127.19; 123.05; 122.18; 90.94; 60.88. HR-MALDI-MS (DHB): 491.8947 (MH^+, $C_{15}H_{12}I_2NO_2^+$; calc. 491.8961). Anal. calc. for $C_{15}H_{11}I_2NO_2$ (491.07): C 36.69, H 2.26, N 2.85, O 6.52; found: C 36.60, H 2.51, N 2.62, O 6.58.

4′-(3,5-Dibromo-4-methoxyphenyl)[2,2′:6′,2″]terpyridine (**1a**). A mixture of **6a** (3.0 g, 7.56 mmol), **7** (3.2 g, 9.07 mmol), NH_4OAc (30 g), and glacial AcOH (160 ml) was heated under Ar and vigorous mechanical stirring to 120° for 16 h, then to 160° for 8 h. After cooling to 20°, a brown precipitate was collected by filtration. The filtrate was washed with H_2O and dried. CC (300 g neutral Al_2O_3 (+6% H_2O); hexane/AcOEt 2 : 1 → 1 : 2), followed by precipitation from a concentrated soln. in CH_2Cl_2 with hexane, afforded **1a** (1.1 g, 29%). Tan solid. M.p. 235°. IR (KBr): 1605*m*, 1584*s*, 1568*m*, 1527*m*, 1482*m*, 1467*s*, 1425*m*, 1411*m*, 1362*m*, 1358*m*, 1268*m*, 985*m*, 981*m*, 865*m*, 788*m*, 736*m*, 734*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.75 (*m*, 2 H); 8.68 (*m*, 2 H); 8.66 (*s*, 2 H); 8.06 (*s*, 2 H); 7.91 (*m*, 2 H); 7.39 (*m*, 2 H); 3.97 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.07; 155.68; 154.83; 149.05; 147.21; 137.18; 137.01; 131.45; 124.17; 121.53; 118.81; 118.57; 60.83. HR-MALDI-MS (DHB): 495.9642 (MH^+, $C_{22}H_{16}Br_2N_3O^+$; calc. 495.9660); 517.9479 ($[M + Na]^+$, $C_{22}H_{15}Br_2N_3NaO^+$; calc. 517.9480).

4′-(3,5-Diiodo-4-methoxyphenyl)[2,2′:6′,2″]terpyridine (**1b**). A mixture of **6b** (9.0 g, 18.3 mmol), **7** (7.2 g, 21.96 mmol), NH_4OAc (80 g), and glacial AcOH (160 ml) was heated under Ar and vigorous mechanical stirring to 160° for 16 h. After evaporation of AcOH *in vacuo*, the residue was treated with boiling MeCN (1500 ml). Filtration, followed by CC (1000 g neutral Al_2O_3, act. IV (+12% H_2O); hexane → hexane/AcOEt 1 : 1) and recrystallization (MeCN), afforded **1b** (6.96 g, 64%). Tan needles. M.p. 216°. IR (KBr): 1583*m*, 1564*m*, 1518*m*, 1466*m*, 1403*m*, 1355*m*, 1256*m*, 1234*m*, 994*m*, 872*m*, 789*s*, 705*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.76 (*m*, 2 H); 8.68 (*m*, 2 H); 8.65 (*s*, 2 H); 8.29 (*s*, 2 H); 7.91 (*m*, 2 H); 7.40 (*m*, 2 H); 3.93 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.55; 156.15; 155.85; 149.16; 146.82; 138.50; 138.29; 137.0; 124.10; 121.45; 118.52; 91.03; 60.88. HR-MALDI-MS (DHB): 591.9375 (MH^+, $C_{22}H_{16}I_2N_3O^+$; calc. 591.9383). Anal. calc. for $C_{22}H_{15}I_2N_3O$ (591.19): C 44.70, H 2.56, N 7.11, O 2.71; found: C 44.91, H 2.85, N 6.84, O 2.98.

4′-(4-Methoxy-3,5-bis{[tris(1-methylethyl)silyl]ethynyl}phenyl)[2,2′:6′,2″]terpyridine (**9**). A degassed suspension of **1a** (500 mg, 1.01 mmol), $(i\text{-}Pr)_3Si{-}C{\equiv}CH$ (1.35 ml, 1.1 g, 6.04 mmol), and $(i\text{-}Pr)_2NH$ (2.7 ml) in freshly distilled THF (8 ml) was frozen with liquid N_2. A previously prepared mixture of CuI (60 mg, 30 mol-%), $[Pd(PPh_3)_2Cl_2]$ (106 mg, 15 mol-%), and Bu_4NBr (64 mg, 20 mol-%), that was dried at 0.1 Torr for 1 h, was added. The reaction vessel was evacuated and recharged with Ar three times before allowing it to warm to 20°. After stirring for 16 h under Ar at 60°, sat. aq. NH_4Cl soln. (50 ml) and CH_2Cl_2 (100 ml) were added. The org. phase was washed with sat. aq. NH_4Cl soln. (2 ×) and H_2O (1 ×), dried ($MgSO_4$), and concentrated. The residue was taken up in CH_2Cl_2 and precipitated with MeOH to yield **9** (630 mg, 90%). Silver-gray plates. M.p. 174°. IR (KBr): 3435*m*, 2941*m*, 1583*m*, 1467*s*, 1411*m*, 1367*m*, 1250*m*, 1072*w*, 1006*s*, 883*s*, 783*m*, 740*m*, 667*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.75 (*m*, 2 H); 8.68 (*m*, 2 H); 8.64 (*s*, 2 H); 7.89 (*m*, 2 H); 7.88 (*s*, 2 H); 7.37 (*m*, 2 H); 4.09 (*s*, 3 H); 1.17 (*m*, 42 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 163.55; 156.12; 155.91; 149.16; 148.86; 136.98; 132.74; 123.99;

121.51; 118.73; 118.52; 109.96; 101.87; 96.49; 61.25; 18.46; 11.37. HR-MALDI-MS (DHB): 700.4134 (MH^+, $C_{44}H_{58}N_3OSi_2^+$; calc. 700.4118).

4′-(3,5-Diethynyl-4-methoxyphenyl)[2,2′:6′,2″]-terpyridine **(8).** To a soln. of **9** (50 mg, 71.42 μmol) and one drop of H_2O in freshly distilled THF (5 ml), 1M Bu_4NF in THF (290 μl, 290 μmol) was added. After stirring at 20° for 30 min, sat. aq. NH_4Cl soln. (5 ml) and CH_2Cl_2 (25 ml) were added. The org. phase was washed with sat. aq. NH_4Cl soln. (2 ×) and H_2O (1 ×), dried ($MgSO_4$), and concentrated. The residue was taken up in CH_2Cl_2 (1 ml) and precipitated with MeOH at – 20°. After filtration, the mother liquor was concentrated to one half of its volume and, a second precipitate was collected by filtration to yield **8** (25 mg, 90%). M.p. 203° (dec.). IR (KBr): 3421*m*, 3310*m*, 3243*m*, 2922*m*, 2343*w*, 1602*m*, 1584*s*, 1563*m*, 1544*m*, 1469*s*, 1411*s*, 1372*m*, 1250*m*, 1074*m*, 876*m*, 787*m*, 734*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.73 (*m*, 2 H); 8.67 (*m*, 2 H); 8.66 (*s*, 2 H); 8.01 (*s*, 2 H); 7.88 (*m*, 2 H); 7.36 (*m*, 2 H); 4.15 (*s*, 3 H); 3.37 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 163.55; 156.07; 155.91; 149.12; 147.92; 137.01; 133.81; 133.60; 124.04; 121.45; 118.41; 116.76; 82.52; 79.06; 61.60. HR-MALDI-MS (DHB): 388.1448 (MH^+, $C_{26}H_{18}N_3O^+$; calc. 388.1450).

N,N′-*Didodecyl-4,4′-{[2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis(ethyne-2,1-diyl)}dibenzamide* (**11**). A degassed soln. of **1b** (20 mg, 33.8 μmol) and (i-Pr)$_2$NH (1 ml) in freshly distilled THF (2 ml) was frozen with liquid N_2. A previously prepared mixture of CuI (2.0 mg, 32 mol-%), $[Pd(PPh_3)_2Cl_2]$ (4.75 mg, 20 mol-%), and Bu_4NBr (2.1 mg, 20 mol-%), dried at 0.1 Torr for 1 h, was added. The reaction vessel was evacuated and recharged with Ar (3 ×) before allowing it to warm to 20°. A degassed soln. of **10a** (42.4 mg, 135.2 μmol) in freshly distilled THF (1 ml) was added slowly. After stirring for 16 h under Ar at 20°, sat. aq. NH_4Cl soln. (5 ml) and CH_2Cl_2 (25 ml) were added. The org. phase was washed with sat. aq. NH_4Cl soln. (2 ×) and H_2O (1 ×), dried ($MgSO_4$), and concentrated. CC (Al_2O_3 (+6% H_2O); hexane/AcOEt 3 : 1 → 1 : 1 + 0.5% Et_3N) and GPC (*Bio-Beads S-X1*; THF then CH_2Cl_2) afforded **11** (32.5 mg, 63%). Yellowish solid. IR (KBr): 3315*m*, 2922*s*, 2849*s*, 1725*w*, 1633*s*, 1605*m*, 1583*m*, 1567*m*, 1534*s*, 1500*m*, 1468*m*, 1411*m*, 1378*w*, 1303*m*, 1262*m*, 1183*w*, 1081*m*, 1019*m*, 878*m*, 853*m*, 793*m*, 769*w*, 738*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.75 (*ddd*, *J* = 4.8, 1.8, 0.9, 2 H); 8.71 (*s*, 2 H), 8.68 (*ddd*, *J* = 7.9, 1.0, 1.0, 2 H); 8.05 (*s*, 2 H); 7.90 (*ddd, J* = 7.7, 1.8, 2 H); 7.78, 7.63 (*AA′BB′*, '*J*' = 8.5, 8 H); 7.38 (*ddd*, *J* = 7.5, 4.8, 1.2, 2 H); 6.17 (*t*, *J* = 5.8, 2 H); 4.25 (*s*, 3 H); 3.46 (*q*, *J* = 7.0, 4 H); 1.60 – 1.66 (br. *m*, 4 H); 1.2 – 1.4 (br. *m*, 36 H); 0.88 (*t*, *J* = 7.0, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 166.73; 162.35; 156.04; 155.94; 149.09; 148.11; 137.01; 134.53; 133.94; 132.76; 131.74; 126.94; 126.10; 124.02; 121.48; 118.41; 117.51; 93.64; 87.10; 61.62; 40.23; 31.90; 29.66; 29.64; 29.62; 29.58; 29.55; 29.35; 29.34; 27.02; 22.67; 14.11. HR-MALDI-MS (DHB): 962.5943 (MH^+, $C_{64}H_{76}N_5O_3^+$; calc. 962.5948).

Hexa(tert-*butyl) 3,3′,3″,3‴,3⁗,3′⁗-{[2-Methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]}hexapropanoate* (**12**). According to the protocol for the synthesis of **11**, **1b** (20 mg, 33.83 μmol) and (i-Pr)$_2$NH (160 μl) in THF (1 ml) was reacted with CuI (2.06 mg, 32 mol-%), $[Pd(PPh_3)_2Cl_2]$ (4.75 mg, 20 mol-%), Bu_4NBr (2.14 mg, 20 mol-%), and **10b** (110 mg, 203 μmol) in THF (2 ml). CC (20 g neutral Al_2O_3 (+6% H_2O); hexane/AcOEt 10 : 1 → 3 : 1) afforded **12** (40 mg, 84%). M.p. 117°. IR (KBr): 3374*w*, 2977*m*, 2932*m*, 1730*s*, 1665*m*, 1605*m*, 1584*m*, 1536*m*, 1500*m*, 1468*m*, 1367*s*, 1314*m*, 1256*m*, 1152*s*, 848*m*, 794*m*, 766*w*, 745*w*. ^{1}H-NMR ($CDCl_3$, 500 MHz): 8.76 (*d*, *J* = 4.1, 2 H); 8.73 (*s*, 2 H); 8.70 (*d*, *J* = 7.9, 2 H); 8.07 (*s*, 2 H); 7.90 (*dt*, *J* = 7.7, 1.7, 2 H); 7.83, 7.64 (*AA′BB′*, '*J*' = 8.2, 8 H); 7.38 (*m*, 2 H); 7.11 (*s*, 2 H); 4.26 (*s*, 3 H); 2.33, 2.15 (*AA′BB′*, '*J*' = 7.6, 24 H); 1.44 (*s*, 54 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 173.21; 165.96; 162.36; 156.13; 156.03; 149.16; 148.20; 136.97; 134.78; 133.99; 132.71; 131.61; 127.09; 126.01; 124.01; 121.46; 118.44; 117.58; 93.78; 87.03; 80.88; 61.65; 57.95; 30.26; 29.97; 28.08. HR-MALDI- MS (DHB): 1422.7513 (MH^+, $C_{84}H_{104}N_5O_{15}^+$; calc. 1422.7529).

Hexa(tert-*butyl)* N,N′,N″,N‴,N⁗,N′⁗-*([2-Methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis{[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]tris(ethane-2,1-diyl)})hexacarbamate* (**13**). According to the protocol reported for the synthesis of **11**, **1b** (20 mg, 33.8 μmol) and (i-Pr)$_2$NH (1 ml) in THF (2 ml) were reacted with CuI (2.0 mg, 32 mol-%), $[Pd(PPh_3)_2Cl_2]$ (4.75 mg, 20 mol-%), Bu_4NBr (2.1 mg, 20 mol-%), and **10c** (80 mg, 135.2 μmol) in THF (1 ml). CC (Al_2O_3 (+6% H_2O); hexane/AcOEt) and GPC (*Bio-Beads S-X1*; CH_2Cl_2) afforded **13** (37 mg, 72%). Yellowish solid. M.p. 136°. IR (KBr): 3382*s*, 2976*m*, 2932*m*, 1693*s*, 1502*s*, 1366*s*, 1250*s*, 1170*s*, 854*w*, 792*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.70 (*m*, 2 H); 8.67 (*s*, 2 H); 8.63 (*d*, *J* = 8.0, 2 H); 8.01 (*s*, 2 H); 7.9, 7.57 (*AA′BB′*, '*J*' = 8.0, 10 H); 7.85 (*dt*, *J* = 8.1, 1.8, 2 H); 7.33 (*ddd*, *J* = 7.5, 4.8, 1.0, 2 H); 4.95 (*s*, 6 H), 4.21 (*s*, 3 H); 3.15, 2.06 (*AA′BB′*, 24 H); 1.38 (*s*, 54 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 166.66; 162.25; 156.12; 155.95; 155.81; 149.00; 148.02; 136.88; 134.68; 133.84; 132.46; 131.34; 127.36; 125.80; 123.91; 121.33; 118.26; 117.50; 93.78; 86.77; 79.25; 61.48; 56.97; 36.16; 35.98; 28.30. HR-MALDI-MS (DHB): 1534.7987 ($[M + Na]^+$, $C_{84}H_{109}N_{11}NaO_{15}^+$; calc. 1534.8002).

N,N′,N″,N‴,N⁗,N′⁗-*Hexadodecyl-3,3′,3″,3‴,3⁗,3′⁗-{[2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]}hexapropanamide*

(**14**). According to the protocol reported for the synthesis of **11**, **1b** (10 mg, 16.9 μmol) and $(i\text{-}Pr)_2NH$ (0.5 ml) in THF (1 ml) were reacted with CuI (1.0 mg, 32 mol-%), $[Pd(PPh_3)_2Cl_2]$ (2.4 mg, 20 mol-%), Bu_4NBr (1 mg, 20 mol-%), and **10d** (60 mg, 135.2 μmol) in THF (0.5 ml). CC (Al_2O_3 (+6% H_2O; hexane/AcOEt) and GPC (*Bio-Beads S-X1*; CH_2Cl_2) afforded **14** (19 mg, 54%). Yellowish solid. M.p. 119°. IR (KBr): 3297*m*, 2924*s*, 2852*s*, 1643*s*, 1547*s*, 1467*m*, 1377*m*, 1324*m*, 1296*m*, 1276*m*, 880*w*, 855*w*, 793*w*, 765*w*, 738*w*, 721*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.75 (*d*, $J=4.7$, 2 H); 8.72 (*s*, 2 H); 8.68 (*d*, $J=7.9$, 2 H); 8.12 (*s*, 2 H); 8.05 (*s*, 2 H); 7.91, 7.63 (*AA′BB′*, '*J*' = 8.4, 8 H); 7.88 (*m*, 2 H); 7.37 (*m*, 2 H); 5.89 (*t*, $J=5.5$, 6 H); 4.25 (*s*, 3 H); 3.20 (*q*, $J=6.7$, 12 H); 2.31, 2.21 (*AA′BB′*, '*J*' = 7.3, 24 H); 1.46 (*t*, $J=6.8$, 12 H); 1.28–1.22 (*m*, 108 H); 0.86 (*t*, $J=7.1$, 18 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 173.15; 166.42; 162.33; 156.09; 156.01; 149.13; 148.12; 136.94; 134.51; 133.90; 133.72; 131.61; 127.29; 126.09; 123.98; 121.42; 118.37; 117.55; 93.81; 87.10; 61.55; 58.57; 39.77; 31.89; 31.86; 31.29; 29.65; 29.62; 29.60; 29.54; 29.34; 29.30; 26.94; 22.67; 14.09; one CH_2 resonance around 29 ppm was not resolved. HR-MALDI-MS (DHB): 2111.5809 ($[M+Na]^+$, $C_{132}H_{205}N_{11}NaO_9^+$; calc. 2111.5819).

*Octadeca(*tert-*butyl)* $N,N^{I},N^{II},N^{III},N^{IV},N^{V},N^{VI},N^{VII},N^{VIII},N^{IX},N^{X},N^{XI},N^{XII},N^{XIII},N^{XIV},N^{XV},N^{XVI},N^{XVII}$-*([2-Methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis{(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)tris[(1-oxopropane-3,1-diyl)(iminomethanetetrayl)tris(ethane-2,1-diyl)]})octadecacarbamate* (**15**). According to the protocol reported for the synthesis of **11**, **1b** (10 mg, 16.9 μmol) and $(i\text{-}Pr)_2NH$ (0.5 ml) in THF (1 ml) were reacted with CuI (1.0 mg, 32 mol-%), $[Pd(PPh_3)_2Cl_2]$ (2.4 mg, 20 mol-%), Bu_4NBr (1 mg, 20 mol-%), and **10e** (115 mg, 135.2 μmol) in THF (0.5 ml). CC (SiO_2; CH_2Cl_2/MeOH) and GPC (*Bio-Beads S-X1*; CH_2Cl_2) afforded **15** (22 mg, 35%). Yellowish solid. M.p. 156°. IR (KBr): 3353*m*, 2978*m*, 1696*s*, 1529*s*, 1454*m*, 1392*m*, 1367*s*, 1274*s*, 1251*s*, 1170*s*, 867*w*, 780*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.75 (*d*, $J=4.2$, 2 H); 8.74 (*s*, 2 H); 8.71 (*d*, $J=8.0$, 2 H); 8.4–8.2 (br. *m*, 2 H); 8.08 (*s*, 2 H); 7.94, 7.62 (*AA′BB′*, '*J*' = 8.0, 8 H); 7.90 (*t*, $J=8.3$, 2 H); 7.40 (*t*, $J=6.0$, 2 H); 6.97 (br. *m*, 6 H); 4.81 (br. *m*, 18 H); 4.27 (*s*, 3 H); 3.10, 1.91 (*AA′BB′*, 72 H); 2.34, 2.16 (*AA′BB′*, 24 H); 1.39 (*s*, 162 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 173.71; 165.97; 162.31; 156.12 (3 C); 149.10; 148.29; 143.42; 134.74; 133.93; 132.33; 131.48; 127.56; 125.79; 124.08; 121.52; 118.54; 117.66; 93.99; 86.87; 79.29; 61.61; 58.62; 56.32; 35.85; 35.14; 33.04; 31.86; 28.44. HR-MALDI-MS (DHB): 3762.2500 ($[M+Na]^+$, $C_{192}H_{307}N_{29}NaO_{45}^+$; calc. 3762.2524).

Bis[1,3-Diiodo-2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene]ruthenium(II) Bis(hexafluorophosphate) ($[Ru(\mathbf{1b})_2](PF_6)_2$) (**21**). A soln. of **1b** (50 mg, 85 μmol) and $RuCl_3 \cdot H_2O$ (84% $RuCl_3$, 210 mg, 850 μmol) in EtOH (25 ml) was heated for 3 h to reflux under Ar. After cooling, the volume was reduced to one third. A brownish precipitate was collected by filtration, washed with EtOH, and dried to give crude $[Ru(\mathbf{1b})Cl_3]$ (**19**) (64 mg, 95%). A suspension of **19** (g, 38 μmol) and $AgBF_4$ (22 mg, 113 μmol) in dry acetone (40 ml) and abs. EtOH (10 ml) was heated to 75° for 6 h. The resulting soln. was filtered through *Celite*. EtOH (10 ml) was added to the filtrate, and acetone was removed by evaporation *in vacuo* without heating. Compound **1b** (22 mg, 38 μmol) was added to the soln. of crude **22**, and the mixture was heated to reflux under Ar in the dark for 6 h. The solvent was evaporated, and the residue was dissolved in a minimum volume of MeCN. This soln. was added dropwise to sat. aq. KPF_6 soln. The resulting red precipitate was washed with H_2O and dried to give $[Ru(\mathbf{1b})_2](PF_6)_2$ (**21**) (53 mg, 88%). Red solid. M.p. 256° (dec.). IR (KBr): 3432*m*, 1611*w*, 1520*w*, 1475*w*, 1462*w*, 1427*w*, 1395*m*, 1255*w*, 1030*w*, 993*w*, 844*s*, 786*m*, 752*w*, 707*w*, 557*m*. ^{1}H-NMR ($CDCl_3$, 500 MHz): 9.46 (*s*, 4 H); 9.13 (*d*, $J=8.2$, 4 H); 8.90 (*s*, 4 H); 8.07 (*ddd*, $J=7.9, 7.8, 1.4$, 4 H); 7.52 (*d*, $J=5.8$, 4 H); 7.28 (*ddd*, $J=7.4, 5.8, 1.4$, 4 H); 3.33 (*s*, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 159.98; 157.83; 154.94; 152.04; 143.38; 138.42; 137.90; 135.69; 127.65; 124.90; 121.14; 92.55; 60.50. HR-MALDI-MS (DCTB): 1282.764 ($[M-2\,PF_6]^+$, $C_{44}H_{30}I_4N_6O_2Ru^+$; calc. 1282.7569).

*Bis(*N,N′*-Didodecyl-4,4′-{[2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3- diyl]bis(ethyne-2,1-diyl)}dibenzamide)ruthenium(II) Bis(hexafluorophoshate)* (**23**). A soln. of **11** (50 mg, 52 μmol) and $RuCl_3 \cdot H_2O$ (84% $RuCl_3$, 6 mg, 26 μmol) in *N*-ethylmorpholine (0.5 ml) and EtOH (2 ml) was heated for 6 h to reflux under Ar. After cooling, the volume was reduced to one third. This soln. was then added dropwise to sat. aq. KPF_6 soln. The resulting red precipitate was washed with H_2O and EtOH, and then dried. GPC (*Bio-Beads S-X1*; CH_2Cl_2) gave **23** (48 mg, 80%). Red solid. M.p. 173°. IR (KBr): 3439*w*, 2958*s*, 2927*s*, 2856*s*, 1728*s*, 1641*w*, 1606*w*, 1537*w*, 1464*m*, 1404*w*, 1383*w*, 1275*s*, 1123*m*, 1072*m*, 846*m*, 788*w*, 742*w*, 557*w*. ^{1}H-NMR ($CDCl_3$, 500 MHz): 9.58 (*s*, 4 H); 9.17 (*d*, $J=7.3$, 4 H); 8.74 (*s*, 4 H); 8.59 (*t*, $J=5.6$, 4 H); 8.1 (*t*, $J=7.8$, 4 H); 7.98, 7.76 (*AA′BB′*, '*J*' = 8.5, 16 H); 7.56 (*d*, $J=5.7$, 4 H); 7.31 (*t*, $J=7.9$, 4 H); 4.33 (*s*, 6 H); 3.28 (*q*, $J=6.6$, 8 H); 1.54 (*m*, 8 H); 1.35–1.15 (*m*, 72 H); 0.86 (*t*, $J=6.9$, 12 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 165.13; 162.59; 157.97; 155.11; 152.13; 144.52; 138.03; 134.98; 133.17; 131.87; 131.25; 127.71; 124.94; 124.35; 121.06; 117.03; 94.00; 86.63; 61.64; 31.25; 29.03; 29.02; 28.99; 28.97; 28.96; 28.74; 28.68; 26.44; 22.05; 13.91; one CH_2 and one aromatic C-atom resonance were not resolved. HR-MALDI-MS (DCTB): 2025.0827 ($[M-2\,PF_6]^+$, $C_{128}H_{150}N_{10}O_6Ru^+$; calc. 2025.0897).

*[(*N,N′*-Didodecyl-4,4′-{[2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis(ethyne-2,1-diyl)}dibenzamide)[Hexa*(tert-*butyl)* N,N′,N″,N‴,N⁗,N′′′′′*-([2-Methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis{[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]tris(ethane-2,1-diyl)})hexacarbamate]ruthenium(II) Hexafluorophosphate* (**25**). A suspension of **11** (50 mg, 52 μmol) and $RuCl_3 \cdot H_2O$ (84% $RuCl_3$, 128 mg, 520 μmol) in abs. EtOH (10 ml) was heated to reflux under Ar for 6 h. After cooling, a brown precipitate was collected by filtration, washed with H_2O and EtOH, and dried to give crude **24** (60.8 mg, 99%). Complex **24** (60.8 mg, 51.5 μmol) and **13** (78 mg, 51 μmol) were subsequently suspended in abs. EtOH (5 ml) and *N*-ethylmorpholine (500 μl). The mixture was heated to reflux under Ar for 6 h. The volume was then reduced to one fifth. The red soln. was added dropwise to sat. aq. KPF_6 soln. The resulting red precipitate was collected by filtration and washed with EtOH and dilute aq. KPF_6 soln. GPC (*Bio-Beads S-X1*; CH_2Cl_2) gave **25** (81 mg, 66%). Red transparent glass. M.p. 206°. IR (KBr): 3431*m*, 2925*m*, 2852*m*, 1696*s*, 1648*s*, 1533*s*, 1501*s*, 1404*m*, 1366*m*, 1250*m*, 1167*s*, 845*s*, 557*m*. ^{1}H-NMR ($(CD_3)_2SO$, 500 MHz): 9.52 (*s*, 4 H); 9.10 (*d*, *J* = 7.3, 4 H); 8.69 (*s*, 4 H); 8.58 (*t*, *J* = 5.8, 2 H); 8.06 (‘*t*’, *J* = 7.8, 4 H); 7.94, 7.90, 7.74, 7.72 (2 *AA′BB′*, ‘*J*’ = 8.6, 16 H); 7.61 (br. *m*, 2 H); 7.53 (*d*, *J* = 5.5, 4 H); 7.28 (‘*t*’, *J* = 6.3, 4 H); 6.72 (br. *m*, 6 H); 4.30 (*s*, 3 H); 4.29 (*s*, 3 H); 3.26 (br. *m*, 4 H); 2.95 (br. *m*, 12 H); 1.91 (br. *m*, 12 H); 1.52 (br. *m*, 4 H); 1.34 (*s*, 54 H); 1.30–1.15 (*m*, 36 H); 0.83 (*t*, *J* = 7.0, 6 H). ^{13}C-NMR (125 MHz, $(CD_3)_2SO$): 165.81; 165.57; 162.81; 162.75; 158.21; 158.13; 155.82; 155.76; 155.25; 152.30 (br.); 144.83; 144.80; 138.25; 138.18; 136.01; 135.12; 135.08; 133.46 (br.); 132.22; 132.20; 131.48; 131.24; 128.20; 127.89; 125.18; 125.11; 124.59; 124.47; 121.35; 121.23; 117.24; 117.23; 94.26; 94.20; 86.82; 86.77; 77.79; 61.84; 61.81; 56.51; 35.46; 35.33; 34.41; 31.43; 29.17; 19.14; 29.11; 19.10; 28.88; 28.83; 28.40; 26.59; 22.23; 14.10; three C-atom resonances missing. HR-MALDI-MS (DHB): 2575.2999 ($[M - 2\ PF_6]^+$, $C_{148}H_{184}N_{16}O_{18}Ru^+$; calc. 2575.3054).

*[(*N,N′*-Didodecyl-4,4′-{[2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis(ethyne-2,1-diyl)}dibenzamide)[*N,N′,N″,N‴,N⁗,N′′′′′*-([2-Methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis{[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]tris(ethane-2,1-diyl)})hexaammonium]ruthenium(II) Octakis(2,2,2-trifluoroacetate)* (**26**). A soln. of **25** (50 mg, 17μmol) in 30% CF_3COOH in CH_2Cl_2 (5 ml) was stirred under Ar at 20° for 2 h. After reducing the volume to one third *in vacuo* at 20°, a red solid was precipitated with Et_2O (2 ml). The entire mixture was evaporated, re-suspended in Et_2O, and sonicated. This procedure was repeated twice, and final evaporation afforded **26** (48 mg, 95%). Red solid. M.p. 227° (dec.). IR (KBr): 3439*s*, 2920*m*, 2849*m*, 1676*m*, 1633*m*, 1536*w*, 1405*w*, 1298*w*, 1204*m*, 1134*m*, 836*w*, 799*w*, 722*w*. ^{1}H-NMR ($(CD_3)_2SO + D_2O$, 300 MHz): 9.42 (*s*, 2 H); 9.41 (*s*, 2 H); 9.05–8.98 (*m*, 4 H); 8.63 (*s*, 4 H); 8.05–7.99 (*m*, 4 H); 7.91, 7.88, 7.74, 7.73 (2 *AA′BB′*, ‘*J*’ = 8.3, 16 H); 7.52 (*d*, *J* = 5.4, 2 H); 7.49 (*d*, *J* = 5.6, 2 H); 7.29–7.24 (*m*, 4 H); 4.27 (*s*, 3 H); 4.26 (*s*, 3 H); 3.24 (*t*, *J* = 6.9, 4 H); 2.80, 2.07 (*AA′BB′*, 24 H); 1.50 (*m*, 4 H); 1.6–1.2 (*m*, 36 H); 0.81 (*t*, *J* = 7.0, 6 H). HR-MALDI-MS (DHB): 1974.9863 ($[M - 8\ CF_3COOH]^+$, $C_{118}H_{136}N_{16}O_6Ru^+$; calc. 1974.991).

*Bis(*N,N′,N″,N‴,N⁗,N′′′′′*-Hexadodecyl-3,3′,3″,3‴,3⁗,3′′′′′-{[2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]}hexapropanamide)ruthenium(II) Bis(hexafluorophosphate)* (**28**). A soln. of **14** (12 mg, 6 μmol) and $RuCl_3 \cdot H_2O$ (84% $RuCl_3$, 0.7 mg, 3 μmol) in dry 2-methoxyethanol (2 ml) was heated for 6 h to reflux under Ar. After cooling, the volume was reduced to one third. This soln. was then added dropwise to sat. aq. KPF_6 soln. The resulting red precipitate was washed with H_2O and EtOH, and then dried. GPC (*Bio-Beads S-X1*; CH_2Cl_2) gave **28** (8 mg, 61%). Red solid. M.p. 185°. IR (KBr): 3426*s*, 2925*s*, 2853*m*, 1693*s*, 1649*s*, 1536*s*, 1466*m*, 1366*m*, 1251*m*, 1171*m*, 845*m*, 790*w*. HR-MALDI-MS (DHB): 4279.0808 ($[M - 2\ PF_6]^+$, $C_{264}H_{410}N_{22}O_{18}Ru^+$; calc. 4279.0882).

*[(*N,N′,N″,N‴,N⁗,N′′′′′*-Hexadodecyl-3,3′,3″,3‴,3⁗,3′′′′′-{[2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]}hexapropanamide)-[Hexa*(tert-*butyl)* N,N′,N″,N‴,N⁗,N′′′′′*-([2-Methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis{[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]tris(ethane-2,1-diyl)})hexacarbamate]ruthenium(II) Bis(hexafluorophosphate)* (**29**). A suspension of **14** (30 mg, 14 μmol) and $RuCl_3 \cdot H_2O$ (84% $RuCl_3$, 35 mg, 144 μmol) in dry 2-methoxyethanol (2 ml) was heated to reflux under Ar for 6 h. After cooling, wet MeOH was added. A brown precipitate was formed, and it was collected by filtration, washed with H_2O and MeOH, and dried to give crude **27** (30 mg, 91%). Complex **27** (12.1 mg, 5.3 μmol) and **13** (8.1 mg, 5.3 μmol) were suspended in dry 2-methoxyethanol (2 ml) and *N*-ethylmorpholine (2 ml), and the mixture was heated to reflux under Ar for 6 h. After cooling, CH_2Cl_2 (5 ml) and sat. aq. KPF_6 soln. (10 ml) were added. The phases were separated, and the aq. phase was extracted with CH_2Cl_2 (3 ×). The combined org. phases were dried ($MgSO_4$) and evaporated. The resulting solid was taken up in CH_2Cl_2 and stirred with sat. aq. KPF_6 soln. for 1 h. The phases were separated, and the procedure was repeated twice. Evaporation and drying over P_2O_5 (0.01 Torr), followed by GPC (*Bio-Beads S-X1*; CH_2Cl_2), gave **29** (18 mg, 52%). Red solid. M.p. 212°. IR (KBr): 3432*m*, 2925*m*, 2854*w*, 1697*m*, 1653*m*, 1534*m*, 1367*w*, 1256*w*, 1170*m*, 833*s*, 558*m*. ^{1}H-NMR ($CDCl_3$,

500 MHz): 8.82 (br. *m*, 4 H); 8.53 (br. *m*, 4 H); 8.17 (br. *m*, 4 H); 7.9 – 7.35 (*m*, 34 H); 7.11 (br. *m*, 4 H); 5.68 (br. *m*, 6 H); 4.20 (br. *m*, 6 H); 3.17 (br. *m*, 12 H); 2.98 (br. *m*, 12 H); 2.1 – 1.8 (*m*, 36 H); 1.4 – 1.0 (*m*, 174 H); 0.69 (br., 18 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 173.92; 167.60; 167.23; 162.91; 157.49; 156.60; 155.09; 146.88; 146.57; 138.08; 135.05; 134.74; 134.46; 132.85; 131.90; 131.29; 131.23; 127.19; 127.09; 126.39; 126.29; 125.70; 125.56; 124.91; 124.57; 121.14; 117.96; 96.00; 94.16; 86.35; 86.23; 79.15; 58.40; 56.95; 56.93; 39.38; 35.36; 35.24; 31.57; 31.01; 30.34; 29.31; 29.30; 29.28; 29.27; 29.22; 29.00; 28.90; 27.92; 26.63; 22.31; 13.60; eight C(sp^2)-atom resonances were not resolved. HR-MALDI-MS (DHB): 3702.3000 ($[M - 2\,PF_6]^+$, $C_{216}H_{314}N_{22}O_{24}Ru^+$; calc. 3702.3064).

*[(*N,N′,N″,N‴,N⁗,N′⁗*-Hexadodecyl-3,3′,3″,3‴,3⁗,3′⁗-{[2-methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]}hexapropanamide)-[*N,N′N″,N‴,N⁗,N′⁗*-([2-Methoxy-5-(2,2′:6′,2″-terpyridin-4′-yl)benzene-1,3-diyl]bis{[(ethyne-2,1-diyl)(benzene-4,1-diyl)(oxomethanediyl)(iminomethanetetrayl)]tris(ethane-2,1-diyl)})hexaammonium]ruthenium(II) Octakis(2,2,2-trifluoroacetate)* (**30**). A soln. of **29** (10 mg, 3 μmol) in 30% CF_3COOH in CH_2Cl_2 (1 ml) was stirred under Ar at 20° for 1 h. After reducing the volume to one third *in vacuo* at 20°, a red solid was precipitated with Et_2O (1 ml). The entire mixture was evaporated, re-suspended in Et_2O, and sonicated. This procedure was repeated twice, and evaporation provided **30** (10 mg, 99%). Red solid. M.p. 225° (dec.). IR (KBr): 3441*s*, 2924*m*, 2853*m*, 1712*m*, 1644s, 1537*m*, 1457*w*, 1261*w*, 1089*m*, 1022*m*, 803*w*. HR-MALDI-MS (DHB): 3102.9990 ($[MH - 8\,CF_3COOH]^+$, $C_{186}H_{267}N_{22}O_{12}Ru^+$; calc. 3102.9997).

X-Ray Crystal Structures. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Compound **1b**. Crystal data at 293(2) K for $C_{22}H_{15}I_2N_3O$ (M_r 591.17): triclinic, space group $P\bar{1}$, $D_c = 1.908$ g cm^{-3}, $Z = 4$ (2 conformers), $a = 5.016(4)$, $b = 18.761(10)$, $c = 23.66(2)$ Å, $\alpha = 111.53(5)$, $\beta = (94.97(6)$, $\gamma = 92.11(6)°$, $V = 2058(2)$ Å^3, MoK_α radiation, $\lambda = 0.71073$ Å, linear crystal dimensions *ca.* 0.3 × 0.1 × 0.1 mm. The structure was solved by direct methods (SHELXS 86) and refined by full-matrix least-squares analysis (SHELXTL PLUS (VMS)). All heavy atoms were refined anisotropically, H-atoms isotropically; H-positions are based on stereochemical considerations. Final $R(F) = 0.0576$, w$R(F^2) = 0.1789$ for 506 parameters and 3012 reflections with $I > 2\sigma(I)$ and $1.78 < \theta < 20.04°$. *Cambridge Crystallographic Data Centre* Deposition No. CCDC-245959.

Compound **19**. Crystal data at 293(2) K for $C_{22}H_{15}Cl_3I_2N_3ORu \cdot 0.5\,MeCN$ (M_r 819.12): monoclinic, space group $P2(1)/n$, $D_c = 2.048$ g cm^{-3}, $Z = 8$ (2 conformers), $a = 13.772(9)$, $b = 15.23(2)$, $c = 24.93(2)$ Å, $\beta = 97.87(6)°$, $V = 5179(8)$ Å^3, CuK_α radiation, $\lambda = 1.54178$ Å, linear crystal dimensions *ca.* 0.08 × 0.04 × 0.04 mm. The structure was solved by direct methods (SHELXS 86) and refined by full-matrix least-squares analysis (SHELXTL PLUS (VMS)). All heavy atoms were refined anisotropically, H-atoms isotropically; H-positions are based on stereochemical considerations. Final $R(F) = 0.0777$, w$R(F^2) = 0.192$ for 604 parameters, 841 restraints, and 3979 reflections with $I > 2\sigma(I)$ and $3.41 < \theta < 50.00°$. *Cambridge Crystallographic Data Centre* Deposition No. CCDC-245960.

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