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Formation of a Series of [{Methylphenylenebis(terpyridine)}$_n$Ru$^{II}_{n-1}$] (n = 2–6) Oligomers in a Single-Pot Reaction

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A series of oligomeric [{methylphenylenebis(terpyridine)}$_n$-Ru$^{II}_{n-1}$] complexes, where n = 2–6, possessing metal-free terpyridine end groups was formed and isolated from a single-pot reaction. These oligo complexes were analyzed by ^{1}H NMR spectroscopy and mass spectrometry. Macrocyclization of combinations of these oligomers gave rise to the known hexagonal metallomacrocycle **7**. Cyclic voltammetry (CV) data of these linear oligomers are discussed and compared to that of the corresponding metallomacrocycle **7**. Diffusion coefficients were obtained by means of the Randles–Sevcik equation.

Introduction

Supramolecular[1] self-assembly is based on a combination of inherent structural information and bonding potential, such as the ligand juxtaposition within the polytopic building blocks and H-bonding ability, respectively. Lehn,[2] Stang,[3,4] Fujita,[5] Atwood,[6] and many others[7–13] have elegantly demonstrated the resultant structural beauty arising from the application of such parameters. This has prompted our investigation of a new series of self-assembling macrocycles through the use of a terpyridine–metal–terpyridine connectivity. Terpyridine-based monomers[14] have been used in the formation of numerous ordered assemblies,[15] such as in layered polyelectrolyte films,[16] grids,[17,18] racks,[19–21] Ru^{II}-based dendrimers,[22] helicating ligands,[23] photoactive molecular-scale wires,[24,25] luminescent complexes,[26–30] photovoltaic devices,[31] conducting polymers,[32] metallocycles,[33–37] metallodendritic spiranes,[38] fullerene–terpyridine complexes,[39–41] and combined biotin–terpyridine systems[42] as well as the generation of novel metallopolymers.[14,15]

More recently, we reported the creation of a series of bis(terpyridine) ligands each possessing a 120° bond angle with respect to the two ligating moieties (**1**) and their stepwise, as well as one-step, assembly to give hexagonal metal(II)-based macrocyclic complexes.[43–45] The potential to synthesize such constructs, with little equilibration (i.e., metal/ligand exchange) under mild physicochemical conditions, is predicated on the unique strength and stability of the terpyridine–metal coordination.[46] In the stepwise protocol,[43–45] we described the construction of linear bis(terpyridine)Ru^{II} complexes, as precursors to the construction of these hexagons; thus, the realization that these linear constructs could, in their own right, provide unique building blocks to afford access to new utilitarian materials has prompted us to devise conditions which would lead to a series of metallo-oligomers.[47,48] Herein, we report the formation and characterization of a linear [{methylphenylenebis(terpyridine)}$_n$Ru$^{II}_{n-1}$] oligomeric family possessing metal-free terpyridine end groups.

Results

In previous reports,[43–45] a key target was the preparation of the bis(Ru^{II}) oligomer **5**, which was intended for use in the stepwise construction of the hexagonal macrocycle **9**. During the course of our work, this trimer was obtained as the dominant product from the reaction of bis(terpyridine) ligand **1** with the bis(Ru^{III}) adduct **2**, however, it was later found that oligomeric side products could be generated as major components by adjusting the metal stoichiometry; thus, the metal/bis(terpyridine) ratio could be manipulated to determine the reaction outcome. Also, the formation of dimer **4** is not possible when starting with *pure* bis(Ru^{III}) monomer **2**, because there is no literature evidence of metal (Ru^{III}) loss or exchange under typical reaction conditions to generate [bis(terpyridine)Ru^{II}] complexes. Therefore, in

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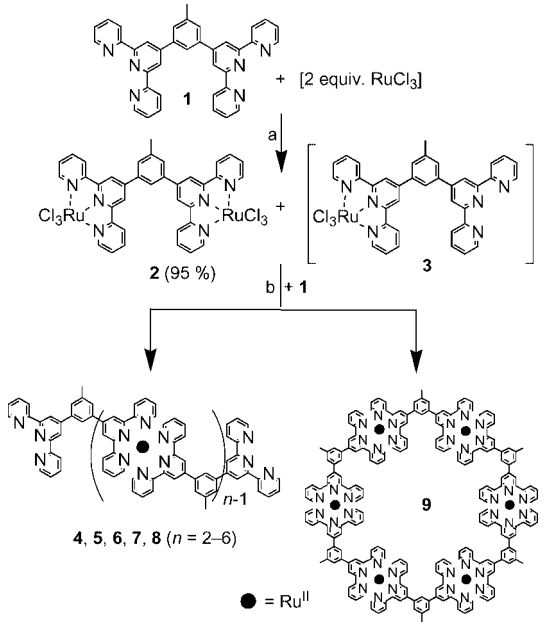
the initial preparation of the bis(Ru^{III}) adduct **2**, the formation of a bis(terpyridine)mono(Ru^{III}) adduct **3** (Scheme 1) occurs in measurable quantities. Conventionally, purification of the solid **2** is accomplished by repeated washings with MeOH to remove any unreacted starting materials; however, minor amounts of the mono(Ru^{III}) adduct **3** impurity remained under these extraction conditions. Subsequent treatment of **3** with the metal-free ligand **1** then gave the bis(terpyridine) dimer **4**.



Scheme 1. Synthesis of the bis(Ru^{III}) and mono(Ru^{III}) adducts (**2** and **3**) and the formation of the linear [{methylphenylenebis(terpyridine)}$_n$$Ru^{II}_{n-1}$] complexes **4**–**8** and macrocycle **9** by single-pot reaction; a) EtOH, reflux 12 h; b) (i) 2 equiv. **1**, MeOH, *N*-ethylmorpholine, reflux 12 h, (ii) NH_4PF_6, MeOH.

Thus, to see if it is possible to generate other non-cyclized materials, the series of oligomeric [{methylphenylenebis(terpyridine)}$_n$$Ru^{II}_{n-1}$] complexes [$n$ = 2 (**4**), 3 (**5**), 4 (**6**), 5 (**7**), 6 (**8**)] was accessed using a single-pot reaction (Scheme 1) by refluxing a mixture of 3,5-bis(4′-terpyridinyl)toluene (**1**) and 0.5 equiv. of the related bis(Ru^{III}) adduct **2** in MeOH with a catalytic amount of *N*-ethylmorpholine. Isolation of each member in the series was accomplished employing column chromatography (basic Al_2O_3; solution of MeCN/satd. aq. KNO_3/water, 10:1:1 v/v), and followed by preparative TLC (basic Al_2O_3; solution of MeCN/satd. aq. KNO_3/water, 10:1:1 v/v; R_f = 0.7, 0.6, 0.55, 0.45, and 0.4, respectively) which gave the desired linear complexes as deep red microcrystals in 6, 40, 9, 7, and 5% yields for **4**, **5**, **6**, **7**, and **8**, respectively.

Evidence (^{1}H NMR) for the formation of [{methylphenylenebis(terpyridine)}$_n$$Ru^{II}_{n-1}$] oligomers with bis(terpyridine) chain lengths with $n > 6$ has been observed; however, attempted isolation and purification of these trace products have to date not been successful. Notably, connecting combinations of the isolated oligomers by stepwise procedures should give access to the larger cyclic and noncyclic members of this series. As expected, the macrocyclic hexamer **9** was also isolated (8%) using different preparative TLC (silica; solution of MeCN/satd. aq. KNO_3/water, 7:1:1 v/v) conditions. Under the TLC conditions in which the oligomers move, the cyclic complex fortunately does not and vice versa.

These results triggered us to investigate the possibility of the generation of oligo complexes under different reaction conditions (Table 1). Reaction combinations of [**1** + 0.5 equiv. $RuCl_3$] and [**1** + 1 equiv. **2**] with *N*-ethylmorpholine were designed to maximize the yield of dimer **4** and hexagon **9**, respectively. These reaction conditions resulted in similar products, albeit with different product distributions.

Table 1. Overall results of the formation of linear [{methylphenylenebis(terpyridine)}$_n$$Ru^{II}_{n-1}$] complexes **4**–**8** and macrocycle **9** with variable reaction conditions.

Reactants [equiv.]			Complexes [%][a]					
1	**2**	$RuCl_3$	**4**	**5**	**6**	**7**	**8**	**9**
1	–	0.5	30	8	6	5	6	10
1	0.5	–	6	40	9	7	5	8
1	1		2	6	8	6	4	39

[a] Isolated weight-% yield.

Structural support (^{1}H NMR) for the bis[bis(terpyridine)]Ru^{II} dimer **4** includes resonances for the 5,5′′- and 6,6′′-tpy*H* atoms of the coordinated terpyridine moiety [δ = 7.31 (4 H), 7.62 (4 H) ppm], and the analogous metal-free terpyridine protons [δ = 7.55 (4 H), 8.76 (4 H) ppm]. Resonances attributed to 2,6-Ar*H* atoms and 3′,5′-tpy*H* atoms of the coordinated bis(terpyridine) units are observed at δ = 8.31 (2 H), and 9.43 (4 H) ppm, respectively. Whereas, peaks assigned to the metal-free units are observed at δ = 8.11 (2 H), and 8.95 (4 H) ppm and are similar to that of the starting ligand **1**. The aryl methyl groups appear as a singlet [δ = 2.77 (6 H) ppm] due to an equivalent environment. These aryl methyl absorptions are diagnostic for all the oligomers in that the inner and outer methyl moieties on the chains display different chemical shifts. Thus, the integrated ratios of these two signals are diagnostic for each oligomer. COSY experiments confirmed these assignments. The HR-ESI mass spectrum for the dimer **4** displays a molecular ion peak at m/z = 605.1757 amu [M – 2 PF_6]$^+$ (calcd. 605.1741 amu).

Unlike the simple dimer **4**, the bis(Ru^{II}) trimer **5** contains three different kinds of terpyridine units, as depicted in Figure 1 (**5**), in which there are (1) the central complexed terpyridines [Figure 1 (c)] that constitute the inner half of the complex, (2) the complexed terpyridines [Figure 1 (b)] of the two terminal bis(ligands), and (3) the free terminal terpyridines [Figure 1 (a)]. Each absorption attributed to the 5,5′′-, 6,6′′-, 3′,5′-tpy*H* atoms and 2,6-Ar*H* atoms of trimer **5** exhibits different chemical shifts based on its chain location as well as coordination. Signals for the 5,5′′-tpy*H* are observed at δ = 7.34 (4 H), 7.31 (4 H), 7.54 (4 H) ppm and 6,6′′-tpy*H* atoms are found at δ = 7.67 (4 H), 7.62 (4 H), 8.77 (4 H) ppm. The resonances attributed to the 2,6-Ar*H* and 3′,5′-tpy*H* positions are also assigned as three distinguishable peaks at δ = 8.41 (2 H), 8.31 (2 H), 8.11 (2 H)

ppm and at δ = 9.55 (4 H), 9.43 (4 H), 8.95 (4 H) ppm. The methyl protons appear as two singlets at δ = 2.78 and 2.88 ppm that integrate in a 2:1 ratio; COSY experiments further confirm these assignments. The HR-ESI mass spectrum for **5** displays a mass peak at m/z = 466.6273 amu $[M - 4\ PF_6]^+$, z = 4 (calcd. 466.6286 amu).

As expected, the oligomers **6**–**8** display similar chemical shift patterns but different proton integration ratios, as shown in Figure 1. Diagnostic signals for the aryl methyl groups of these oligomers exhibit two well-separated singlets at δ = 2.78 and 2.89 ppm (**6**; 1:1 ratio), 2.77 and 2.88 ppm (**7**; 2:3 ratio), as well as 2.77 and 2.89 ppm (**8**; 1:2 ratio), which are in agreement with the assignments. These assignments, along with the remaining proton chemical shifts, are confirmed by COSY NMR experiments and are reported in Table 2. The corresponding HR-ESI mass spectra for these oligomers exhibit molecular ion peaks for **6** at m/z = 420.4505 amu $[M - 6\ PF_6]^+$, z = 6 (calcd. 420.4334 amu); for **7** at m/z = 939.6541 amu $[M - 4\ PF_6]^+$, z = 4 (calcd. 939.6459 amu); and for **8** at m/z = 735.8165 amu $[M - 6\ PF_6]^+$, z = 6 (calcd. 735.7850 amu).

UV spectra of the oligomers **4**–**8** revealed the metal-to-ligand charge transfer (MLCT) band characteristic of [bis(terpyridine)Ru^{II}] coordination at 496 nm (λ_{max}) with extinction coefficients (ε) of 1.9 (**5**), 2.7 (**6**), 4.1 (**7**), 5.0 (**8**), and 5.5 (**9**) when compared to that of the dimeric complex **4** (see Experimental Section).

Further evidence supporting the formation and functionalities of the linear structures of **4**–**8** was provided by the treatment of the linear structures with the appropriate rea-

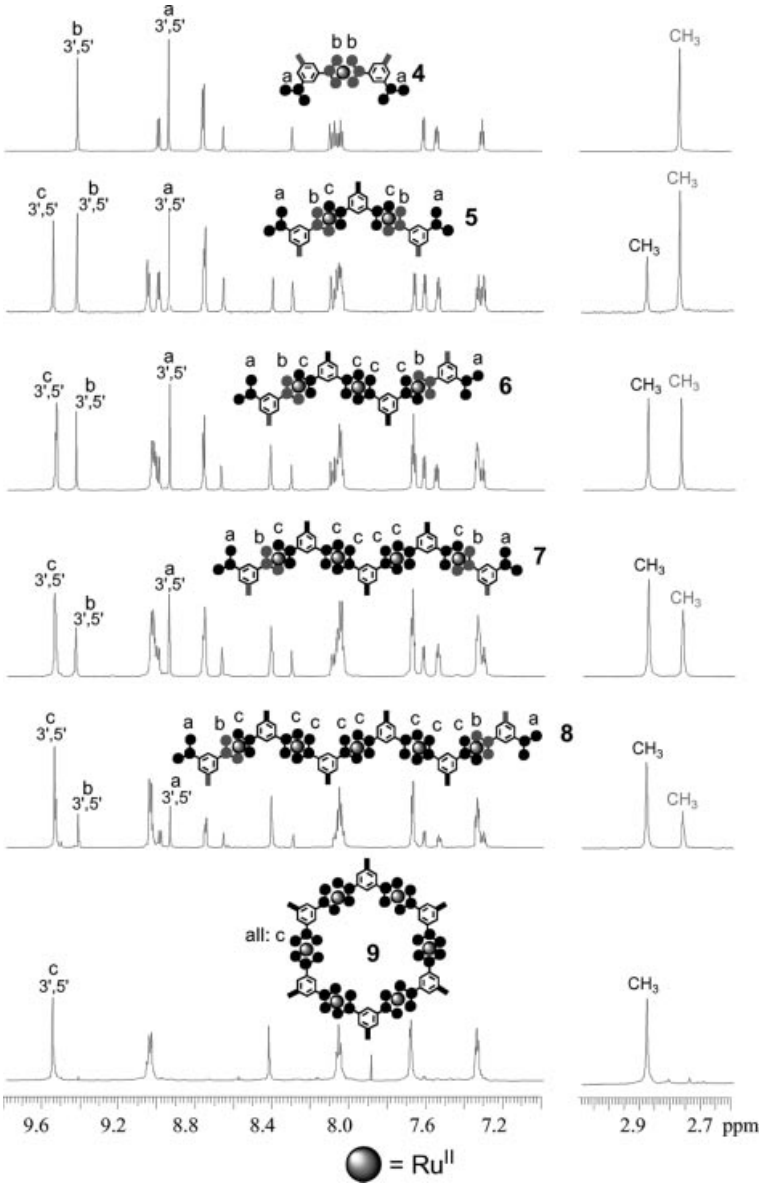


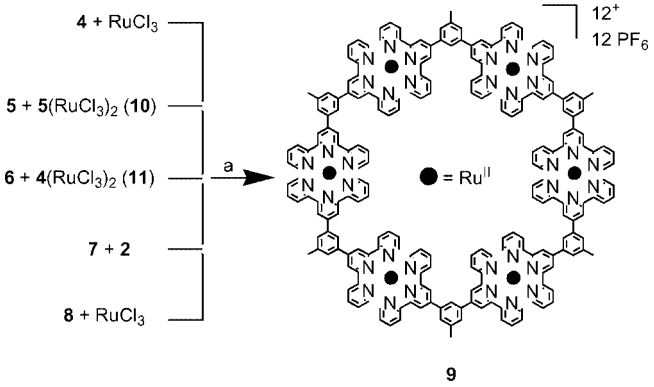
Figure 1. ^{1}H NMR spectra (Cl^- counterion, CD_3OD) of the linear [{methylphenylenebis(terpyridine)}$_n$Ru$^{II}_{n-1}$] complexes **4**–**8** and the macrocycle **9**.

Table 2. Proton chemical shifts of the linear [{methylphenylenebis(terpyridine)}$_n$Ru$^{II}_{n-1}$] complexes **4**–**8** and the hexagonal macrocycle **9**.

	Ar^4	Ar^{2,6}	3′,5′	3,3"	4,4′′	5,5′′	6,6′′	Methyl
4	8.66, s 2 H	8.11, s 2 H[a] 8.31, s 2 H[b]	8.95, s 4 H[a] 9.43, s 4 H[b]	8.76, d 4 H[a] 9.01, d 4 H[b]	8.08, m 8 H	7.55, dd 4 H[a] 7.31, dd 4 H[b]	8.76, d 4 H[a] 7.62, d 4 H[b]	2.77, s 6 H
5	9.06, s 1 H[c] 8.67, s 2 H[d]	8.11, s 2 H[a] 8.31, s 2 H[b] 8.41, s 2 H[c]	8.95, s 4 H[a] 9.43, s 4 H[b] 9.55, s 4 H[c]	8.77, d 4 H[a] 9.00, d 4 H[b] 9.05, d 4 H[c]	8.07, m 12 H	7.54, dd 4 H[a] 7.31, dd 4 H[b] 7.34, dd 4 H[c]	8.77, d 4 H[a] 7.62, d 4 H[b] 7.67, d 4 H[c]	2.78, s 6 H[d] 2.88, s 3 H[c]
6	9.05, s 2 H[c] 8.69, s 2 H[d]	8.12, s 2 H[a] 8.32, s 2 H[b] 8.43, s 4 H[c]	8.96, s 4 H[a] 9.44, s 4 H[b] 9.55, s 8 H[c]	8.78, d 4 H[a] 9.01, d 4 H[b] 9.04, d 8 H[c]	8.07, m 16 H	7.57, dd 4 H[a] 7.33, dd 4 H[b] 7.36, dd 8 H[c]	8.78, d 4 H[a] 7.63, d 4 H[b] 7.69, d 8 H[c]	2.78, s 6 H[d] 2.89, s 6 H[c]
7	9.05, s 3 H[c] 8.68, s 2 H[d]	8.11, s 2 H[a] 8.32, s 2 H[b] 8.43, s 6 H[c]	8.96, s 4 H[a] 9.44, s 4 H[b] 9.55, s 12 H[c]	8.77, d 4 H[a] 9.01, d 4 H[b] 9.04, d 12 H[c]	8.07, m 20 H	7.56, dd 4 H[a] 7.32, dd 4 H[b] 7.35, dd 12 H[c]	8.77, d 4 H[a] 7.64, d 4 H[b] 7.69, d 12 H[c]	2.77, s 6 H[d] 2.88, s 9 H[c]
8	9.05, s 4 H[c] 8.67, s 2 H[d]	8.10, s 2 H[a] 8.31, s 2 H[b] 8.42, s 8 H[c]	8.94, s 4 H[a] 9.42, s 4 H[b] 9.54, s 16 H[c]	8.76, d 4 H[a] 9.00, d 4 H[b] 9.04, d 16 H[c]	8.08, m 24 H	7.54, dd 4 H[a] 7.31, dd 4 H[b] 7.35, dd 16 H[c]	8.76, d 4 H[a] 7.62, d 4 H[b] 7.68, d 16 H[c]	2.77, s 6 H[d] 2.89, s 12 H[c]
9	9.07, s 6 H	8.43, s 12 H	9.56, s 24 H	9.05, d 24 H	8.07, dd 24 H	7.35, dd 24 H	7.70, d 24 H	2.89, s 18 H

[a] Metal-free terpyridine. [b] Coordinated part of end bis(terpyridine). [c] Fully coordinated bis(terpyridine). [d] End bis(terpyridine).

gents to construct the known hexameric metallocycle **9** (Scheme 2). To a methanolic solution of **4**, 1 equiv. of $RuCl_3$ and a catalytic amount of *N*-ethylmorpholine were added and the mixture refluxed for 12 h.



Scheme 2. Formation of macrocycle **9** by the reaction of linear complexes combination: a: i) MeOH, *N*-ethylmorpholine, reflux 12 h; ii) NH_4PF_6, MeOH.

After the reaction, the product was purified by column chromatography (silica) to give the red microcrystalline metallocycle **9** (33%). Stepwise reaction of **5** + [**5**$(RuCl_3)_2$ (**10**)] for the formation of **9** has been reported previously.[43] The reaction combinations of **6** + [**4**$(RuCl_3)_2$ (**11**)], **7** + **2**, and **8** + 1 equiv. of $RuCl_3$ with *N*-ethylmorpholine in refluxing methanol gave the expected product **9** with 30, 26, and 35% yields, respectively.

The ^{1}H NMR spectra of **9** (PF_6^- counterion) prepared by these procedures are identical in all respects to the known **9** (PF_6^- counterion) obtained by the self-assembly method.[43]

Electrochemical responses of the Ru^{II} linear complexes **4**–**8** and the corresponding metallomacrocycle **9** were analyzed by cyclic voltammetry (CV) experiments conducted at 298 K with 0.2 mM solutions in 0.1 M Bu_4NBF_4 in DMF (Figure 2 and related data in Table 3). All oligomeric complexes showed a reversible wave at ca. 0.7 V vs. Fc^+|Fc; the size increased with the number of (terpyridine)Ru units present in the molecule, which presumably corresponds to the Ru^{III}|Ru^{II} couple.[44,45] Inspection of the cathodic region showed two reversible monoelectronic reduction processes at approximately –1.7 and –1.9 V vs. Fc^+|Fc which, based

on previous observations,[44,45] correspond to the sequential one-electron reduction of each of the two terpyridine ligands surrounding the complexed ruthenium metal atom (Tpy|Tpy$^-$ and Tpy$^-$|Tpy^{2-}). In contrast to that of oligomers **4**–**8**, the 2e$^-$ terpyridine reduction of **9** results in a neutral compound for which any further electron transfer process is characterized by a sharp peak whose shape is typical of a species adsorbed on the electrode surface.[44]

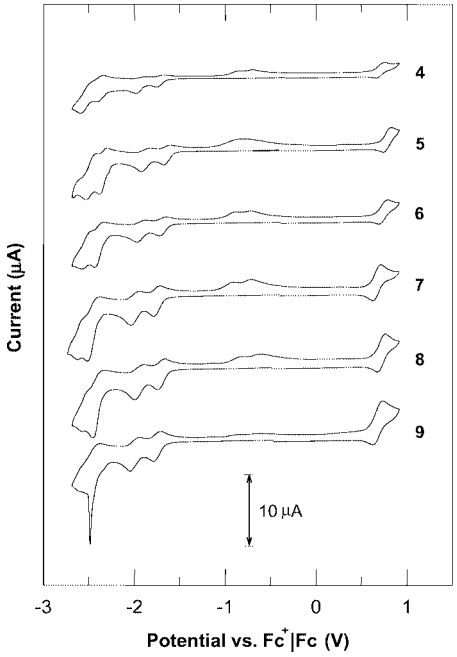


Figure 2. CV responses of [{methylphenylenebis(terpyridine)}$_n$-Ru$^{II}_{n-1}$] complexes **4**–**8**, and macrocycle **9** (0.2 mM for each sample in 0.1 M Bu_4NBF_4 in DMF using a glassy carbon electrode) at 298 K and a scan rate of 0.1 V s^{-1}.

Inspection of the cathodic region in Figure 2 reveals that following the two-wave terpyridine reduction processes, a third reduction event occurs. The corresponding signal was observed to increase progressing from **4** to **8** and assuming reversible conditions,[49] analysis of its peak current, reveals that it is related to a 2e$^-$ reduction process at each one of the equivalent methylphenylene (MP) linking units.

During the cathodic scan, this reduction process is followed by a fourth cathodic peak which, in contrast to the third peak, was observed to be constant as the number of (terpyridine)Ru units is increased in the series, thus suggesting electron uptake of the terminal units (TU) of **4**–**8**.

Analysis of the data obtained from the CV experiments suggests that during the cathodic scan, the reduction events result in a decomposition of the relevant molecules. The lack of definition in the corresponding anodic responses, as well as the oxidation peaks observed at ca. –1 to –0.5 V vs. Fc$^+$|Fc also suggest this interpretation.

From the CV data obtained for the first reversible one-electron reduction of the terpyridine ligand, it was possible to calculate approximate values for the diffusion coefficients (Table 3) of the oligomers using the Randles–Sevcik equation.[49] The corresponding values roughly follow an inversely proportional relationship with the number of ruthenium metal atoms in the molecule suggesting that the smaller the molecule, the larger its diffusion coefficient [Figure 3 (●)].

These values can also be incorporated in the Stokes–Einstein equation to calculate the radius, *r*, of a spherical diffusing particle in a continuous medium.[50] Using this approximation, the values of *r* were graphed as a function of the number of Ru atoms in each oligomer [Figure 3 (▲)]; and an approximate linear relationship was obtained. Using the slope of the adjusted straight line, it was determined that each (terpyridine)Ru unit in the molecule increased the radius of the equivalent spherical molecule by approximately 1.4 Å, a value that is in the order of what should be expected for this series of related linear structures.

Table 3. Electrochemical data of [{methylphenylenebis(terpyridine)}$_n$Ru$^{II}_{n-1}$] complexes **4**–**8**, and macrocycle **9** (0.2 mM for each sample in 0.1 M Bu_4NBF_4 in DMF using a glassy carbon electrode) at 298 K and a scan rate of 0.1 V s^{-1}.

Complex	$E_{1/2}$ (ΔE_p) / V vs. Fc$^+$|Fc					D / 10^{-8} cm^2 s^{-1}
	TU|TU^{2-}	MP|MP^{2-}	Tpy$^-$|Tpy^{2-}	Tpy|Tpy$^-$	Ru^{III}|Ru^{II}	
4	-2.532 (0.080)	-2.379 (0.109)	-1.934 (0.067)	-1.720 (0.119)	0.699 (0.090)	49.82
5	-2.481 (0.077)	-2.354 (0.096)	-1.884 (0.091)	-1.651 (0.118)	0.775 (0.090)	17.30
6	-2.536 (0.076)	-2.394 (0.096)	-1.929 (0.100)	-1.694 (0.098)	0.734 (0.090)	5.13
7	-2.611 (0.063)	-2.469 (0.098)	-2.011 (0.120)	-1.772 (0.085)	0.658 (0.086)	5.54
8	-2.554 (0.072)	-2.406 (0.106)	-1.964 (0.144)	-1.725 (0.082)	0.702 (0.083)	2.83
9	-	-2.428 (0.103)	-1.991 (0.115)	-1.747 (0.083)	0.593 (0.099)	2.08

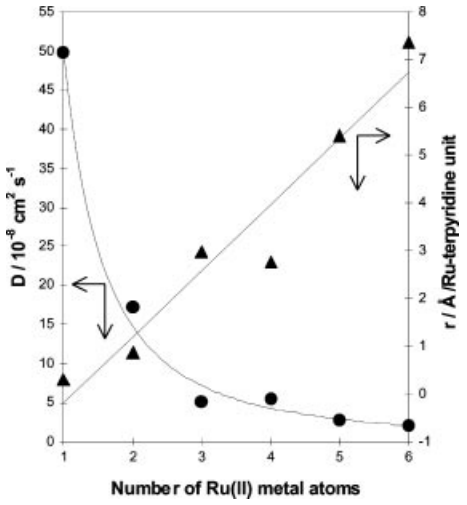


Figure 3. Diffusion coefficients (●) and approximate radii (▲) vs. the number of Ru atoms for the linear [{methylphenylenebis(terpyridine)}$_n$Ru$^{II}_{n-1}$] complexes **4**–**8** and the macrocycle **9**.

Conclusions

In conclusion, we synthesized and identified oligomeric [{methylphenylenebis(terpyridine)}$_n$Ru$^{II}_{n-1}$] complexes where n = 2–6, which include free terminal terpyridine moieties. NMR spectroscopy and mass spectrometry studies support the structural assignments of these linear complex chains. The electrochemical studies further support the oligomeric structure using the Randles–Sevcik equation. Also, we showed the positive complexation functionality of free terpyridines at the end-of-the-chain through the formation of hexagonal macrocycle **9** by cyclic complexation of linear structures **4**–**8** with Ru atoms or Ru-containing reagents. Combinations of these oligomers with diverse metals afford new opportunities to tailor the permanent or reversible incorporation of specific metal atoms within polymeric chains.

Experimental Section

Materials and Methods: Chemicals were purchased from Aldrich and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets precoated with aluminum oxide or silica gel and visualized by UV light. Column chromatography was conducted using neutral/basic alumina, (activity I, 60–325 mesh) or silica gel (60–200 mesh). ^{1}H (750 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a Varian Unity Inova 750 and Gemini 300 spectrometers, respectively. [^{1}H NMR of all linear complexes and **9** were measured in CD_3OD using chloride counterions due to their enhanced splitting patterns relative to using PF_6 counterions. Furthermore, **9** (PF_6^- counterion) was also measured in CD_3CN to verify the structural identification in all respects to the known **9** (PF_6^- counterion) obtained by the self-assembly method.] ESI mass spectra were obtained with an electrospray ion-trap mass spectrometer. High-resolution ESI mass spectra were recorded with a Micromass LCT spectrometer. The cyclic voltammetry (CV) experiments were conducted at 298 K using a 5-mL cell [3 mL solution of 0.2 mM of each compound dissolved in 0.1 M Bu_4NBF_4 (99%) in DMF (99.9%)] equipped with a glassy carbon working electrode (exposed area of 0.0787 cm^2), a platinum counter electrode, and a silver wire, which worked as a pseudo-reference electrode. All the potentials reported in this work were measured against the ferrocinium/ferrocene (Fc^+|Fc) redox couple. All of the electrolyte solutions were deoxygenated by bubbling of ultrapure nitrogen gas through the solution for at least 10 min.

Representative Oligomerization Procedure: 3,5-Bis(4′-terpyridinyl)-toluene (**1**; 125 mg, 226 μmol) was added to a suspension of the 3,5-bis(4′-terpyridinyl)toluene·2$RuCl_3$ adduct **2** (100 mg, 103 μmol) in MeOH (100 mL), then *N*-ethylmorpholine (100 μL) was added; the mixture was refluxed for 12 h. After the reaction mixture was cooled, the resulting deep red solution was filtered through Celite. After the solvent and volatiles were removed in vacuo, the residue was column-chromatographed (Al_2O_3) eluting with an H_2O/MeCN/satd. aq. KNO_3 (1:10:1) solution to afford a red solid, which was dried to give the linear complex series. Each complex was subjected to a second purification through preparative TLC [basic alumina on glass, solution of MeCN/ satd. aq.KNO_3/water (10:1:1, v/v)] for NMR study (**4**: 6%, R_f = 0.7; **5**: 40%, R_f = 0.6; **6**: 9%, R_f = 0.55; **7**: 7%, R_f = 0.45; **8**: 5%, R_f = 0.4). To a methanol solution of purified complex (Cl^- counterion) a slight excess of methanolic NH_4PF_6 was added to precipitate the counterion-exchanged complex (PF_6^-), which was washed with MeOH, then dried in vacuo to afford red microcrystals in quantitative yield.

[Ru(1)$_2$(Cl)$_2$] (4): Yield 13 mg; m.p. > 320 °C. ^{1}H NMR (CD_3OD): Table 2. [Ru(**1**)$_2$(PF_6)$_2$]: ^{13}C NMR (CD_3CN): δ = 21.78, 119.73, 122.12, 122.85, 124.79, 125.42, 125.67, 128.38, 130.32, 131.20, 138.38, 138.88, 140.52, 141.46, 148.60, 150.19, 151.30, 153.31, 156.31, 157.04, 159.17 ppm. HR ESI MS: m/z = 605.1757 ([M – 2 PF_6]$^+$, z = 2; calcd. 605.1741). UV/Vis (PF_6^- counterion, MeCN, MLCT band only): λ_{max} (ε) = 496 (26200) nm.

[Ru$_2$(1)$_3$(Cl)$_4$] (5): Yield 86 mg; m.p. > 400 °C. ^{1}H NMR (CD_3OD): Table 2. [Ru$_2$(**1**)$_3$(PF_6)$_4$]: ^{13}C NMR (CD_3CN): δ = 21.81, 21.92, 120.94, 122.99, 123.16, 124.96, 125.51, 125.75, 126.40, 128.71, 130.86, 130.93, 131.34, 139.08, 139.23, 139.36, 140.07, 140.39, 141.98, 142.29, 148.84, 149.02, 149.29, 151.72, 153.62, 154.66, 155.52, 156.63, 156.71, 159.32, 159.38 ppm. HR ESI MS: m/z = 670.4797 ([M – 3 PF_6]$^+$, z = 3; calcd. 670.4795), 466.6273 ([M – 4 PF_6]$^+$, z = 4; calcd. 466.6286). UV/Vis (PF_6^- counterion, MeCN, MLCT band only): λ_{max} (ε) = 496 (50000) nm.

[Ru$_3$(1)$_4$(Cl)$_6$] (6): Yield 19 mg; m.p. > 400 °C. ^{1}H NMR (CD_3OD): Table 2. [Ru$_3$(**1**)$_4$(PF_6)$_6$]: ^{13}C NMR (CD_3CN): δ = 21.82, 21.93, 119.94, 122.38, 123.07, 124.89, 125.56, 125.76, 128.70, 128.77, 130.48, 130.85, 131.36, 138.47, 139.03, 139.25, 139.38, 140.99, 141.96, 142.33, 148.82, 148.88, 149.28, 150.47, 150.84, 153.67, 156.65, 156.76, 156.86, 157.54, 159.40 ppm. HR ESI MS: m/z = 420.4505 ([M – 6 PF_6]$^+$, z = 6; calcd. 420.4334). UV/Vis (PF_6^- counterion, MeCN, MLCT band only): λ_{max} (ε) = 496 (70100) nm.

[Ru$_4$(1)$_5$(Cl)$_8$] (7): Yield 15 mg; m.p. > 400 °C. ^{1}H NMR (CD_3OD): Table 2. [Ru$_4$(**1**)$_5$(PF_6)$_8$]: ^{13}C NMR (CD_3CN): δ = 21.78, 21.92, 119.91, 122.31, 123.06, 124.89, 125.54, 125.82, 128.67, 128.73, 130.50, 130.81, 131.33, 138.43, 139.08, 139.25, 139.37, 140.98, 141.92, 142.28, 148.80, 148.86, 149.27, 150.46, 150.81, 153.64, 156.62, 156.75, 156.84, 158.21, 159.40 ppm. HR ESI MS: m/z = 939.6541 ([M – 4 PF_6]$^+$, z = 4; calcd. 939.6459). UV/Vis (PF_6^- counterion, MeCN, MLCT band only): λ_{max} (ε) = 496 (108300) nm.

[Ru$_5$(1)$_6$(Cl)$_{10}$] (8): Yield 11 mg; m.p. > 400 °C. ^{1}H NMR (CD_3OD): Table 2. [Ru$_5$(**1**)$_6$(PF_6)$_{10}$]: ^{13}C NMR (CD_3CN): δ = 21.79, 21.91, 119.89, 122.32, 123.08, 124.89, 125.54, 125.82, 128.65, 128.73, 130.49, 130.81, 131.34, 138.43, 139.06, 139.25, 139.37,

140.98, 141.93, 142.28, 148.81, 148.86, 149.27, 150.45, 150.81, 153.64, 156.62, 156.74, 156.84, 157.51, 159.40 ppm. HR ESI MS: m/z = 735.8165 ([M – 6 PF_6]$^+$, z = 6; calcd. 735.7850). UV/Vis (PF_6^- counterion, MeCN, MLCT band only): λ_{max} (ε) = 496 (132000) nm.

[5(RuCl$_3$)$_2$] (10) and [4(RuCl$_3$)$_2$] (11). General Method: Solid RuCl$_3$·3H$_2$O (2 equiv.) was added to a solution of the terminal bis(terpyridine) linear complex (50 μmol) in EtOH (25 mL), then the solution was refluxed for 12 h. After the mixture had been cooled, the resultant dark brown solid was filtered, washed with EtOH and MeOH, then dried in vacuo to yield the bis(Ru^{III}) adduct **10** or **11** as a dark brown solid (88–92%). These materials were used without further purification.

[Ru$_6$(1)$_6$(Cl)$_{12}$] (9): Individual combinations of [**4** + 1 equiv. of RuCl$_3$], [**6** (1 equiv.) + **11** (1 equiv.)], [**7** (1 equiv.) + **2** (1 equiv.)], or [**8** + RuCl$_3$] were combined in MeOH with a catalytic amount of *N*-ethylmorpholine, then the reaction mixture was refluxed for 12 h. Each reaction combination in this series was treated with a same workup and purification procedures as follows. After the reaction mixture had been cooled, the resulting deep red solution was filtered through Celite. After the solvent and volatiles were removed in vacuo, the residue was column-chromatographed (silica) eluting with an H$_2$O/MeCN/satd. aq. KNO$_3$ (1:7:1) solution to afford (25–35%) **9** as a red solid. For the NMR study, each derived hexacomplex was then subjected to preparative TLC (silica on glass) before exchange of the counterion to PF_6^-. To a methanol solution of purified complex (Cl^- counterion) a slight excess of methanolic NH_4PF_6 was added to precipitate the product (PF_6^-), which was washed with MeOH, then dried in vacuo to afford red microcrystals in quantitative yield; m.p. > 400 °C. ^{1}H NMR (Cl^- counterion, CD_3OD): Table 2. [Ru$_6$(**1**)$_6$(PF$_6$)$_{12}$]: ^{13}C NMR (CD_3CN): δ = 21.92, 122.50, 125.05, 125.11, 128.75, 138.41, 138.68, 148.44, 152.77, 154.76, 155.87, 158.56 ppm. ESI MS (PF_6^- counterion): m/z = 485.7 ([M – 9 PF_6]$^+$, z = 9; calcd. 485.5), 564.2 ([M – 8 PF_6]$^+$, z = 8; calcd. 564.3), 664.4 ([M – 7 PF_6]$^+$, z = 7; calcd. 665.7), 800.1 ([M – 6 PF_6]$^+$, z = 6; calcd. 800.8), 1273.0 ([M – 4PF_6]$^+$, z = 4; calcd. 1273.6), 1745.8 ([M – 3 PF_6]$^+$, z = 3; calcd. 1746.5). UV/Vis (PF_6^- counterion, MeCN, MLCT band only): λ_{max} (ε) = 496 (143400) nm.

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