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14 Step-15 Electron Reversible Redox Behavior of Tetrameric Oligomer of Oxo-Bridged Triruthenium Cluster

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Pyrazine-bridged trimeric and tetrameric oligomers of triruthenium clusters, $[\{Ru_3O(CH_3CO_2)_6(CO)(py)\}\text{-}(\mu\text{-pz})\text{-}\{Ru_3O(CH_3CO_2)_6(CO)\}\text{-}(\mu\text{-pz})\text{-}\{Ru_3O(CH_3CO_2)_6(py)_2\}]^+$ (**1**) and $[\{Ru_3O(CH_3CO_2)_6(CO)(py)\}\text{-}(\mu\text{-pz})\text{-}\{Ru_3O(CH_3CO_2)_6(CO)\}\text{-}(\mu\text{-pz})\text{-}\{Ru_3O(CH_3CO_2)_6(py)\}\text{-}(\mu\text{-pz})\text{-}\{Ru_3O(CH_3CO_2)_6(dmap)_2\}]^{2+}$ (**2**), were prepared (pz = pyrazine, py = pyridine, dmap = 4-dimethylaminopyridine). Trimer **1** and tetramer **2** show closely spaced 11 step-12 electron and 14 step-15 electron reversible redox waves, respectively, in their cyclic voltammograms in CH_3CN. These compounds were designed specifically to incorporate the above-mentioned electrochemical behavior, using the unique redox properties characteristic of triruthenium clusters: (i) each Ru_3 cluster unit generally exhibits four reversible single electron waves from $Ru_3^{IV,III,III}$ to $Ru_3^{II,II,II}$ state; (ii) the redox potentials of the cluster units strongly depend on the basicity of the ancillary ligand; (iii) redox potentials of the Ru_3 cluster units vary by 300–500 mV depending on the presence or the absence of a carbonyl ligand on the cluster unit; (iv) in the negative potential region, electronic interaction through the bridging pyrazine between adjacent Ru_3 units containing a carbonyl ligand makes the difference in redox potential of each unit larger. **1** and **2** were synthesized by linking Ru_3 cluster units with the desired ancillary ligand set in the appropriate order.

Molecules possessing multiple redox processes are fundamentally interesting and attractive candidates for use in multilevel electronic devices.[1] However, single molecules usually have a limited degree of multiplicity. For example, although fullerenes C_{60} and C_{70} exhibit six reversible single-electron reductions, these processes are spread over a large and extremely negative potential window (−0.98 V to −3.26 V vs Fc/Fc^+).[2] A few examples of multinuclear complexes having redox-active ligands which possess a large number of redox processes are known.[3–5] Balzani and co-workers reported 26 successive redox processes for a hexanuclear ruthenium complex with bridging polypyridyl ligands, but their redox processes are highly overlapped.[3] Recently, Lehn and co-workers reported a [2 × 2] grid type Co^{II}_4 complex that can be electrochemically reduced by 11 electrons in 10 well-resolved reversible steps.[4] Metal-assembled complexes with redox-active metal centers and their oligomers should be useful for making multi-redox systems.

In this paper we report the design, syntheses and electrochemical properties of a pyrazine-bridged triruthenium cluster trimer and tetramer which show well separated multistep one-electron redox waves. The triruthenium clusters that we used are a class of oxo-centered triruthenium clusters bridged by six acetate ligands with the general formulae of $[Ru_3O(CH_3CO_2)_6(L)_3]^+$ and $[Ru_3O(CH_3CO_2)_6(CO)(L)_2]$. In general, the ancillary ligand L is a neutral monodentate ligand such as a pyridine derivative, triphenylphosphine, isocyanide and/or a solvent molecule. In the isolated state, $[Ru_3O(CH_3CO_2)_6(L)_3]^+$ without a carbonyl or isocyanide ligand formally has three Ru(III) centers and an overall charge of +1 ($Ru_3^{III,III,III}$), whereas $[Ru_3O(CH_3CO_2)_6(CO)(L)_2]$ formally contains one Ru(II) and two Ru(III) centers and thus has an overall charge of 0 ($Ru_3^{III,III,II}$). The non-carbonyl cluster $[Ru_3O(CH_3CO_2)_6(L)_3]^+$ has, in addition to four reversible cluster-based single-electron redox waves from +3 ($Ru_3^{IV,IV,III}$) to −1 ($Ru_3^{III,II,II}$) state, a quasi-reversible ligand-based one electron wave at the most negative potentials. On the other hand, the carbonyl cluster $[Ru_3O(CH_3CO_2)_6(CO)(L)_2]$ shows four reversible single-electron redox waves from +2 ($Ru_3^{IV,III,III}$) to −2 (possibly $Ru_3^{II,II,II}$)[6] state in a normally accessible potential region.[7,8] In addition, the redox potentials of the carbonyl Ru_3 complexes are 300–500 mV more positive than those of corresponding waves of the non-carbonyl Ru_3 complexes, and the redox po-

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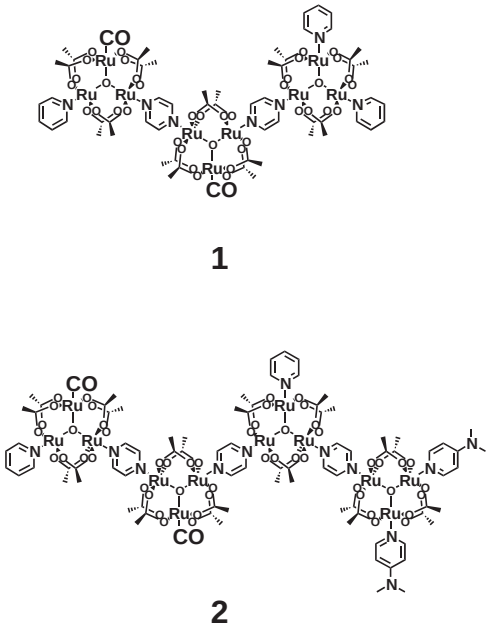
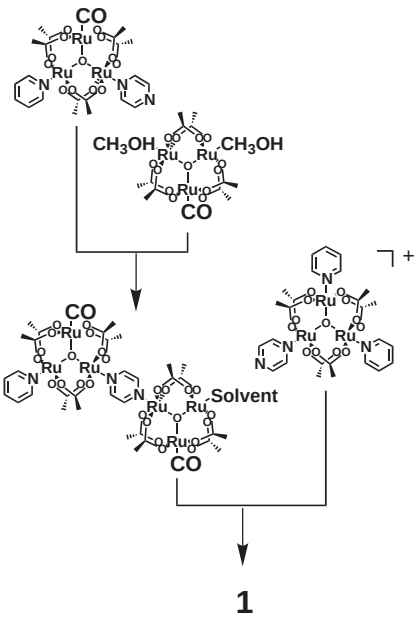


Fig. 1. Molecular structures of Ru_3 trimer **1** and Ru_3 tetramer **2**.



Scheme 1.

tential of Ru_3 complexes strongly depends on the basicity, or pK_a, of the ancillary ligand L. For example, redox potentials shift toward negative potentials by 200–500 mV upon changing L from 4-cyanopyridine ($pK_a = 1.7$) to 4-dimethylaminopyridine (9.7).[8e] Moreover, oligomers of Ru_3 clusters are easily obtained when a linear didentate bridging ligand such as pyrazine (pz)[8c,9,10] or 4,4′-bipyridine[8c,10,11] is used and each Ru_3 unit in the oligomers maintains a redox potential controllable ligand site. Thus, we can control the redox potential of the Ru_3 cluster oligomers by choosing the appropriate ligands, L and/or CO, for each Ru_3 cluster unit. Using these unique properties, we designed the pyrazine-bridged Ru_3 trimer **1** and tetramer **2** that show multiple one-electron redox waves. The molecular structures of **1** and **2** are shown in Fig. 1. To reduce the complexity of chemical formulae, we have abbreviated the pyrazine-bridged Ru_3 oligomers such that the ancillary ligand set, excluding the bridging pyrazine, for each Ru_3 unit is in parentheses and hyphens represent the bridging pyrazines, e.g., the trimer $[\{Ru_3O(CH_3CO_2)_6(L^1)(L^2)\}\text{-}(\mu\text{-pz})\text{-}\{Ru_3O(CH_3CO_2)_6(L^3)\}\text{-}(\mu\text{-pz})\text{-}\{Ru_3O(CH_3CO_2)_6(L^4)(L^5)\}]$ is abbreviated as $[(L^1,L^2)\text{–}(L^3)\text{–}(L^4,L^5)]$. When the oxidation state of Ru or the ligand set in an oligomer unit must be shown, abbreviations such as $Ru_3^{III,III,II}$ or $\{Ru_3(L^1,L^2)\}$, in which μ_3-oxo, six acetate ligands, and pyrazine ligand are omitted, are used. In this study, pyridine and 4-dimethyaminopyridine are used as ancillary ligands L, and are abbreviated as py and dmap, respectively. Meyer and coworkers reported a similar pyrazine-bridged Ru_3 trimer $[(py,py)\text{–}(CO)\text{–}(py,py)]^{2+}$, in which the onset of band-like electronic properties was observed.[9b] However, oligomers **1** and **2** are the first examples of this type which have well-separated multiple one-electron redox waves.

Results

Trimer, $[(CO,py)\text{–}(CO)\text{–}(py,py)]^+$ (1). The synthesis of **1** was carried out by the stepwise addition of terminal Ru_3 units to the central carbonyl Ru_3 unit as shown in Scheme 1. Complex **1** was purified by silica-gel and gel filtration column chromatography and isolated as a hexafluorophosphate salt, $[Ru_3^{III,III,II}(CO,py)\text{–}Ru_3^{III,III,II}(CO)\text{–}Ru_3^{III,III,III}(py,py)](PF_6)$. Its ^1H NMR and mass spectra were fully consistent with the chemical formula (see Discussion for the NMR assignment). The cyclic voltammogram of **1** in acetonitrile shows 11 reversible redox waves involving 12 electrons overall (Fig. 2, Table 1). Each wave is a single electron process and is well separated from the other waves except for two waves at $E_{1/2}$ = ca 1.4 and 0.70 V, where two single electron proc-

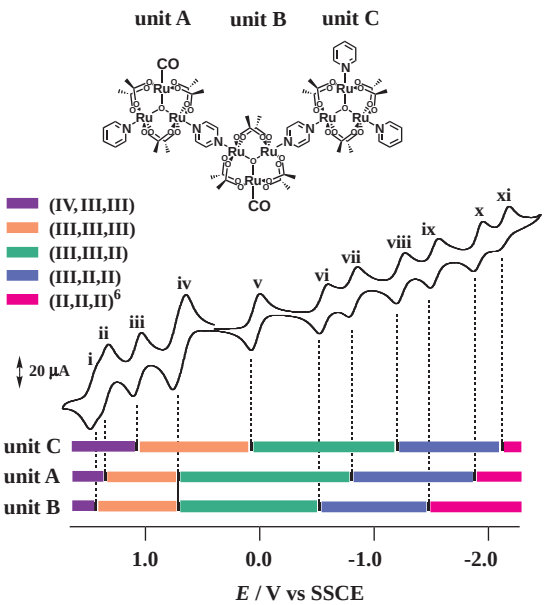


Fig. 2. Cyclic voltammogram and redox wave assignments of Ru_3 trimer **1**. The oxidation state of each unit is shown in the colored regions in the chart below: violet = (IV, III, III), orange = (III, III, III), green = (III, III, II), blue = (III, II, II), pink = (II, II, II).[6]

Table 1. Electrochemical Data for Ru_3 Trimer **1** in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$–$CH_3CN$

Redox wave	Assignment	$E_{1/2}$,[a] V vs SSCE (ne)[b]
i	(IV,III,III)/(III,III,III) in unit B	1.44 (1e)
ii	(IV,III,III)/(III,III,III) in unit A	1.36 (1e)
iii	(IV,III,III)/(III,III,III) in unit C	1.07 (1e)
iv	(III,III,III)/(III,III,II) in unit B and A	0.70 (2e)
v	(III,III,III)/(III,III,II) in unit C	0.09 (1e)
vi	(III,III,II)/(III,II,II) in unit B	−0.50 (1e)
vii	(III,III,II)/(III,II,II) in unit A	−0.76 (1e)
viii	(III,III,II)/(III,II,II) in unit C	−1.16 (1e)
ix	(III,II,II)/(II,II,II) in unit B[c]	−1.46 (1e)
x	(III,II,II)/(II,II,II) in unit A[c]	−1.84 (1e)
xi	(III,II,II)/(II,II,II) in unit C[c]	−2.07 (1e)

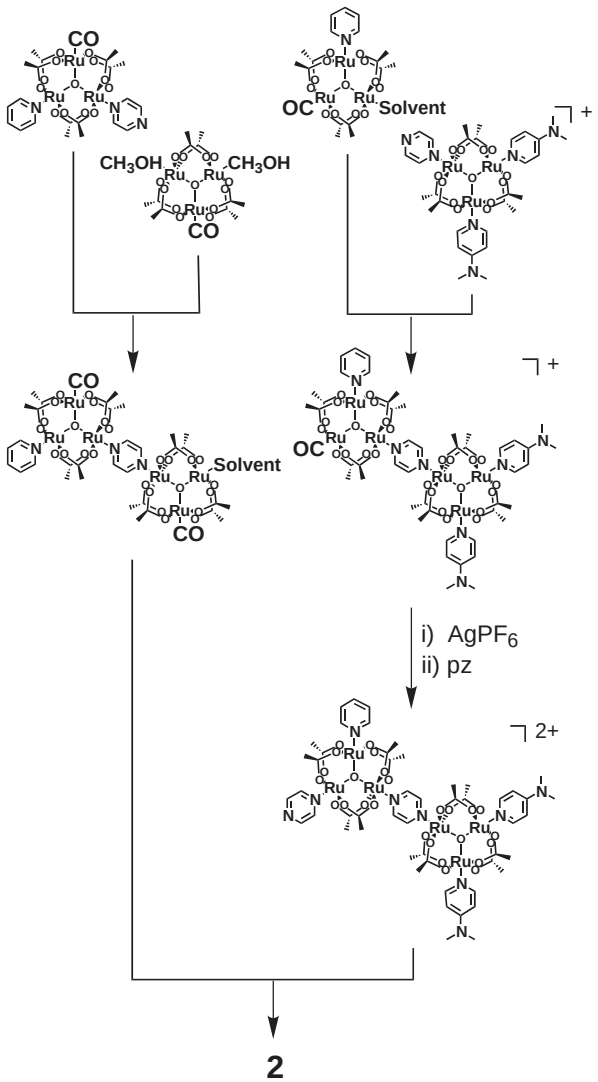
a) $E_{1/2}$'s are determined from the differential pulse voltammetry. b) ne = number of electrons exchanged. c) See text for Discussion of the $Ru_3^{II,II,II}$ state.

esses overlap. All of the redox waves can be easily assigned by comparing the Ru_3 monomers bearing the same ligand set ($[Ru_3^{III,III,II}O(CH_3CO_2)_6(CO)(py)(pz)]$ (corresponding to unit A in Fig. 2): $E_{1/2} = 1.23, 0.58, -0.83, -1.64$; $[Ru_3^{III,III,II}O(CH_3CO_2)_6(CO)(pz)_2]$ (corresponding to unit B): $E_{1/2} = 1.37, 0.70, -0.65, -1.30$; $[Ru_3^{III,III,III}O(CH_3CO_2)_6(py)_2(pz)]^+$ (corresponding to unit C): $E_{1/2} = 0.96, -0.03, -1.17, -1.74$ V). In assigning the waves based on the comparison with the component Ru_3 monomers, two important points were considered: (i) the electron-donating ability of the bridging pyrazine is much lower than that of the coordinated monodentate pyrazine, and (ii) in the negative potential region, electronic interaction through the bridging pyrazine between adjacent Ru_3 units makes the difference in redox potentials of each unit larger.[8c,9a,10] The redox wave assignments are shown in Fig. 2. On going from the most positive potential to the most negative potential, the successive waves were assigned to ($Ru_3^{IV,III,III}/Ru_3^{III,III,III}$), ($Ru_3^{III,III,III}/Ru_3^{III,III,II}$), ($Ru_3^{III,III,II}/Ru_3^{III,II,II}$), and ($Ru_3^{III,II,II}/Ru_3^{II,II,II}$) processes in each cluster unit, where the reduction of the cluster units occurs in the order B to A to C unit for each redox couple (see Fig. 2). Waves ix–xi are tentatively assigned to the ($Ru_3^{III,II,II}/Ru_3^{II,II,II}$) processes (Fig. 2 and Table 1). However, they might be ligand-based redox waves (see Discussion).

Tetramer, [(CO,py)–(CO)–(py)–(dmap,dmap)]$^{2+}$ (2). The synthesis of **2** was carried out by connecting two Ru_3 dimer units, [(CO,py)–(CO,solvent)][12] and [(py,pz)–(dmap,dmap)] (Scheme 2), and isolated as a hexafuluorophosphate salt, $[Ru_3^{III,III,II}(CO,py)\text{–}Ru_3^{III,III,II}(CO)\text{–}Ru_3^{III,III,III}(py)\text{–}Ru_3^{III,III,III}(dmap,dmap)](PF_6)_2$ (**2**$(PF_6)_2$). The non-carbonyl Ru_3 dimer, [(py,pz)–(dmap,dmap)], was synthesized using a method similar to the "stepwise elongation strategy" described previously.[9c]

The ESI-mass spectrum of **2** has a peak envelope centered at $m/z = 1697$ with peak separation of 0.5 (Fig. 3), meaning the overall charge of the tetramer is +2 and the molecular weight corresponds to $\mathbf{2}^{2+}$. Since ruthenium has five isotopes with a natural abundance greater than 10% and complex **2** has twelve ruthenium atoms within a molecule, **2** consists of many isotopomers and the peak envelope shape approaches that of a Gaussian-like curve. The simulated mass spectrum of $\mathbf{2}^{2+}$ is consistent with the observed spectrum (Fig. 3).

Even though the ^{1}H NMR spectrum of **2** (Fig. 4) spans a relatively wide region from −2 ppm to 9 ppm, indicating that $\mathbf{2}^{2+}$ is paramagnetic, we could unambiguously assign the spectrum (see Discussion for the assignment). Figure 5 shows the cyclic voltammogram of **2** in acetonitrile, which consists of 14 re-



Scheme 2.

verssible step waves involving 15 electrons in all (Table 2). Except for the wave at 0.70 V which corresponds to two overlapping single-electron redox processes, all of the waves involve single electron processes and are well separated. Redox wave assignment of tetramer **2** was made in the following manner. Cyclic voltammogram pattern of **2** can be understood as a sum of CV's of trimer **1** and the Ru_3 monomer $[Ru_3O(CH_3CO_2)_6(dmap)_2(pz)]$ added to trimer **1** (unit D, see Fig. 5). Since unit D has two dmap ligands, which are strong electron donating ligands, the redox potentials of the ($Ru_3^{IV,III,III}/Ru_3^{III,III,III}/Ru_3^{III,III,II}/Ru_3^{III,II,II}/Ru_3^{II,II,II}$) couples are more negative than those of units A, B, and C. Note that a wave corresponding to the $Ru_3^{III,II,II}/Ru_3^{II,II,II}$ process of unit D is at a potential more negative than the accessible potential

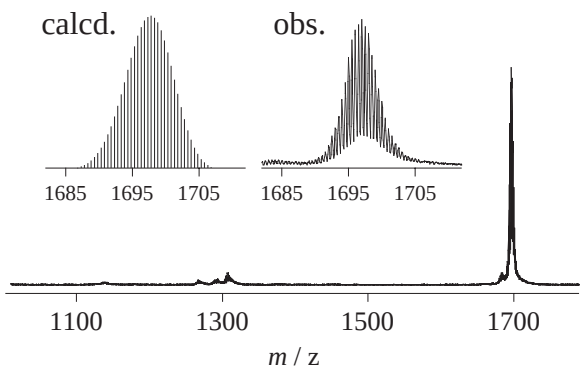


Fig. 3. ESI Mass spectrum of Ru_3 tetramer **2**.

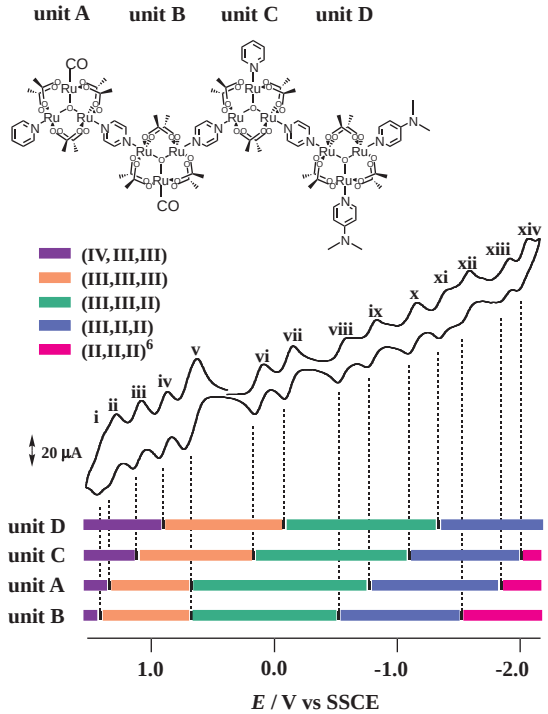


Fig. 5. Cyclic voltammogram and redox wave assignments of Ru_3 tetramer **2**. The oxidation state of each unit is shown in the colored regions in the chart below: violet = (IV, III, III), orange = (III, III, III), green = (III, III, II), blue = (III, II, II), pink = (II, II, II)).[6]

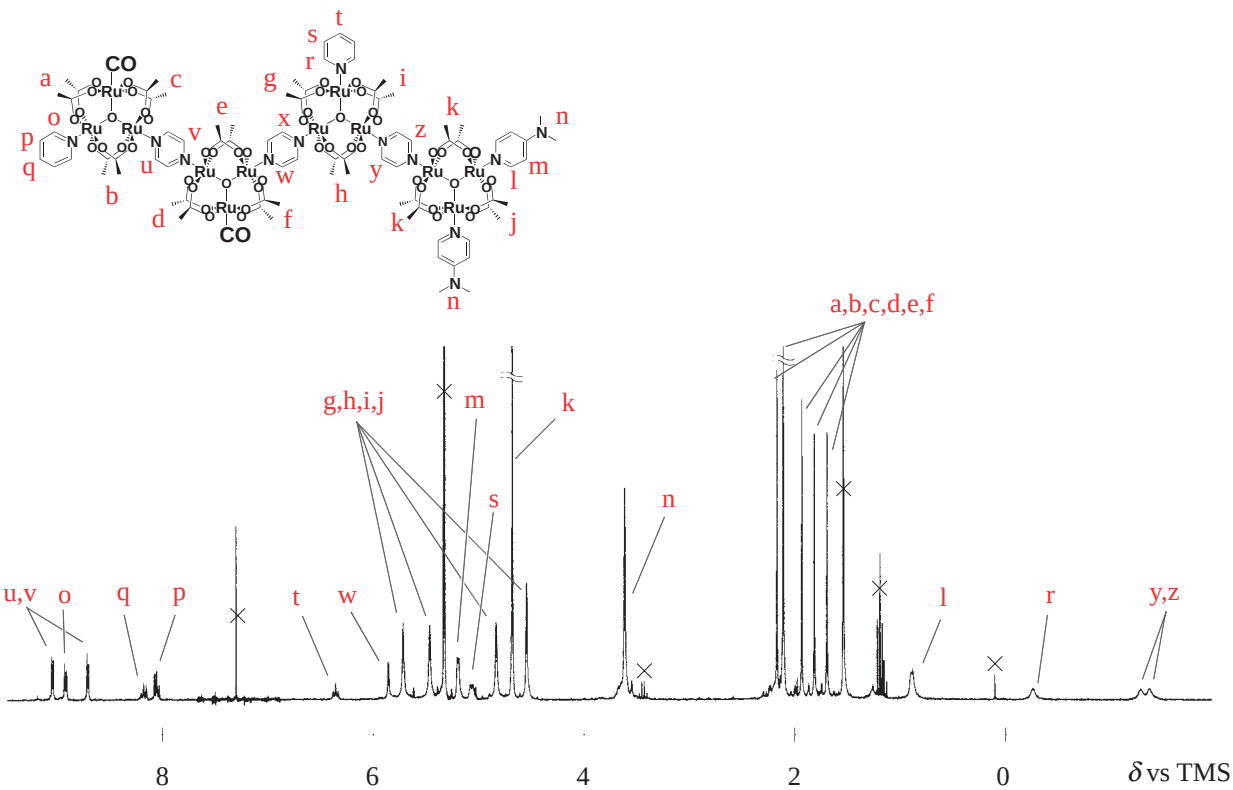


Fig. 4. ^{1}H NMR spectrum of Ru_3 tetramer **2** in CD_2Cl_2. × denotes impurities and solvent.

Table 2. Electrochemical Data for Ru_3 Tetramer **2** in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$–$CH_3CN$

Redox wave	Assignment	$E_{1/2}$,[a] V vs SSCE (ne)[b]
i	(IV,III,III)/(III,III,III) in unit B	1.44 (1e)
ii	(IV,III,III)/(III,III,III) in unit A	1.36 (1e)
iii	(IV,III,III)/(III,III,III) in unit C	1.15 (1e)
iv	(IV,III,III)/(III,III,III) in unit D	0.93 (1e)
v	(III,III,III)/(III,III,II) in unit B and A	0.70 (2e)
vi	(III,III,III)/(III,III,II) in unit C	0.19 (1e)
vii	(III,III,III)/(III,III,II) in unit D	−0.06 (1e)
viii	(III,III,II)/(III,II,II) in unit B	−0.50 (1e)
ix	(III,III,II)/(III,II,II) in unit A	−0.75 (1e)
x	(III,III,II)/(III,II,II) in unit C	−1.08 (1e)
xi	(III,III,II)/(III,II,II) in unit D	−1.32 (1e)
xii	(III,II,II)/(II,II,II) in unit B[c]	−1.50 (1e)
xiii	(III,II,II)/(II,II,II) in unit A[c]	−1.83 (1e)
xiv	(III,II,II)/(II,II,II) in unit C[c]	−1.99 (1e)

a) $E_{1/2}$'s are determined from the differential pulse voltammetry. b) ne = number of electrons exchanged. c) See text for Discussion of the $Ru_3^{II,II,II}$ state.

window and thus does not appear in the CV. On going from the most positive potential to the most negative potential, the reduction of the cluster units occurs in the order B to A to C to D unit for each redox couple (Fig. 5). Waves xii–xiv are tentatively assigned to the ($Ru_3^{III,II,II}$/$Ru_3^{II,II,II}$) processes (Fig. 5 and Table 2). However, these might be ligand-based redox waves (see Discussion).

Discussion

The syntheses of oligomers **1** and **2** were easily carried out using "complexes as metal and complexes as ligand" strategy,[13] as shown in Schemes 1 and 2. The coordinated solvent molecules in the Ru_3 complexes ("complex as metal") were easily replaced by those containing pyrazine with a free donor nitrogen atom ("complex as ligand"). This strategy worked nicely to couple Ru_3 unit(s) one at a time to the growing oligomers via a μ-pz ligand. Compounds **1** and **2** were obtained as PF_6^- salts in relatively good yields.

It deserves a special comment that all the ^{1}H NMR signals of **1** and **2** were unambiguously assigned in spite of the fact that the compounds are large and paramagnetic. It is well known for monomeric Ru_3 complexes that the $Ru_3^{III,III,II}$ cluster core having an even number of d electrons is diamagnetic whereas the $Ru_3^{III,III,III}$ cluster core is paramagnetic. However, the paramagnetism of the $Ru_3^{III,III,III}$ core is weak because only one electron spin is delocalized over three ruthenium centers. Thus the ^{1}H NMR spectrum of the monomeric $Ru_3^{III,III,III}$ complexes generally spans the region from −2 to 9 ppm, and the highly shifted signals around 0 ppm are assigned to the ortho protons of coordinated pyridines and pyrazine ligands. The acetate methyl peaks are observed around 5 ppm. Trimer **1** has one paramagnetic $Ru_3^{III,III,III}$ unit, {$Ru_3^{III,III,III}$(py,py)}, and tetramer **2** has two paramagnetic units, {$Ru_3^{III,III,III}$(py)} and {$Ru_3^{III,III,III}$(dmap,dmap)}. Their NMR spectral regions were similar to those of monomeric $Ru_3^{III,III,III}$ complexes. This observation indicates the magnetic interaction between the two paramagnetic units through the bridged pyrazine in **2** is very weak. That is, **2** has two uncoupled electron spins that are localized on each paramagnetic cluster unit. Nuclear spin–spin couplings in **1** and **2** were successfully analyzed by means of their COSY spectra.

The objective of this study was to prepare Ru_3-based compounds which show many reversible well-separated one-electron redox waves. To accomplish this purpose, the selection of the ancillary ligands and their location within the oligomer, i.e., how to arrange the Ru_3 cluster units with appropriate ancillary ligand sets in the oligomers is extremely important. This study was motivated by our finding that Ru_3 dimer, [$Ru_3^{III,III,II}$(CO,py)–$Ru_3^{III,III,III}$(py,py)](PF_6),[9c] exhibits eight well separated single-electron redox waves.[14] Trimer **1** was designed in such a way that a {$Ru_3^{III,III,II}$(CO,py)} unit is linked to the left-hand side of this dimmer. All the Ru_3 units in the resulting trimer have different ancillary ligand sets and thus each unit should have different redox potentials. Furthermore, when two Ru_3 units with the CO ligand are adjacent to each other, the redox waves of two units corresponding to the ($Ru_3^{III,III,II}$/$Ru_3^{III,II,II}$) and ($Ru_3^{III,II,II}$/$Ru_3^{II,II,II}$) couples should be well separated due to a strong inter-Ru_3 unit electronic interactions.[8c,9a,10] As is expected, all of the waves for **1** in the negative potential region are well separated, while the waves for the ($Ru_3^{IV,III,III}$/$Ru_3^{III,III,III}$) and ($Ru_3^{III,III,III}$/$Ru_3^{III,III,II}$) processes are more or less overlapped in the positive potential region. Tetramer **2** was designed in such a way that a {$Ru_3^{III,III,III}$(dmap,dmap)} unit is linked to the right-hand side of trimer **1** to give [$Ru_3^{III,III,II}$(CO,py)–$Ru_3^{III,III,II}$(CO)–$Ru_3^{III,III,III}$(py)–$Ru_3^{III,III,III}$(dmap,dmap)]$^{2+}$. The strong electron donating dmap ligands cause the redox waves from the {Ru_3(dmap,dmap)} unit to shift toward more negative potentials and thus these waves do not overlap with other waves (Fig. 5).

As described in earlier sections, the assignments to the ($Ru_3^{III,II,II}$/$Ru_3^{II,II,II}$) processes in **1** and **2** are tentative. A redox wave based likely on the bridging pyrazine is often observed in these potential regions; in actual fact, Meyer and co-worker assigned the wave that corresponds to our tentative assignment to the ($Ru_3^{III,II,II}$/$Ru_3^{II,II,II}$) process to a ligand-based process for similar Ru_3 complexes.[8c] There is a possibility that the waves observed at potentials more negative than −1.45 V are due to reduction to an electronic state created by mixing of the reduced states of pyrazine and Ru_3 cluster core. This pa-

per deals with compounds showing multistep one-electron redox waves and not the detailed assignments for the observed waves. Therefore, waves observed at extremely negative potentials are tentatively assigned to the ($Ru_3^{III,II,II}/Ru_3^{II,II,II}$) processes in this paper.

To the best of our knowledge, the present compounds show the largest number of well-characterized and well-separated single-electron redox processes reported thus far.

Experimental

Preparation. $[Ru_3O(CH_3CO_2)_6(CO)(CH_3OH)_2]$,[9b] $[Ru_3O(CH_3CO_2)_6(CO)(py)_2]$,[8a,8b] $[Ru_3O(CH_3CO_2)_6(CO)(py)(solvent)]$,[9c,12] and $[Ru_3O(CH_3CO_2)_6(py)_2(pz)](PF_6)$[8b] were synthesized according to reported methods.

$[Ru_3O(CH_3CO_2)_6(CO)(py)(pz)]$. A mixture of $[Ru_3O(CH_3CO_2)_6(CO)(py)(solvent)]$ (250 mg, 0.505 mmol) and pyrazine (487 mg, 6.08 mmol) in CH_2Cl_2 (30 cm^3) was stirred at room temperature overnight. The solution was evaporated to dryness using a rotary evaporator. The residue was dissolved in a minimal amount of dichloromethane, and a large amount of *n*-hexane was added to the solution. The precipitate was collected via filtration and washed with *n*-hexane. The precipitate was chromatographed over silica gel (Wakogel C-200) with $CH_3OH/CH_2Cl_2 = 0.5:100$ (v/v) as the eluent. The main fraction was collected and evaporated to dryness. Yield 190 mg (71%). Anal. Calcd for $Ru_3C_{22}H_{27}O_{14}N_3$: C, 30.70; H, 3.16; N, 4.88%. Found: C, 30.16; H, 3.22; N, 4.71%. FAB-MS: *m*/*z* 862 (calcd (M) = 861). ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.21 (2H, pz), 8.98 (2H, py-*o*), 8.71 (2H, pz), 8.15 (1H, py-*p*), 8.02 (2H, py-*m*), 2.15 (6H, acetate methyl), 2.11 (6H, acetate methyl), 1.90 (6H, acetate methyl).

$[Ru_3O(CH_3CO_2)_6(CO)(dmap)_2](PF_6)$. This complex was prepared by the method similar to that for $[Ru_3O(CH_3CO_2)_6(CO)(pz)_2]$.[9b] Anal. Calcd for $Ru_3C_{27}H_{38}O_{14}N_4 \cdot 0.5H_2O$: C, 33.96; H, 4.12; N, 5.87%. Found: C, 33.83; H, 3.99; N, 5.85%. ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.01 (4H, dmap-*o*), 7.23 (4H, dmap-*m*), 3.32 (12H, dmap methyl), 2.03 (12H, acetate methyl), 1.76 (6H, acetate methyl).

$[Ru_3O(CH_3CO_2)_6(dmap)_2(pz)](PF_6)$. A methanol solution (25 cm^3) of NH_4PF_6 (84 mg, 0.515 mmol) and a methanol solution (10 cm^3) of $AgPF_6$ (142 mg, 0.562 mmol) were added to a dichloromethane solution (25 cm^3) of $[Ru_3O(CH_3CO_2)_6(CO)(dmap)_2]$ (410 mg, 0.434 mmol). After stirring for 30 min in the dark, the solution was evaporated to dryness using a rotary evaporator. The residue was dissolved in a minimal amount of dichloromethane, and filtered to eliminate the insoluble materials. After the solution was evaporated to dryness using a rotary evaporator, dichloromethane (40 cm^3) and pyrazine (1.07 g, 13.4 mmol) were added, and the solution was stirred for 15 h at room temperature. The solution was evaporated to dryness using a rotary evaporator. The residue was dissolved in a minimal amount of dichloromethane, and a large amount of *n*-hexane was added to the solution. The precipitate was collected via filtration and washed with *n*-hexane. The precipitate was purified by silica gel column chromatography with $CH_3OH/CH_2Cl_2 = 1:100$ (v/v) as the eluent and gel chromatography with dichloromethane as the eluent. In each case, the main fraction was collected and evaporated to dryness. Yield 210 mg (42%). Anal. Calcd for $Ru_3C_{30}H_{42}O_{13}N_6PF_6$: C, 31.53; H, 3.70; N, 7.36%. Found: C, 31.26; H, 3.68; N, 7.32%. FAB-MS: *m*/*z* 1138 (calcd (M) = 1142), 999 (calcd (M − PF_6) = 997). ^{1}H NMR (270 MHz, CD_3CN) δ 6.23 (2H, pz-*m*), 5.81 (4H, dmap-*m*), 5.38 (12H, acetate methyl), 3.64 (12H, dmap methyl), 3.53 (6H, acetate methyl), 0.52 (2H, pz-*o*).

$[\{Ru_3O(CH_3CO_2)_6(CO)(py)\}$-($\mu$-pz)-$\{Ru_3O(CH_3CO_2)_6(CO)(solvent)\}]$.[12] A dichloromethane solution (20 cm^3) of $[Ru_3O(CH_3CO_2)_6(CO)(py)(pz)]$ (30 mg, 0.035 mmol) was added to a methanol/dichloromethane(3/5 (v/v)) solution (8 cm^3) of $[Ru_3O(CH_3CO_2)_6(CO)(CH_3OH)_2]$ (142 mg, 0.193 mmol). After standing for 18 h, the solution was evaporated to dryness using a rotary evaporator. This residue was purified by gel chromatography with dichloromethane as the eluent. The main fraction was collected and evaporated to dryness. Yield 36 mg (66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.27 (4H, pz), 8.95 (2H, py-*o*), 8.17 (1H, py-*p*), 8.07 (2H, py-*m*), 2.28 (6H, acetate methyl), 2.27 (6H, acetate methyl), 2.22 (6H, acetate methyl), 2.17 (6H, acetate methyl), 2.10 (6H, acetate methyl), 2.02 (6H, acetate methyl).

$[\{Ru_3O(CH_3CO_2)_6(CO)(py)\}$-($\mu$-pz)-$\{Ru_3O(CH_3CO_2)_6(dmap)_2\}](PF_6)$. A dichloromethane solution (15 cm^3) of $[Ru_3O(CH_3CO_2)_6(dmap)_2(pz)](PF_6)$ (400 mg, 0.350 mmol) and $[Ru_3O(CH_3CO_2)_6(CO)(py)(solvent)]$ (277 mg, 0.350 mmol) was stood for 14 h. The solution was evaporated to dryness using a rotary evaporator. This residue was purified by gel chromatography with dichloromethane as the eluent. The main fraction was collected and evaporated to dryness. Yield 470 mg (70%). Anal. Calcd for $Ru_6C_{48}H_{65}O_{27}N_7PF_6 \cdot 2H_2O$: C, 29.41; H, 3.55; N, 5.00%. Found: C, 29.40; H, 3.51; N, 5.21%. FAB-MS: *m*/*z* 1779 (calcd (M − PF_6) = 1778). ^{1}H NMR (270 MHz, CD_3CN) δ 8.92 (2H, py-*o*), 8.25 (1H, py-*p*), 8.05 (2H, py-*m*), 6.59 (2H, pz($Ru_3^{III,III,II}$)), 5.67 (4H, dmap-*m*), 5.41 (12H, acetate methyl($Ru_3^{III,III,III}$)), 3.95 (6H, acetate methyl($Ru_3^{III,III,III}$)), 3.60 (12H, dmap methyl), 2.25 (2H, pz($Ru_3^{III,III,III}$)), 1.90 (6H, acetate methyl($Ru_3^{III,III,II}$)), 1.81 (6H, acetate methyl($Ru_3^{III,III,II}$)), 1.74 (4H, dmap-*o*), 1.61 (6H, acetate methyl($Ru_3^{III,III,II}$)).

$[\{Ru_3O(CH_3CO_2)_6(py)(pz)\}$-($\mu$-pz)-$\{Ru_3O(CH_3CO_2)_6(dmap)_2\}](PF_6)_2$. A methanol solution (5 cm^3) of NH_4PF_6 (52 mg, 0.32 mmol) and a methanol solution (5 cm^3) of $AgPF_6$ (92 mg, 0.36 mmol) were added to a dichloromethane solution (10 cm^3) of $[\{Ru_3O(CH_3CO_2)_6(CO)(py)\}$-($\mu$-pz)-$\{Ru_3O(CH_3CO_2)_6(dmap)_2\}](PF_6)$ (470 mg, 0.248 mmol). After stirring for 1 h in the dark, the solution was evaporated to dryness using a rotary evaporator. The residue was dissolved in a minimal amount of dichloromethane and filtered to eliminate the insoluble materials. After the solution was evaporated to dryness using a rotary evaporator, the residue was dissolved in CH_2Cl_2 (20 cm^3) and to this solution a dichloromethane solution (5 cm^3) of pyrazine (793 mg, 9.90 mmol) was added. After the mixture stood for 15 h, the solution was evaporated to dryness using a rotary evaporator. The residue was dissolved in a minimal amount of dichloromethane, and a large amount of *n*-hexane was added to the solution. A precipitate was collected via filtration and washed by *n*-hexane. The precipitate was purified by silica gel column chromatography with $CH_3OH/CH_2Cl_2 = 1:100$ (v/v) as the eluent and gel chromatography with dichloromethane as the eluent. The main fraction was collected and evaporated to dryness. Yield 81 mg (16%). Anal. Calcd for $Ru_6C_{51}H_{69}O_{26}N_9P_2F_{12} \cdot 2H_2O$: C, 28.40; H, 3.41; N, 5.85%. Found: C, 28.51; H, 3.44; N, 5.74%. FAB-MS: *m*/*z* 1973 (calcd (M − PF_6) = 1975), 1831 (calcd (M − $(PF_6)_2$) = 1830) ^{1}H NMR (270 MHz, CD_3CN) δ 6.62 (1H, py-*p*), 5.70 (6H, acetate methyl), 5.68 (2H, py-*m* or pz), 5.45 (4H + 2H, dmap-*m* + py-*m* or pz-*m*), 5.36 (12H, acetate methyl), 5.17 (6H, acetate methyl), 4.91 (6H, acetate methyl), 3.97 (6H, acetate methyl), 3.17 (12H, dmap methyl), 1.41 (4H, dmap-*o*), 0.32,

0.04–0.11 (6H, py-*o* + pz-*o*).

[{$Ru_3O(CH_3CO_2)_6(CO)(py)$}-($\mu$-pz)-{$Ru_3O(CH_3CO_2)_6$-(CO)}-($\mu$-pz)-{$Ru_3O(CH_3CO_2)_6(py)_2$}]($PF_6$) (1($PF_6$)). A dichloromethane solution (10 cm^3) of [{$Ru_3O(CH_3CO_2)_6$(CO)-(py)}-(μ-pz)-{$Ru_3O(CH_3CO_2)_6$(CO)(solvent)}] (36 mg, 0.024 mmol) and [$Ru_3O(CH_3CO_2)_6(py)_2(pz)$]($PF_6$) (32 mg, 0.030 mmol) was stood for 14 h. The solution was evaporated to dryness using a rotary evaporator. The residue was purified by gel chromatography with dichloromethane as the eluent. The main fraction was collected and evaporated to dryness. Yield 28 mg (45%). Anal. Found: C, 27.74; H, 3.22; N, 3.61%. Calcd for $C_{61}H_{77}F_6N_7O_{41}P_1Ru_9$: C, 27.98; H, 2.96; N, 3.74%. FAB-MS: m/z 2565 (calcd ($M - PF_6$) = 2563) ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.11 (2H, pz($Ru_3^{III,III,II}$)), 8.93 (2H, py-*o*($Ru_3^{III,III,II}$)), 8.76 (2H, pz($Ru_3^{III,III,II}$)), 8.20 (1H, py-*p*($Ru_3^{III,III,II}$)), 8.07 (2H, py-*m*($Ru_3^{III,III,II}$)), 6.40 (2H, py-*p*($Ru_3^{III,III,II}$)), 6.32 (2H, pz($Ru_3^{III,III,III}$)), 5.76 (6H, acetate methyl($Ru_3^{III,III,III}$)), 5.29 (4H, py-*m*($Ru_3^{III,III,III}$)), 5.03 (12H, acetate methyl($Ru_3^{III,III,III}$)), 3.42 (4H, pz($Ru_3^{III,III,III}$)), 2.18 (6H, acetate methyl($Ru_3^{III,III,II}$)), 2.14 (6H, acetate methyl($Ru_3^{III,III,II}$)), 2.10 (6H, acetate methyl-($Ru_3^{III,III,II}$)), 1.94 (6H, acetate methyl($Ru_3^{III,III,II}$)), 1.89 (6H, acetate methyl($Ru_3^{III,III,II}$)), 1.76 (6H, acetate methyl($Ru_3^{III,III,II}$)), −0.29 (4H, py-*o*($Ru_3^{III,III,III}$)). For ^{1}H NMR signal assignments, COSY spectrum has been used.

[{$Ru_3O(CH_3CO_2)_6(CO)(py)$}-($\mu$-pz)-{$Ru_3O(CH_3CO_2)_6$-(CO)}-($\mu$-pz)-{$Ru_3O(CH_3CO_2)_6(py)$}-($\mu$-pz)-{$Ru_3O(CH_3CO_2)_6$-(dmap)$_2$}]($PF_6$)$_2$ (2(PF_6)$_2$). A solution of dichloromethane (10 cm^3) of [{$Ru_3O(CH_3CO_2)_6$(CO)(py)}-(μ-pz)-{$Ru_3O(CH_3CO_2)_6$-(CO)(solvent)}] (39 mg, 0.026 mmol) and [{$Ru_3O(CH_3CO_2)_6$-(py)(pz)}-(μ-pz)-{$Ru_3O(CH_3CO_2)_6$(dmap)$_2$}](PF_6)$_2$ (81 mg, 0.040 mmol) was stirred for 2 days in the dark. The solution was evaporated to dryness using a rotary evaporator. This residue was purified by gel chromatography with dichloromethane as the eluent. The main fraction was collected and evaporated to dryness. Yield 72 mg (75%). Anal. Found: C, 27.85; H, 3.42; N, 4.39%. Calcd for $C_{86}H_{114}F_{12}N_{12}O_{54}P_2Ru_{12}$: C, 28.05; H, 3.12; N, 4.56%. ESI-MS: m/z 1697 (calcd ($M - (PF_6)_2$) = 1698), ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.07 (2H, pz($Ru_3^{III,III,II}$)), 8.95 (2H, py-*o*($Ru_3^{III,III,II}$)), 8.73 (2H, pz($Ru_3^{III,III,II}$)), 8.20 (1H, py-*m*-($Ru_3^{III,III,II}$)), 8.07 (2H, py-*p*($Ru_3^{III,III,II}$)), 6.36 (1H, py-*p*-($Ru_3^{III,III,II}$)), 5.86 (2H, pz($Ru_3^{III,III,II}$)), 5.71 (acetate methyl-($Ru_3^{III,III,III}$)), 5.46 (6H, acetate methyl($Ru_3^{III,III,III}$)), 5.19 (4H, dmap-*m*), 5.06 (2H, py-*m*($Ru_3^{III,III,III}$)), 4.82 (6H, acetate methyl-($Ru_3^{III,III,III}$)), 4.67 (12H, acetate methyl($Ru_3^{III,III,III}$)), 4.54 (6H, acetate methyl($Ru_3^{III,III,III}$)), 3.60 (12H, dmap methyl), 2.17 (6H, acetate methyl($Ru_3^{III,III,II}$)), 2.11 (6H, acetate methyl($Ru_3^{III,III,II}$)), 2.10 (6H, acetate methyl($Ru_3^{III,III,II}$)), 1.93 (6H, acetate methyl-($Ru_3^{III,III,II}$)), 1.81 (6H, acetate methyl($Ru_3^{III,III,II}$)), 1.69 (6H, acetate methyl($Ru_3^{III,III,II}$)), 0.88 (4H, dmap-*o*), −0.29 (2H, py-*o*-($Ru_3^{III,III,III}$)), −1.31 (2H, pz($Ru_3^{III,III,III}$)), −1.39 (2H, pz-($Ru_3^{III,III,III}$)).

Measurements. ^{1}H NMR spectra were measured with a Bruker DPX 300 or JEOL GSX-270 FT-NMR spectrometer. Chemical shifts were referenced to TMS except for trimer **1** and tetramer **2** which were referenced to dichloromethane signal at 5.32 ppm, corresponding to TMS at 0 ppm. ESI-Mass spectra and FAB Mass spectra were recorded on a Micromass LCT and JEOL JMS-HX100 mass spectrometer, respectively. All cyclic voltammerty and differential pulse voltammetry experiments were carried out using a BAS CV-50W Voltammetric Analyzer. Cyclic voltammetry was performed at a scan rate of 100 mV/s. Differential pulse voltammetry was performed at a scan rate of 20 mV/s with a pulse amplitude of 50 mV. The working electrode was glassy carbon. The counter electrode was a platinum coil, and the reference electrode was a sodium saturated calomel electrode, SSCE. $E_{1/2}$ of the ferrocene/ferrocenium ion (Fc/Fc^+) was 0.40 V vs SSCE. All voltammograms were measured using 0.1 M solutions of tetrabutylammonium hexafluorophosphate (TBAH) in acetonitrile (1 M = 1 mol dm^{-3}).

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6 See Discussion for the $Ru_3^{II,II,II}$ state.

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14 Unpublished result.