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Charge Gating and Electronic Delocalization over a Denderimeric Assembly of Trinuclear Ruthenium Clusters

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A zeroth-order dendrimer was formed using a tridentate bridging ligand, 2,4,6-tri-4-pyridyl-*S*-triazine, and the redox-active trinuclear ruthenium cluster $Ru_3O(OAc)_6(CO)(py)(H_2O)$. The electronic properties of this dendrimer were probed using cyclic voltammetry. IR spectroelectrochemistry was performed at both low (–30 °C) and room temperature. The IR spectroelectrochemical response at –30 °C was straightforward, but at room temperature, the dendrimer exhibits an unusual and complex series of electronic behaviors, including intramolecular cluster-to-bridging-ligand charge transfer, gated electron transfer, and dynamic exchange on the IR time scale.

Previous work in our research laboratory has focused on dimers of trinuclear ruthenium clusters of the type $[Ru_3O(OAc)_6(CO)(L)]_2$-μ_2-BL (BL = bridging ligand), which, in the mixed-valence state, provide a sensitive probe of ground-state electron transfer (ET) in the class II−III regime.[1] The ability to effect small electronic changes within the cluster assemblies by varying the bridging and ancillary ligands allowed for an in-depth study into the effects of small electronic perturbations upon the ET rate (k_{et}).[2] Using these dimers, we have also reported the first observations of “mixed-valence isomers”,[3,4] which provided the ability to experimentally evaluate the Marcus−Hush potential energy surfaces associated with ET.[5]

Given the ability of these “dimers of trimers” to probe ET, we now extend our work to study ET across greater distances and between multiple sites. To this end, we have synthesized the zeroth-generation ligand-centered dendrimer (LCD) $[Ru_3O(OAc)_6(CO)(L)]_3$-μ_3-2,4,6-tri-4-pyridyl-*S*-triazine.[6] This cluster assembly is prepared by mixing 3 equiv of $Ru_3O(OAc)_6(CO)(py)(H_2O)$ [ref] with 1 equiv of 2,4,6-tri-4-pyridyl-*S*-triazine (tz)[7] for 3 days in chloroform, followed by purification on a Biobeads S-X1 (Bio-Rad) size-exclusion column.

The electrochemistry of LCD was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV).[8] In the anodic region, the CV of LCD contains two separate, reversible three-electron-reduction waves (0.95 and 0.17 V), corresponding to the oxidation of the three metal clusters ($Ru^{III}Ru^{III}Ru^{III}/Ru^{III}Ru^{III}Ru^{IV}$ and $Ru^{III}Ru^{III}Ru^{II}/Ru^{III}Ru^{III}Ru^{III}$, respectively). However, in the cathodic region, the reduction of the three metal clusters is not a concerted process. Instead, the reductions are split into two distinct reversible redox processes. Similar behavior has been observed in the CV of the dimers of trimers.[1] On the basis of a comparison of the integrated current obtained from DPV, the waves at −1.24 and −1.36 V are assigned to one- and two-electron reductions, respectively, and correspond to the reduction of one of the clusters followed by a concerted reduction of the other two clusters. This degree of splitting corresponds to $K_c = 1.56 \times 10^4$. The last electrochemical event that we observe in the CV (−1.79 V) is the reduction of the bridging tz ligand.

The IR spectroelectrochemical (SEC) response of LCD in the region of the carbonyl stretching frequency at low temperature (−30 °C) is shown in Figure 1a.[9] As the potential is brought sufficiently negative to reduce LCD (−0.95 V vs Ag wire), we observe a decrease in the intensity of ν(CO) at 1940 cm^{-1} until it is no longer present in the spectrum. At the same time, we observe the growth of a new band at

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(6) LCD was isolated as a powder with the formula $[Ru_3O(OAc)_6(CO)(L)]_3$-μ_3-2,4,6-tri-4-pyridyl-*S*-triazine•CH_3Cl. Yield: 34%. Anal. Calcd for $C_{74}H_{86}Cl_3N_9O_{42}Ru_9$: C, 31.86; H, 3.11; N, 4.52. Found: C, 32.06; H, 2.98; N, 4.52. ^1H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 18H, acetate), 2.10 (s, 18H, acetate), 2.16 (s, 18H, acetate), 8.04 (t, 6H, pyridine), 8.14 (t, 3H, pyridine), 8.93 (d, 6H, triazine), 9.05 (d, 6H, pyridine), 9.24 (d, 6H, triazine). IR (KBr disk): 3399 (s), 2968 (w), 2931 (w), 1946 (s), 1608 (s), 1572 (m), 1578 (m), 1421 (s), 1373 (w) 1349 (w), 689 (w) cm^{-1}.

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(8) Electrochemistry was performed using 0.1 M tetra-*n*-butylammonium hexaflurophosphate in CH_2Cl_2 versus ferrocene/ferrocenium.

(9) IR spectra were recorded in methylene chloride using a custom-built reflectance spectroelectrochemical cell.

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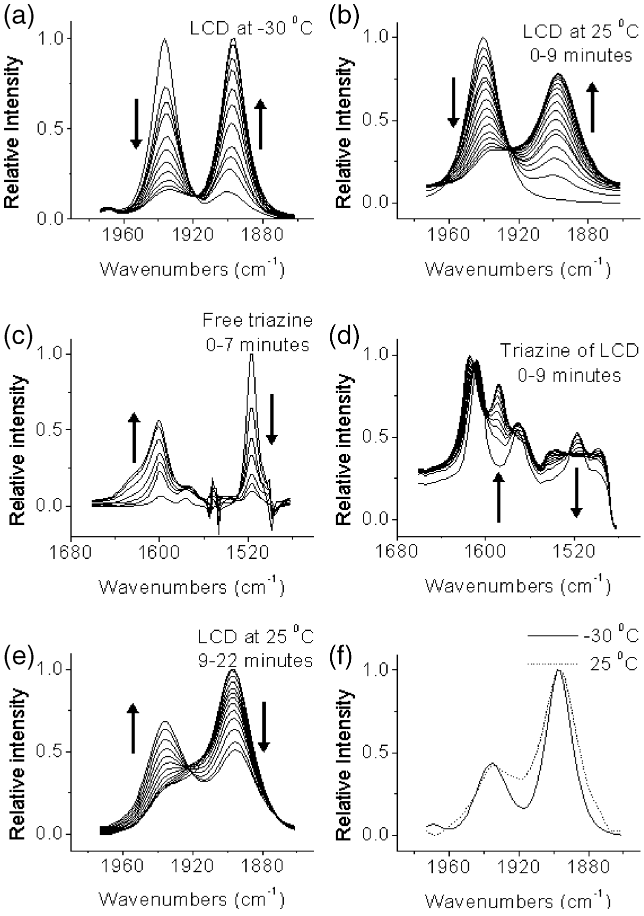

Figure 1. Spectroelectrochemical response of (a) LCD at −30 °C and −0.95 V, (b) LCD at room temperature and −1.05 V, (c) 2,4,6-tri-4-pyridyl-*S*-triazine at room temperature and −1.20 V, (d) LCD at room temperature and −1.05 V, and (e) LCD at room temperature and −1.05 V and (f) a comparison of spectra at the LCD at both −30 °C and room temperature. All potentials are versus Ag wire.

1895 cm^{-1}. On the basis of previous work,[10] we assign the band at 1940 cm^{-1} to ν(CO) of a neutral cluster and the lower energy band to ν(CO) of a reduced cluster. Taking into consideration these assignments, the progression of spectra shown in Figure 1a corresponds to the reduction of the three outer clusters of LCD.

At room temperature, the response of LCD to reducing potentials is more complex. Initially, at −1.05 V (vs Ag wire) a reduction in the intensity of the high-energy ν(CO) band is observed accompanied by the appearance of the low-energy ν(CO) band, a progression associated with the reduction of the outer metal clusters (Figure 1b). However, this evolution of the spectrum ceases at the point when the ratio of intensities of the high- and low-energy bands is 1:2. This indicates that the reduction of LCD has stopped at the point at which only two of the outer clusters are reduced. This is an unexpected behavior because the CV of LCD reveals that the reduction of the second and third clusters in LCD occurs concurrently. Thus, at a potential sufficient to reduce two of the clusters, all three clusters should be reduced. In effect, we observed a two-electron process spectroscopically when a three-electron process is predicted electrochemically.

This result may be explained by considering the SEC response of tz to reduction. For the purposes of our study, we are only concerned with the band at 1515 cm^{-1} because this is the only band arising from tz that both is intense enough in LCD to be useful and does not overlap with bands associated with the ruthenium clusters. Upon reduction, this band is found to disappear (Figure 1c) as a new band grows in at 1600 cm^{-1}. Using these spectroscopic signatures, we find that, in LCD at room temperature, the reduction of the central triazine occurs concomitantly with the reduction of the outer clusters (Figure 1d). Thus, at room temperature, the initial reduction of LCD is a three-electron process. However, the process does not yield a species having three reduced clusters. Rather, the end point of the reduction, as observed spectroscopically, is a species that contains two reduced clusters and a reduced triazine.

When an applied potential of −1.20 V is maintained, the next event observed in the SEC response of LCD at room temperature is also unexpected (Figure 1e). Here, the lower-energy band is seen to decrease in intensity while the intensity of the high-energy band increases. This is a progression of spectra associated with oxidation of the ruthenium clusters. Given that the potential applied has not changed from that used to effect the initial reduction of LCD (Figure 1b), what is occurring is an *oxidation* event at a *reducing* potential.

This reversal in the electrochemical behavior of LCD can be understood by considering that the reduction potential of the ruthenium clusters is found to decrease with increasing electron donation strength of the attached ligands.[11] Because the radical anion tz is expected to be a much stronger electron donor than the neutral tz, reduction of tz pushes the reduction potential of the clusters to lower potential. This has the effect of trapping the electron on tz because upon lowering of the reduction potential of the clusters the tz anion is no longer a strong enough reducing agent to reduce the attached clusters. Additionally, the applied potential is now no longer negative enough to reduce the third and final ruthenium cluster. Recalling that the second and third clusters undergo concerted reduction (as observed in the CV), it follows that if the potential is not negative enough to reduce the third cluster, it is no longer sufficient to maintain the reduction of the second cluster. Accordingly, one of the clusters, which had just been reduced, is now oxidized (Figure 1e).

Scheme 1 is forwarded as a mechanism that accounts for the SEC response of LCD upon reduction at room temperature. The first two steps of Scheme 1 bring together the data obtained from CV and SEC. First, all three clusters of LCD are reduced (step 1), as indicated by CV, but this is followed by a rapid intramolecular ET (step 2), in which one of the outer clusters donates an electron to tz, giving rise to LCD species observed spectroscopically in Figure 1b,d. The reduced tz pushes the reduction potential of the

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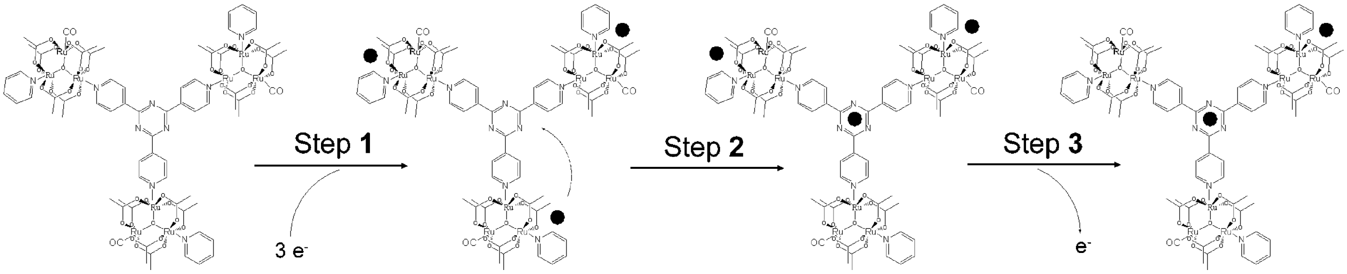
Scheme 1 [a]



[a] The LCD initially undergoes a three-electron reduction (step 1). An intramolecular electronic reorganization follows in which one of the reduced clusters donates an electron to the triazine ligand (step 2). Upon its reduction, the triazine pushes the reduction potential of the clusters more negative, resulting in the subsequent oxidation of one of the clusters (step 3).

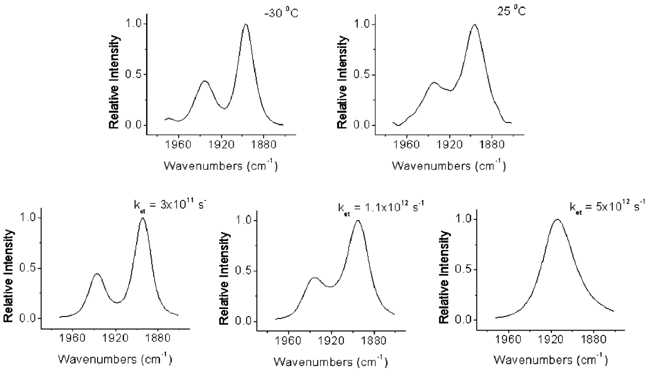


Figure 2. (a) ν(CO) band of LCD at -30 °C. (b) ν(CO) band of LCD at room temperature. (c$-$e) Simulated ν(CO) band assuming ET rates of 3×10^{11}, 1.1×10^{12}, and 5×10^{12} s^{-1}, respectively.

clusters more negative, giving rise to their oxidation at the applied potential (step 3). This is the effect observed in Figure 1e.

At the point where tz becomes reduced (step 2 of Scheme 1), a difference arises between the room- and low-temperature spectra (Figure 1f). Here, the low-temperature spectra were taken at a point during the electrochemical response of LCD such that the intensity ratio of the 1940-cm^{-1} band to the 1895-cm^{-1} band was the same as that seen in the final spectra in Figure 1b (the initial room-temperature spectroelectrochemical response of LCD). The most striking difference between these spectra is the "extra" intensity present in the room-temperature spectrum between the high- and low-energy ν(CO) bands. This extra intensity is an expected result of dynamic exchange on the IR time scale and was predicted by Turner and co-workers when they adapted the Bloch equation used in dynamic NMR for use in dynamic IR.[12]

Just as in dynamic NMR, the band shapes in dynamic IR hold information as to the rate of the dynamic process occurring.[13] In this case, the dynamic process is ET between the outer clusters of LCD and simulation of the spectra provides an estimation of the rate of electron exchange (Figure 2).[14] The low-temperature spectrum is adequately reproduced in the limit of stopped exchange, that is, assuming a k_{et} of less than 10^{11}. The best fit of the simulated spectra to the room-temperature spectra is achieved assuming $k_{et} = 1.1 \times 10^{12}$. The only chemical difference between LCD at low and room temperature is that the species at room temperature contains a reduced tz, while the tz at low temperature retains its intensity in the band at 1515 cm^{-1}. Thus, the reduction of the tz functions appears as an electronic "switch", turning on ET across the molecule.

The LCD presented here is well behaved upon reduction at low temperatures, giving easy to interpret spectra. However, at room temperature, this dendrimer exhibits some unusual electrochemical behavior. This unexpected behavior includes intramolecular electronic reorganization, reversal of the electrochemical behavior of LCD to an applied potential, and an electrochemically controlled switching event. There have been many other reports of gated ET, in which molecular dynamics,[15−19] pH,[20,21] magnetism,[22] ion size,[23] and light[24] function as the gate. While gating of ET is by no means novel, we believe this is the first case in which ET appears to be gated by an electronic event within the molecule. We have presented a mechanism (Scheme 1) to account for this behavior, and we are currently pursuing studies in order to further develop our understanding of this system. Specifically, we hope to discover the origin of the temperature dependence of the SEC response. Additionally, we are investigating whether the switching event observed in LCD may be exploited in the construction of workable molecular electronic devices.

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Supporting Information Available: Cyclic voltammogram of LCD and NMR of LCD. This material is available free of charge via the Internet at http://pubs.acs.org.

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