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A Remarkable Structural Sensitivity toward Electrogeneration of Metallopolyacetylenes

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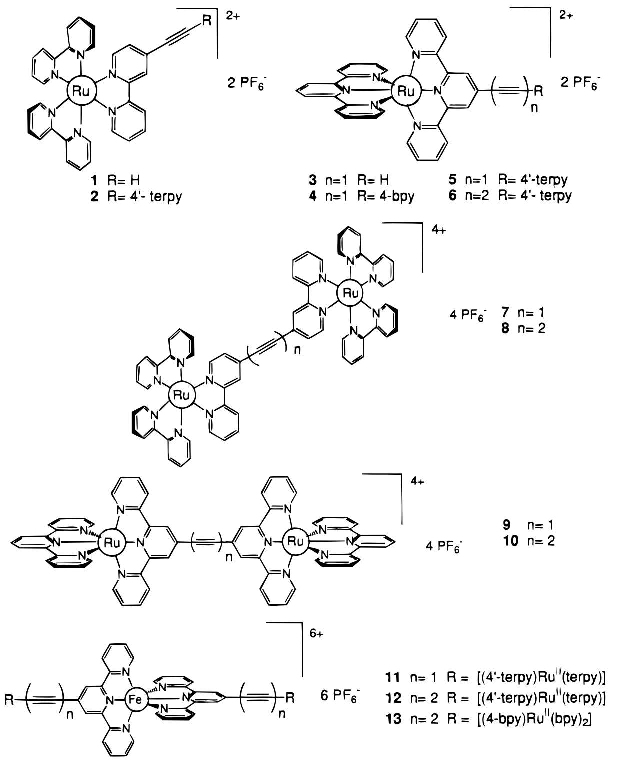
Fabrication of molecular arrays containing discrete redox-active components bound to a macroscopic support is an area of considerable interest for the design of molecular electronic devices, sensors, artificial enzymes, and immobilized catalysts.[1] The most popular polymerizable groups are pyrrole,[2] vinyl,[3] and halobenzyl,[4] and appropriate monomers containing these functionalities can be used to coat electrodes with polymeric films comprising noninteracting metallosites interspersed along a saturated hydrocarbon backbone. Electropolymerization of alkyne-substituted metal complexes is rare[5] but, in principle, could be used to produce *immobilized metallopolymers possessing a conjugated backbone*. We now show that such materials, being forms of doped polyacetylene, are deposited on the working electrode during electroreduction of alkyne-substituted ruthenium(II) bis(2,2′:6′,2″-terpyridyl) complexes.

A series of ruthenium(II) polypyridine (polypyridine = 2,2′-bipyridine (bpy) or 2,2′:6′,2″-terpyridine (terpy)) complexes bearing an alkyne (alkyne = acetylene or buta-1,3-diyne) group was synthesized (Chart 1). These compounds were studied by cyclic voltammetry in deoxygenated acetonitrile containing TBAPF_6 (0.1 M) at a platinum working electrode.

The substituted bpy complexes containing one (i.e., **1** and **2**) or two (i.e., **7** and **8**) ruthenium(II) centers exhibit electrochemical behavior similar to that of $[\text{Ru(bpy)}_3]^{2+}$, with a reversible metal-centered oxidation wave and several reversible, ligand-centered reduction waves (Table 1). The oxidation potentials ($E^{\circ\prime}_{\text{ox}}$) remain comparable to that of $[\text{Ru(bpy)}_3]^{2+}$, but the alkyne substituent raises the reduction potential ($E^{\circ\prime}_{\text{red}}$) for each step to a more positive value (Table 1). With an ethynylene bridge, $E^{\circ\prime}_{\text{red}}$ for addition of the first electron reflects the energy of the LUMO localized on the alkyne (i.e., **1** < **2** < **7**) while the buta-1,3-diynylene bridge gives the most positive $E^{\circ\prime}_{\text{red}}$.

Addition of a second electron to **7** and **8** occurs at a potential more positive than addition of the first electron to $[\text{Ru(bpy)}_3]^{2+}$ suggesting that it is added also to the bridging ligand. The difference in potential between first and second reduction steps, corresponding to 250 and 180 meV, respectively, for **7** and **8**, indicates that the first electron is extensively delocalized over the ditopic ligand.[6−8] The third reduction process for these binuclear complexes involves a two-electron step, presumably due to simultaneous reduction of a bpy ligand bound to each metal center. The voltammograms were not modified on iterative scanning between +1.6 and −1.6 V vs Ag^0 and no insoluble polymer deposited on the working electrode during 100 such cycles. Coulometric studies do not eliminate the possibility that soluble oligomers are generated.

Chart 1



Identical trends are observed in the electrochemistry of the ruthenium(II) bis(terpy) complexes (Table 1). Again, the alkyne substituent renders that ligand easier to reduce. For the binuclear complexes, the first two electrons are added sequentially to the ditopic ligand, giving delocalization energies of 220 and 100 meV, respectively, for **9** and **10**, followed by simultaneous reduction of the two parent terpy ligands. The trinuclear complexes gathered around an iron(II) center (i.e., **11** and **12**) are first reduced at a terpy ligand coordinated to the iron(II) center. The second electron is added to the other terpy coordinated to the same iron(II) center at a slightly more negative potential (Table 1). This small differential $E^{\circ\prime}_{\text{red}}$, being half that of $[\text{Fe(terpy)}_2]^{2+}$, is a consequence of electron delocalization within the ditopic ligand.[6] Addition of a second electron to each ditopic ligand occurs simultaneously and is followed by concurrent one-electron reduction of the unsubstituted terpy ligands coordinated to the ruthenium(II) sites. The mixed bpy−terpy ligand in the trinuclear complex **13** shows less extensive electron delocalization, the differential $E^{\circ\prime}_{\text{red}}$ across the central iron(II) complex being increased to 120 meV.

Unlike the bpy complexes, the voltammograms of these terpy complexes (i.e., **4**, **5**, **6**, **9**−**13**) are modified upon continuous cycling of the potential between +1.6 and −1.6 V vs Ag^0 with simultaneous increases in both reduction and oxidation waves. These changes arise from enhanced redox reactions of the complex in solution and because of material deposited on the electrode surface. After 25 scans, the working electrode was coated with a red, air-stable, insoluble polymeric film. Surface coverage (Γ) was comparable to values reported for other modified electrodes while the efficacy for film formation (Φ_{poly})

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Table 1. Electrochemical Properties of Complexes **1**−**13** in Solution or Polymerized on a Platinum Surface[a]

complex	$E^{\circ\prime}$(ox, soln) V, ΔEp (mV)[b]	E_{pa}-(ox, film) V[c]	$E^{\circ\prime}$(red, soln) V, ΔEp (mV)[d]	Φ_{poly}-(%)[e]	Γ (mmol/cm^2)[f]
1	1.29 (80), 1e$^-$		−1.25 (70), 1e$^-$; −1.36 (70), 1e$^-$; −1.53 (100), 1e$^-$		
3	1.32 (90), 1e$^-$		−1.16 (90), 1e$^-$; −1.29 (90), 1e$^-$; −1.42 (90), 1e$^-$		
2	1.30 (60), 1e$^-$		−1.13 (90), 1e$^-$; −1.30 (60), 1e$^-$; −1.47 (90), 1e$^-$		
7	1.31 (80), 2e$^-$		−0.94 (70), 1e$^-$; −1.19 (70), 1e$^-$; −1.41 (80), 2e$^-$		
8	1.29 (90), 2e$^-$		−0.86 (60), 1e$^-$; −1.04 (60), 1e$^-$; −1.37 (80), 2e$^-$		
4	1.30 (60), 1e$^-$	1.33	−1.12 (60), 1e$^-$; −1.31 (80), 1e$^-$; −1.44 (90), 1e$^-$	27	5.2×10^{-8}
5	1.31 (70), 1e$^-$	1.42	−1.12 (60), 1e$^-$; −1.23 (80), 1e$^-$; −1.38 (90), 1e$^-$	8	1.8×10^{-9}
6	1.30 (90), 1e$^-$	1.48	−1.02 (60), 1e$^-$; −1.24 (90), 1e$^-$; −1.38 (90), 1e$^-$	28	1.0×10^{-8}
9	1.33 (80), 2e$^-$	1.42	−0.97 (70), 1e$^-$; −1.19 (60), 1e$^-$; −1.44 (90), 2e$^-$	5	1.0×10^{-8}
10	1.30 (90), 2e$^-$	1.30	−0.92 (80), 1e$^-$; −1.02 (80), 1e$^-$; −1.37 (80), 2e$^-$	5	1.1×10^{-8}
11	1.31 (80), 2e$^-$; 1.18 (60), 1e$^-$	1.43, −[g]	−0.93 (60), 1e$^-$; −1.01 (60), 1e$^-$; −1.21 (80), 2e$^-$; −1.43 (80), 2e$^-$	54	6.1×10^{-8}
12	1.32 (90), 2e$^-$; 1.17 (70), 1e$^-$	1.30, 1.23	−0.92 (60), 1e$^-$; −0.99 (80), 1e$^-$; −1.22 (80), 2e$^-$; −1.42 (80), 2e$^-$	34	8.6×10^{-8}
13	1.30 (80), 2e$^-$; 1.19 (80), 1e$^-$	1.42, 1.31	−0.91 (80), 1e$^-$; −1.03 (80), 1e$^-$; −1.27 (80), 2e$^-$; −1.42 (80), 2e$^-$	21	1.5×10^{-8}

[a] Electrolyte was 0.1 M TBAPF$_6$/anhydrous CH$_3$CN, complex concentration 0.6 to 1.6×10^{-1} mM. All potentials are reported in volts vs SSCE and using Fc$^+$/Fc as internal reference. [b] M$^{III/II}$ metal oxidation couple, lowest potential M = Fe, highest potential M = Ru. [c] Values for surface-bound complex. [d] Successive ligand-localized reduction, number of electron involved are indicated as *n*e$^-$. [e] Polymerization efficiency obtained as described in ref 3. [f] Surface coverage of complex obtained by cycling through the three reductions and divided by the number of scans. [g] Fe oxidation overlapped with Ru oxidation.

was <1 (Table 1). This latter finding is consistent with polymerization occurring *via* association of reduced species on the electrode surface as opposed to radical-initiated reactions in solution.

Two important caveats emerge from this study. First, it is clearly demonstrated that redox-active, *metallo-doped polyacetylenes* can be formed as stable coatings on the electrode during reductive electrolysis. Second, the reaction demonstrates exquisite structural sensitivity in that a coordinated terpy unit is mandatory for generation of an insoluble polymer. This latter requisite becomes most evident by comparison of the properties of **2** and **4**. This is an extraordinary level of selectivity, especially bearing in mind that both terpy and bpy complexes undergo preferential one- and two-electron reduction of the alkyne-substituted ligand. The polymerization efficiency is markedly higher for the trinuclear complexes where cross-linking may favor formation of less soluble residues. Poor solubility of emerging oligomers, taken together with less inherent steric crowding, might also explain why monomeric terpy complexes appear more polymerizable than their binuclear counterparts (Table 1) but fails to account for the marked disparity between metal bpy and terpy centers. None of the uncomplexed ligands polymerize during reductive cycling despite the ready accessibility of their π-radical anions. It becomes clear that *polymerization occurs only when the Ru^{II} is coordinated to an alkyne-substituted terpy ligand*.

Polymerization requires activation of the alkyne bridge.[9] Electrochemical studies and MO calculations[10] indicate pronounced electron delocalization over an extended π^*-orbital that includes the alkyne for the π-radical anions of the metal bpy and terpy complexes and also for the free ligands. No obvious differences in the extent of electron delocalization over the alkyne at the π-radical anion stage exist between terpy and bpy ligands, before or after complexation. Restricting electrolysis to potentials slightly negative of the first reduction potential results in extremely inefficient, or negligible, polymerization of the metal terpy complexes. Therefore, in contrast to earlier studies,[5,9] generation of the alkyne π-radical anion is, by itself, insufficient to induce polymerization.

Efficacious polymerization demands addition of two or more electrons to a metal terpy complex, and since in most cases studied both electrons are added to the ditopic ligand, we may surmise that the dianion is directly involved in accretion. However, electrochemical studies (Table 1) and MO calculations[10] indicate that dianions formed from bpy and terpy ligands remain closely comparable, such that selective polymerization of terpy ligands is not related to the electronic properties of individual complexes. Molecular modeling studies[10] show that coupling at the alkyne moiety is accompanied by severe steric strain. The bpy-based complexes, which possess nominal 3-fold symmetry, occupy a larger volume than do the corresponding terpy complexes, these having nominal 2-fold symmetry, and are less amenable to close packing. Thus, stereochemical restrictions associated with the oligomers may be largely responsible for the noted inability of bpy complexes to form insoluble polymers, at least for the binuclear complexes.

Although subject to less steric congestion than are the bpy ligands, stereological considerations indicate that the terpy head-group must undergo internal distortion in order to support polymerization around the alkyne. In particular, a linear polyenic chain can only be preserved if individual pyridine units within a terpy head-group are considerably displaced from coplanarity. This, in turn, has the effect of localizing electron density on the central pyridine units during reduction of the oligomer and, at the dianion stage, favoring adoption of a [3]-cumulene-type structure that minimizes electrostatic repulsion. Cumulenes are known to be stabilized by local geometric distortion[11] and have been suggested as intermediates in the multielectron reduction of polyacetylenes.[12] As such, a plausible mechanism for the polymerization process involves coupling of a cumulene-bridged dianionic form of the emerging oligomer with an alkyne or π-radical anion. The resultant metallofilms, which are nonluminescent but stable[13] and electroactive, may possess useful catalytic functions.

Supporting Information Available: The synthesis and characterization of all complexes, putative structures of the polymers, electrochemical and UV absorption properties of the free ditopic ligands, typical cyclic voltammogram, and scanning electron micrographs of the polymeric material (10 pages). See any current masthead page for ordering and Internet access instructions.

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[9] Electropolymerization of mononuclear Ru^{II} bipy and terpy complexes bearing two bis(4-pyridylacetylene) moieties appears to occur *via* indirect population of the alkyne π-radical anion, with the bpy complexes being the more polymerizable. These complexes are less sterically hindered than those described herein but the polymerization mechanism, especially under oxidative conditions, has not been clarified. See ref 5 for details.

[10] Semiempirical molecular orbital calculations using the AM1 orbital basis sets were made with Sybyl v.5.41 on a VAX computer. Coordinates for the parent metal bpy and terpy complexes are available from the Cambridge data bank while the X-ray crystal structure of an alkyne-bridged, terpy-based ditopic ligand was recently acquired in our laboratory.

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[13] After storage in air for more than 1 year, the electrochemical behavior of a modified electrode was unchanged.