Supporting Information for *Angew. Chem. Int. Ed.* Z16983

Supporting Information

The cyclic voltammetric behavior of the cluster in 0.1 M TBA(PF_6)/THF solutions at a Pt working electrode is shown in Figure A. None of the observed voltammetric waves is electrochemically reversible, but two distinct regions of electroactivity are observed. The first occurs at ~ -2.0 V vs. the ferrocenium/ferrocene couple and the second, comprised of two distinct reduction waves, occurs at ~ -3.0 V vs. Fc+/Fc. This latter redox activity is seen to coincide in potential with that for the first 1-e^- reduction of free bipyridine (Fig. 3, bottom). Note, however, that for free bipyridine the first voltammetric wave is electrochemically reversible. It is probable that the voltammetric activity for the cluster in this same region also corresponds to addition of electrons to the two peripheral coordinated bipyridine ligands. The spacing between the voltammetric waves in the cluster is comparable to that observed in other bis(bipyridyl) transition-metal complexes. The lack of distinct oxidative components to these voltammetric waves could be an indication that the electrons, once added to the peripheral bipyridines, can migrate into the U(V) f-orbitals becoming unavailable for subsequent oxidation. The irreversible voltammetric activity for the cluster at ~ -2.0 V is likely attributable to the direct reduction of U(V) centers. The voltammetric characteristics of this process confirm that it is kinetically unfavorable, either because of poor diffusion properties of the bulky cluster or because of intrinsic barriers to adding electrons to the already reduced U centers. Irreversible oxidative voltammetric activity is also observed for the cluster just before the positive potential limit of the solvent/supporting electrolyte system is reached (~ + 1.5 V vs. Fc+/Fc). The peak current associated with this oxidation wave is comparable in magnitude to that for the reduction wave at ~ - 2.0 V. The oxidation process is also most likely attributable to metal-based redox activity, in this case loss of electrons from the U(V) centers.

Figure A. Cyclic voltammetric behavior for **2**.