

Supporting Information

Chemicals

$K_3[Fe(CN)_6]$ (Fisher Scientific Co., ACS grade), $Na_4[Fe(CN)_6]$ (The Coleman and Bell Co., 99% min. assay), $[Ru(NH_3)_6]Cl_3$ (Aldrich Chemical Co., 95% assay), and $[Ru(NH_3)_6]Cl_2$ (Aldrich Chemical Co., 99.9+% assay) were used as obtained without further purification. To prepare $[Co(4'-amino-2,2':6',2''-terpyridine)_2]Cl_2$, the ligand 4'-amino-2,2':6',2''-terpyridine was initially prepared from 4'-chloro-2,2':6',2''-terpyridine (Aldrich Chemical Co.) using previously reported procedures (Mutai *et al.*, 2001). $[Co(4'-amino-2,2':6',2''-terpyridine)_2]Cl_2$, $[Co(2,2':6',2''-terpyridine)_2]Cl_2$, and $[Co(2', 2'-bipyridine)_3]Cl_2$ (abbreviated as $[Co(tpy)_2]Cl_2$, $[Co(atpy)_2]Cl_2$, and $[Co(bpy)_3]Cl_2$, respectively, throughout the manuscript) were then synthesized according to published procedures (Hogg and Wilkins, 1962).

Electrochemical Measurements

Electrochemical measurements were done on a BAS EC Epsilon instrument using a BAS (Japan) RE-1C Ag/AgCl reference electrode, a (99.99%) Pt wire as the counterelectrode and a 25 μm diameter Pt wire ultramicroelectrode as the working electrode. For the controlled electrolysis steps a Pt coil made of a long Pt wire was employed in place of the microelectrode. All experiments were carried out in a three-compartment cell of conventional design where the individual compartments were separated by standard medium porosity frits.

References

- Mutai, T.; Cheon, J.-D.; Arita, S.; Araki, K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 7, 1045.
- Hogg, R.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 341.