

# HETEROMETALLIC SCAFFOLDS IN SOLUTION AND ON SURFACES FOR MULTI-ELECTRON TRANSFER AND DIOXYGEN PRODUCTION.

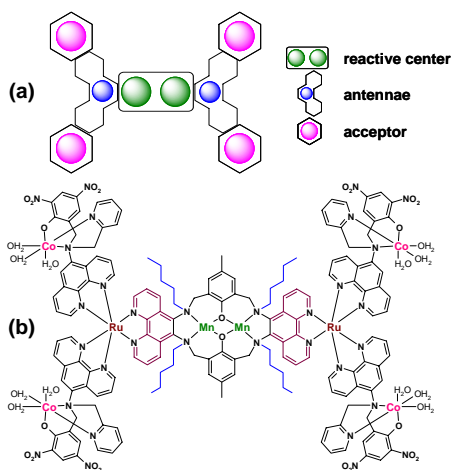
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The Verani and Endicott groups are engaged in systematic studies of multimetallic complexes which should enable the design of efficient photoinduced multi-electron transfer systems in order to facilitate processes such as interfacial electron transfer, O<sub>2</sub> and/or H<sub>2</sub> production, among others. Current studies have involved the design, synthesis, and photophysical and photochemical characterization of a range of multimetallic complexes varying from simple bimetallics to metal containing film precursors. The design approach is modular with the information based on simple complexes being used for selection of the optimal components of arrays such as illustrated in **Figure 1**.

The initial studies are based on the assumptions that: (1) facile multi-electron transfer in complexes with more than one donor metal will depend on strong metal-metal electronic coupling; (2) by analogy with mono-metal systems,<sup>1</sup> we assume that the array must contain a substrate binding site. In addition, our studies with simple model complexes have show that for systems in which excited state reactivity is an issue, additional factors have important effects. These effects are very difficult to predict; e.g.: (1) transition metal complexes tend to have a large number of low and near in energy excited states, and as such, configurational mixing can alter the structure and reactivity of the lowest energy excited state; these alterations differ appreciably from one complex to another;<sup>2,3,4</sup> (2) the interactions among excited states are different in the singlet and triplet (or other) spin manifolds;<sup>3,5</sup> (3) bridging ligands that are effective at mediating ground state electron transfer may not be effective in the MLCT excited states;<sup>6</sup> (4) substituents of the polypyridine ligands, peripheral moieties, etc., can alter excited state distortions.<sup>7</sup> Many of the relevant excited state properties can be inferred from 77 K emission bandshapes and this has been a focus of the initial studies. The initial synthetic studies have focused on the development of routes for:

(1) constructing molecular scaffolds containing multimetallic cores based on phenanthroline derivatives;<sup>8</sup> and (2) the deposition of these metal-yl forming species onto interfaces and surfaces by means of self-assembly, Langmuir monolayers and Langmuir-Blodgett films.<sup>9,10</sup>



**Figure 1.** Illustrative example of an integrated system.

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