Architecture of Supramolecular Metal Complexes for Photocatalytic CO_2 Reduction: Ruthenium–Rhenium Bi- and Tetranuclear Complexes

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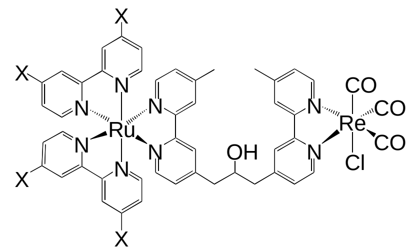
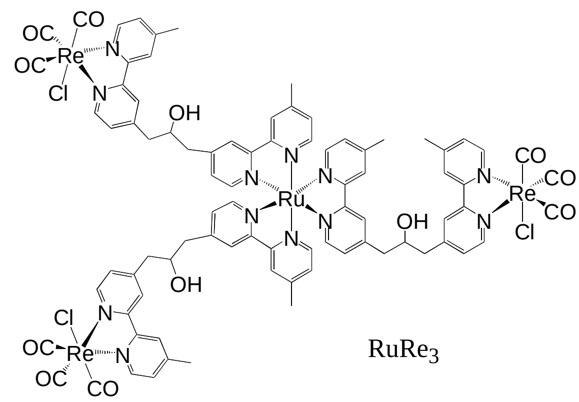
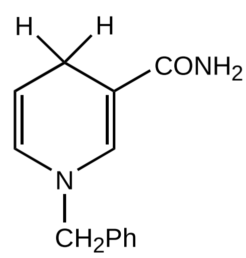


b_2Ru-Re: X = H
d_2Ru-Re: X = CH_3
tfbRu-Re: X = CF_3
Scheme 1



$RuRe_3$

Scheme 2



BNAH
Scheme 3

Multinuclear metal complexes have been playing a central role in the study of supramolecular structures as potential building blocks for photochemical and electrochemical molecular assemblies. Although some examples of mononuclear and multinuclear photocatalysts, such as Ru(II)–Co(III) and Ru(II)–Ni(II), have been appeared in the literature, their activities for CO_2 reduction are not satisfying. In addition, while there are some mechanistic approach, the controlling parameters such as structural requirements and electrochemical properties, which are essential in the design of new supramolecular photocatalysts, have not been systematically investigated yet. Our approach, to explore the present case, is to fabricate supramolecules of the rhenium complex covalently linked to the ruthenium complex as visible-light absorber. To the best of our knowledge, this is the first report regarding the use of heteronuclear Ru and Re multimetallic complexes in the photocatalytic reduction of CO_2.

The electrochemical, spectroscopic and photocatalytic properties of a series of Ru(II)–Re(I) binuclear complexes linked by bridging ligands 1,3-bis(4'-methyl-[2,2']bipyridinyl-4-yl)-propan-2-ol ($bpyC_3bpy$), and 4-methyl-4'-[1,10]phenanthroline-[5,6-*d*]imidazol-2-yl)bipyridine (mfibpy), and a tetranuclear complex in which three $[Re(CO)_3Cl]$ moieties are coordinated to the central Ru using the $bpyC_3bpy$ ligands, were investigated. In the $bpyC_3bpy$ binuclear complexes, 4,4'-dimethyl-2,2'-bipyridine (dmb) and 4,4'-bis(trifluoromethyl)-2,2'-bipyridine ($\{CF_3\}_2$bpy) as well as 2,2'-bipyridine (bpy) were used as peripheral ligands on the Ru moiety. Remarkably improved photocatalytic activities only in the case of $[Ru\{bpyC_3bpyRe(CO)_3Cl\}_3]^{2+}$ (**$RuRe_3$**) and the binuclear complex $[(dmb)_2Ru(bpyC_3bpy)Re(CO)_3Cl]^{2+}$ (**d_2Ru–Re**) were obtained while photocatalytic responses were extended further into the visible region (Schemes 1 and 2).

The excited state of ruthenium in all of the Ru–Re complexes was efficiently quenched by 1-benzyl-1,4-dihydronicotineamide (BNAH, Scheme 3). Following the reductive quenching, in the case of **d_2Ru–Re**, generation of the one-electron reduced (OER) species, for which the added electron resides on the Ru-bound bpy end of the bridging ligand $bpyC_3bpy$, was confirmed by transient absorption spectroscopy. The reduced Re moiety was produced by a relatively slow intramolecular electron transfer, from the reduced Ru-bound bpy to the Re site, occurring at an exchange rate (ΔG ~ 0). The electron transfer needs not to be a rapid process because reaction of the OER species with CO_2 is the rate-determining process. Comparison of the results with those of other bimetallic systems gives us more general architectural "compasses" for constructing supramolecular photocatalysts for CO_2 reduction.