	Osamu Ishitani
	Tokyo Institute of Technology, Professor
	ishitani@chem.titech.ac.jp
	<a href="http://www.chemistry.titech.ac.jp/~ishitani/en/index_en.html">http://www.chemistry.titech.ac.jp/~ishitani/en/index_en.html</a>

**Research keywords:** Ring-shaped Re(I) complexes, CO<sub>2</sub> Reduction, Photosensitizer, Multi-electron accumulation

We have successfully synthesized a novel type of ring-shaped rhenium(I) polymers bridged with bidentate phosphorus ligands (Re-ring) by using photochemical ligand substitution reactions which we have reported previously. These Re-rings can emit at room temperature even in solution, and the emission quantum yields are much higher than those of the corresponding Re(I) mononuclear

complexes. The structure of Re-ring with dppe (PPh<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-PPh<sub>2</sub>) as bridge ligands was determined by X-ray crystallographic analysis as shown in Fig. 1. It has a ship-flapped structure, and intramolecular interactions were observed between the bipyridine ligands and the phenyl groups on the bidentate phosphorus ligands. Some Re-rings can work as redox photosensitizers in photocatalytic CO<sub>2</sub> reduction. For example, The combination of a trinuclear Re-ring photosensitizer with fac-[Re(bpy)(CO)<sub>3</sub>(MeCN)]<sup>+</sup> (bpy = 2,2'-bipyridine) as a catalyst photocatalyzed CO<sub>2</sub> reduction with the highest quantum yield of 82%.

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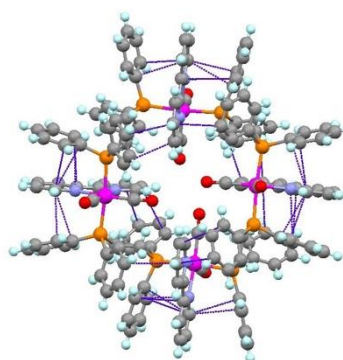


Fig. 1. Ring-shaped Re(I) tetranuclear complex.

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