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Synthesis of Re(I) Rings Comprising Different Re(I) Units and Their Light-Harvesting Abilities

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Trimethylamine N-oxide (Me_3NO) could selectively remove only one CO ligand from *fac*-$[Re(N^N)(CO)_3(PR_2R')]^+$ (N^N = diimine ligand), whereby only the CO ligand in the trans position to the phosphorus ligand was selectively removed to give *cis*,*trans*-$[ReI(N^N)(CO)_2(PR_2R')-(L)]^{n+}$ in good yields. This decarbonylation reaction using Me_3NO was found to be especially useful for synthesizing biscarbonyl Re(I) complexes with electron-withdrawing groups in the diimine ligand, which could not be synthesized or were obtained only in low yields by the photochemical method.

Me_3NO also selectively removed the carbonyl ligands in the trans position to the phosphorus ligands from the edge Re(I) complex units, which have the *fac*-$[Re(N^N)(CO)_3(PR_2R')]^+$ structure, in linear-shaped Re(I) multinuclear complexes. This reaction was successfully applied to synthesize a novel precursor with ring-shaped multinuclear Re complexes (Re-rings) comprising different kinds of Re(I) units (Figure 1). The newly synthesized Re-rings, which consist of one Re unit with a 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (CF_3bpy) ligand and one or two Re unit(s) with a 2,2'-bipyridine (bpy) ligand, showed almost quantitative excitation-energy harvesting ability from the Re unit(s) with bpy to that with CF_3bpy.

The X-ray structure of Re-rings were obtained from the data obtained in KEK NW2A using diffraction set up (2016G084).

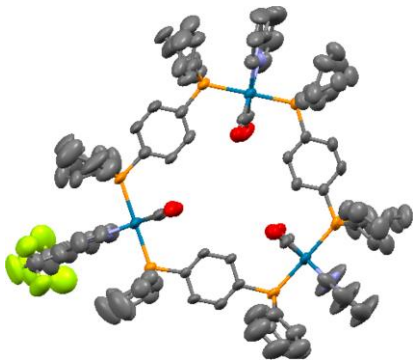

Fig. 2: X-ray structure of R3-Ph(bpy_2,CF_3bpy) from the top view.

References
[1] Y. Yamazaki et. al., *Inorg. Chem.*, **2018**, *57*, 15158.

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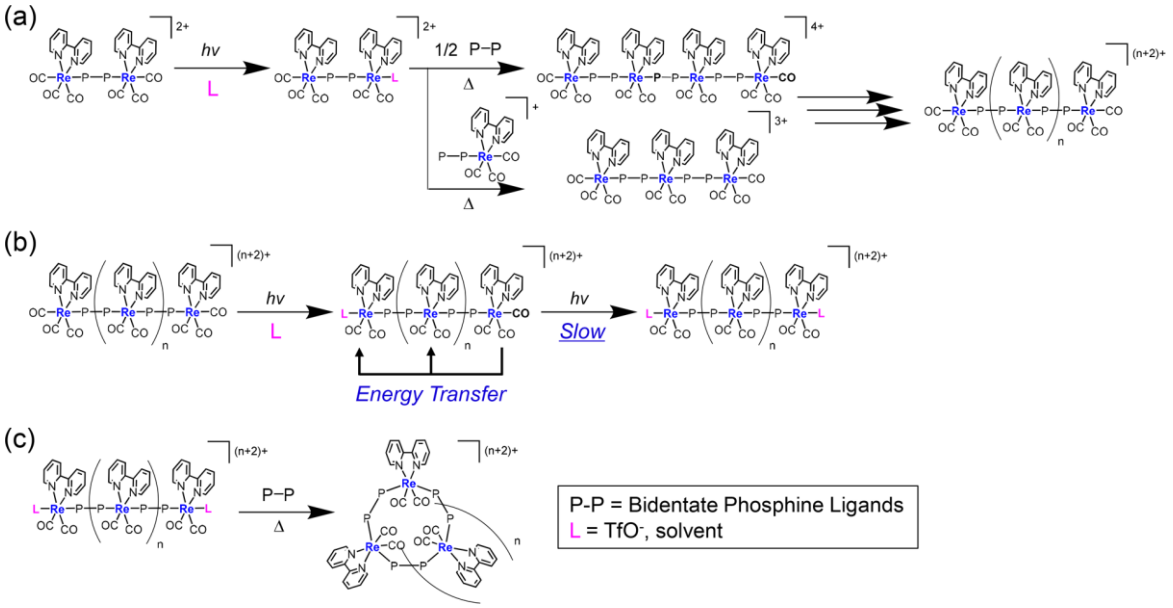

Fig. 1. Syntheses of Linear-Shaped and Ring-Shaped Re(I) Multinuclear Complexes