Review article

Molecular Wire World Having Metal Complexes

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ABSTRACT: Development of molecular and supramolecular systems showing efficient photoinduced energy or electron transfer are of current research interest due to their applications in various chemical and biological processes. Various polypyridine metal complexes including Ru(II), Ru(III), Os(II), Pt(II), Fe(II), Re(I), Ir(III) and so on as a metal center introduce for expanding some more understanding of molecular-scale photoelectronics. Their complexes are concisely classified by the types of relay ligands as follows; (a) metal-direct ligand-metal system; dinuclear or trinuclear systems, (b) metal-nonconjugated ligand-metal system and metal-nonconjugated ligand system having flexible/rigid ligand, (c) metal-conjugated ligand-metal system, and (d) conjugated ligand-metal-conjugated ligand system and metal-self assembly ligand-metal system. It is pointed out that the role played by the relay ligands is important in constructing the metal complexes.

INTRODUCTION

The appearance of the polypyridine metal complexes has triggered an extensive growth in photochemistry and photophysics, because of their highly versatile luminescent and photoredox properties. In the last few years the increasing interest in photoinduced energy- and electron-transfer processes in supramolecular systems[1] has led to important progress in the design and preparation of new relay ligands and in the development of versatile and selective synthetic strategies to assemble mononuclear complexes in supramolecular structures. In particular, Ru(II) polypyridine complexes have been extensively exploited as an ideal component of systems suitable for such investigations, owing to their outstanding excited state[2] and redox properties.[3] Therefore, the choice of suitable relay ligands is crucial to obtain polynuclear complexes capable to showing luminescence, exhibiting interesting electrochemical properties, and giving rise to photoinduced energy- and electron-transfer processes.

It should be pointed out that the role played by the bridging ligands in polynuclear complexes is extremely important from the reasons such as determining the spectroscopic and redox properties of the active metal-based units, determining the structure of the supramolecular system and controling the electronic communication between the metal-based units.

Here, the types of bridging ligands for the preparation of polypyridine metal complexes are introduced by the classification of metal-direct ligand-metal system, metal-nonconjugated ligand-metal system and metal-nonconjugated ligand system, metal-conjugated ligand-metal system, conjugated ligand-metal-conjugated ligand, and metal-self assembly ligand-metal system focusing on the versatile study of the polypyridine metal complexes and those complexes formed in solution including the results of my own work. Also, it is introduced that a flexible dinucleometal complex is fixed in the bilayer lipid system for the efficient electron or energy transfer.
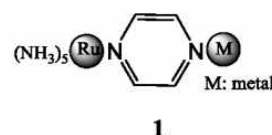
Metal-direct ligand-metal system

There are dinuclear or trinuclear systems in this system, and the polynuclear complexes are initially started from here. This polypyridine complexes have the simple structure and have relatively easily synthesized based on the chemistry of $[Ru(bpy)_3]^{2+}$.[4]

Creutz and Taube had exploited the initial stage of the polypyridine complexes showing electronic communication in the binuclear complexes **1** of ruthenium ammines with the pyrazine as a relay ligand.[5] The physical properties of these complexes are of interest in the growing field of mixed valence compound studies, and the interpretation of their electronic spectra led to deeper understanding of the energetic requirements of electron transfer processes.

After that, so many polypyridine complexes (Fig. 1; **2**, **3**, **4**, and **5**) with the direct bridging ligand[6] were reported, focusing on the simple electronic communication. The bridging ligands used here offer similar chelating sites as bpy (2,2'-bipyridine) or terpy (2,2':6',2''-terpyridine). In addition, as a different trinuclear complexes (Fig. 2; **6**) complexes having ferrocene called as Ru(II) bisferrocene acetylide complex had reported, and it showed the electronic communication between ferrocene terminal group from the result of the different value (0.1 – 0.2 V) of redox potential.[7]

After photochemical and photophysical properties of $Ru(bpy)_3^{2+}$ and related species have been thoroughly examined, attention has turned to incorporating this unit into polynuclear complexes with a view to constructing photochemical devices which can harness its excited-state energy. In fact, these polynuclear complexes shows the simple function not having any switching or control ability as well as a long-range efficient energy or electron transfer, and almost those complexes are classical.

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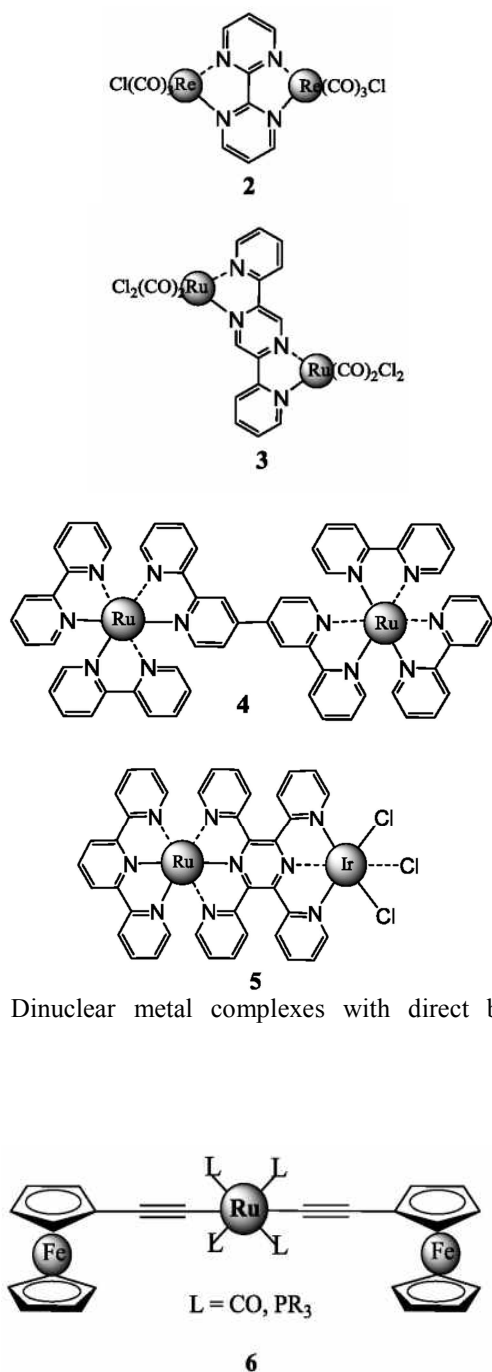E-mail: cschoi@kdu.ac.kr

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Fig 1. Dinuclear metal complexes with direct bridging ligand.

Fig 2. Trinuclear metal complex with direct bridging ligand.

Metal-nonconjugated ligand-metal system and metal-nonconjugated ligand system

In polypyridine complexes, the metal-based components are linked together by relay ligands. In several cases, the coordinating moieties of the relay ligands are linked together (and separated) by spacer. In the last few years, the increasing interest in photoinduced energy- and electron-transfer processes in supramolecular systems has led to important progress in the design and preparation of new relay ligands and in the development of versatile and selective synthetic strategies to assemble mononuclear complexes in supramolecular structures.

As shown in Fig. 3, Fig. 4, Fig. 5, and Fig. 6, polypyridine complexes with nonconjugated relay ligands can be divided into two types; flexible types **7**, **8**, **9** [8], 10, **11, 12, 13, 14, 15,**

15' and rigid systems **16** and **17**.[9] In addition, as the mononuclear Ru(II) complexes, six kinds of complexes (Fig. 7; **18, 19, 20, 21, 22,** and **23**) were synthesized for the emission studies through spacer unit connected by amide bond.

When the spacer linking the coordinating sites of a bridging ligand is flexible (i.e. $-(CH_2)_n-$ chain), the discussion of the experimental results (particularly, the rates of energy- and electron-transfer processes in the frame of current theoretical treatments) can only be vague since the geometry of the system (e.g. the metal-metal distance) is not defined. Such systems are also of limited interest because practical devices usually require the occurrence of vectorial energy- or electron-transfer over long distances. Therefore, rigid spacers, which are of course much more difficult to synthesize, have to be preferred.
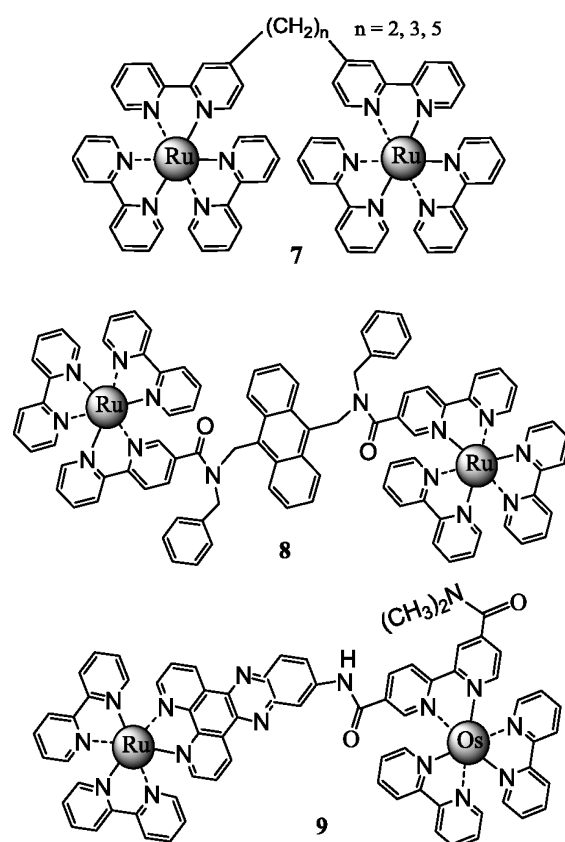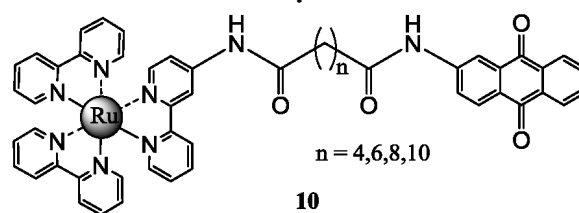

Fig 3. Diunclear metal complexes with flexible nonconjugated bridging ligand.

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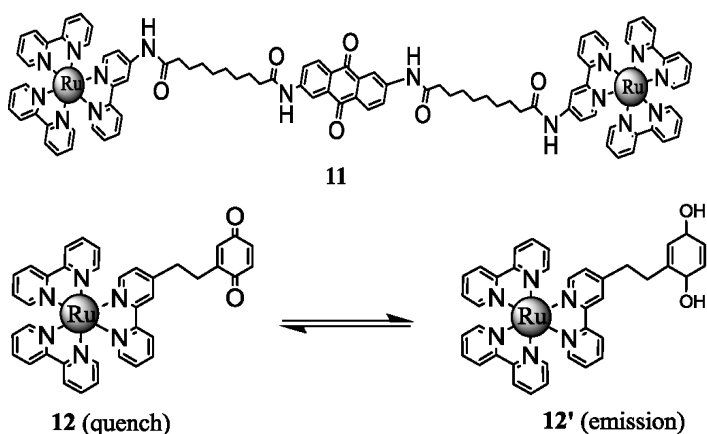**12** (quench)   **12'** (emission)

Fig 4. Mononuclear or dinuclear Ru(II) complexes with flexible nonconjugated bridging ligand including anthraquinone, benzoquinone, and hydroquinone unit.

However, recently, $[Ru(bpy)_2(dppz-NH_2)]^{2+}$ (dppz: 7-amino-dipyrido[3,2-*a*:2',3'-*c*]phenazine) was synthesized as a novel photosensitizing unit for construction of photoinduced energy transfer systems being flexible by the connection of amide bond even if its bridging ligand is nonconjugated one. In particular, heterodinuclear Ru(II)/Os(II) complex **9** having an Os(II) bipyridyl unit as an energy-accepting unit was studied as an efficient intramolecular photoinduced energy transfer system from the Ru(II) to the Os(II) center (the rate of energy transfer: 1.0 x 10^8 s^{-1} in acetonitrile).[8a]

In the case of **10**, **11**, and **12** complexes,[10] those complexes were applicated for the investigation of energy or electron transfer process in vesicle. Energy or electron transfer was not occurred in the case of **10**, while it was occurred in the case of **11**. It was suggested that the length of complex **11** was similar to that of bilayer membrane and anthraquinone spacer was immobilized in the center of bilayer membrane.

In particular, In the case of **12**, the emission from Ru(II) unit was quenched by electron transfer to benzoquinone acceptor, but it was activated when benzoquinone was reduced to hydroquinone as shown in **12'** complex. It was shown that this complex was the typical on/off switching system by redox potential.
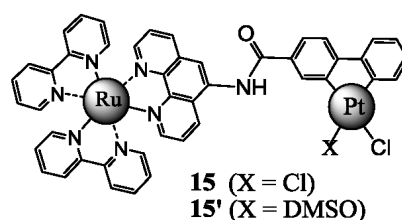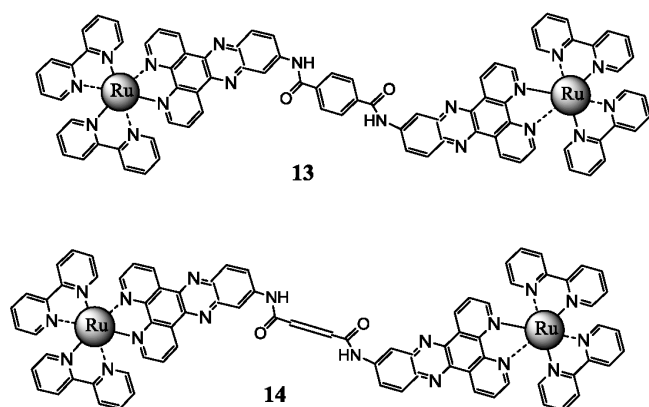

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15 (X = Cl)
15' (X = DMSO)

Fig 5. Dinuclear metal complexes with flexible nonconjugated bridging ligand connected by amide bond.
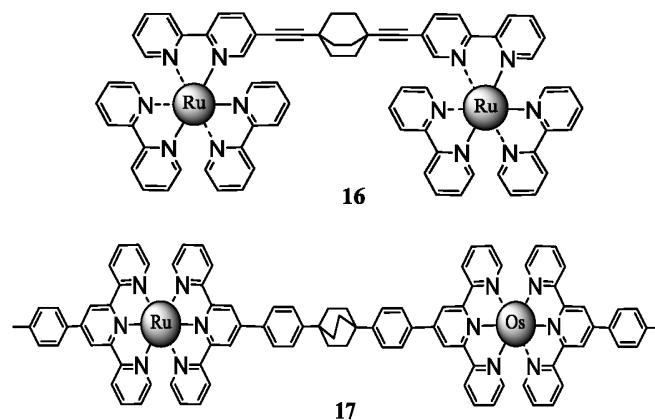

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Fig 6. Dinuclear metal complexes with rigid nonconjugated bridging ligand.

Recently, we synthesized the dinuclear Ru(II) complexes, **13**, and **14** as the moderate yield by one-pot amide formation with $[Ru(bpy)_2(dppz-NH_2)]^{2+}$ and terephthaloyl chloride or fumaryl chloride, respectively, for the construction of the long-ranged photoinduced electron/energy transfer systems. The emission decay curve of Ru(II) complrxes was measured at 610 nm, and showed single exponential component. The life-time of parent complex, $[Ru(bpy)_2(dppz-NH_2)]^{2+}$ showed shorter one as 95 ns, while the life-time of dinuclear Ru(II) complexes, **13**, and **14**, showed longer ones as 172 ns and 185 ns, respectively.[11]

In the resent study, two new heterodinuclear Ru(II)Pt(II) complxes (**15** and **15'**), produced by condensation of $[Ru(bpy)_2(5-amino-phen)]^{2+}$ with $[Pt(cppy)Cl_2]^-$ and Pt(cppy)(DMSO)Cl (cppy = 9-carboxy-phenylpyridinate), respectively, have been prepared and their photo-hydrogen-evolving activities have been evaluated in detail.[12]

In addition, as mononuclear complexes, six kinds of complexes (Fig. 7; **18**, **19**, **20**, **21**, **22**, and **23**) were synthesized for emission studies of Ru(II) center by terminal ligands. The emission from Ru(II) center was almost quenched by terminal ligand such as anthraquinone and anthracence, respectively, while The emission from Ru(II) center was showed by terminal ligand such as cyano group and bipyridyl group, Thus, a variety of acceptor units could easily be attached directly to the rigid dppz unit through the amide bond; the resultant dppz-amide unit was shown to serve as an effective connector in the energy transfer system. These results demonstrated that the $[Ru(bpy)_2(dppz-NH_2)]^{2+}$ complex is a useful building block for constructing efficient energy transfer systems.[8a]
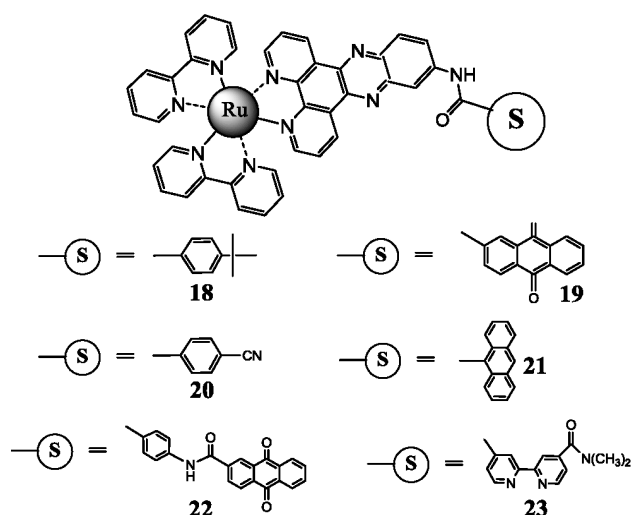
Fig 7. Mononuclear Ru(II) complexes with spacer unit connected by amide bond.

Metal-conjugated ligand-metal system

The polypyridine complexes with the conjugated bridging ligand have been attracting much attention for the realization of the efficient long-range energy- or electron-transfer. In particular, as shown in Fig. 8 (**24**, **25**, **26** and **26'**), these polypyridine complexes have advantage over those with the nonconjugated one because of their rigid and -conjugated skeleton for efficient long-range energy- or electron-transfer, though their syntheses are more difficult.[13]

Design and syntheses of these complexes have further attracted much interest from the viewpoint of molecular devices, and have been investigated intensively. As one of my results, by introducing benzoyl group to the dppz unit (dppz-CO-ph), variety of dinuclear Ru(II) complexes could be prepared in one-step by condensation with various diamino-functionalized connecting units, for which 2,6-diaminoanthraquinone **26** was used as an electron/energy trap.[14] 1,4-Diaminobenzene **26'** was also used as the diamino-functionalized connecting unit in order to clarify the role of the anthraquinone unit in the bridging ligand. Emission around 600 nm was observed by excitation of the MLCT band of **26'** (λex = 440 nm) in acetonitrile at 25 °C, which was similar to those parent complexes showing that the emission was from the excited Ru(II) polypyridyl center. Though emission of **26** appeared at the same region, the intensity was very weak. Relative intensity of the emission was only 0.03 of that of [Ru(bpy)$_3$]$^{2+}$, which was an order of magnitude weaker than that of **26'**. It was well documented that presence of protic solvents induces quenching of the emission of [Ru(bpy)$_2$(dppz-NH$_2$)]$^{2+}$ and anthraquinone derivatives through hydrogen bonding to the phenazine ring nitrogens[15] and quinone oxygens,[16] respectively. The emission of **26** was further quenched in methanolic solvent and no emission was observed in an acetonitrile(10%) containing aqueous solution. However, presence of anionic micelles of sodium dodecylsulfate in the aqueous solution restored roughly half of the emission in acetonitrile. Therefore, hydrogen bonding to the bridging ligand is responsible for the emission quenching of **26** in the protic solvents.
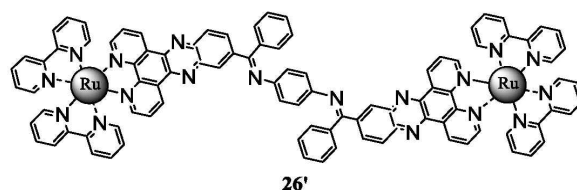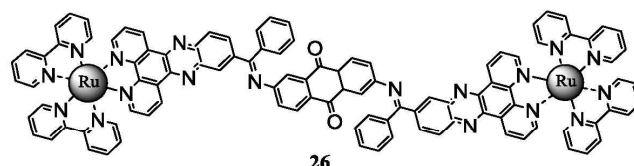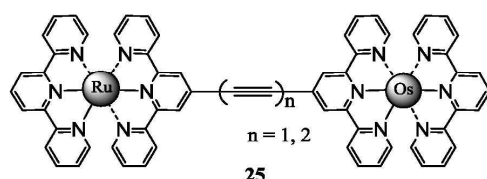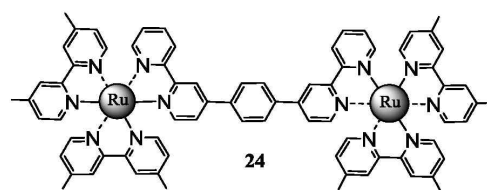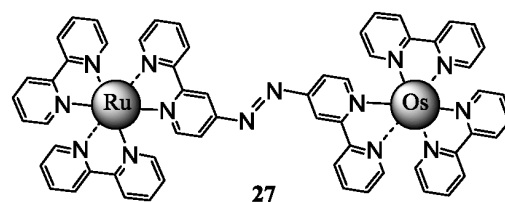

Fig 8. Dinuclear metal complexes with conjugated bridging ligand.

The bridging ligand thus prepared has the extended conjugation through two imine bonds, which will offer novel method for assembling the photosensitizing unit into the rigid and extended structure. As one of the interesting result, heterodinuclear Ru(II)/Os(II) complex **27** in Fig. 9 was recently synthesized by using azo-containing bridging ligand and photoinduced energy transfer from the Ru(II) center to the Os(II) center through the bridging ligand was controlled by redox-switching of the azo group.[17] Also, as shown in Fig. 9, dinuclear Ru(II) complex **28** with aryl/heterocyclic diazo 2,4-pentanediones as a azo-containing bridging ligand was synthesized and antibacterial activity of the complex evaluated against Pseudomonas aeruginosa has been correlated with the change in the absorbances in the presence and absence of the buffered aqueous solution of calf thymus DNA.[18] As above similar Ru(III) complex, dinuclear complex **29** was synthesized for antitumour and anti-HIV studies. This complex did not show activity against tumour cell, while it had a significant effect on the growth of only the glioblastoma cell line.[19]
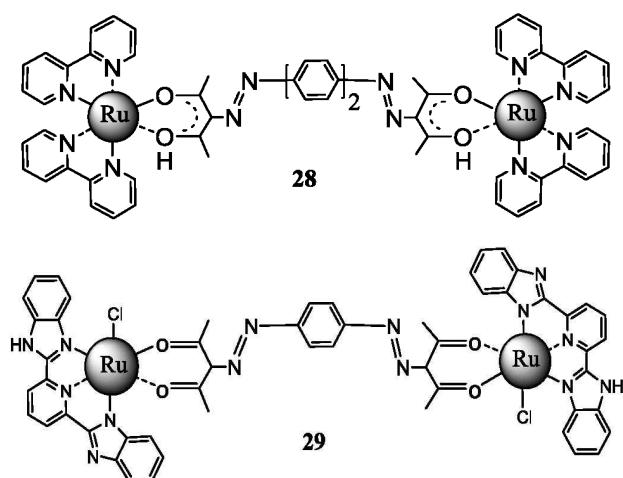
Fig 9. Dinuclear metal complexes with azo-containing conjugated bridging ligand.

Conjugated ligand-metal-conjugated ligand system and metal-self assembly ligand-metal system

We reported recently that 7-(4-methoxybenzoylamino)dipyrido[3,2-a:2',3'-c] phenazine(7-(4-mba)dppz) has a relatively high fluorescence quantum yield (Φ=0.24) comparable to that of the 7-aminodipyrido[3,2-a:2',3'-c]phenazine(7-amino-dppz) (Φ=0.21), despite being a nonrigid л-conjugated system.[20] The photophysical properties of 7-(4-mba)dppz as a ligand in the presence of different metal cations (Mg^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) were investigated in acetonitrile solution in view of potential application as the metal ion sensor. We were known from the fluorescence emission studies that the emission intensities of 7-(4-mba)dppz increase in the presence of Mg^{2+} and Zn^{2+}, respectively, in contrast to decreasing in the presence of Ni^{2+} and Cu^{2+}, respectively. Interestingly, we found from the plotting result of the complexation ratio that all the complexation ratio were the same as [M^{2+} ion] : [1] = 1 : 2 (complex **30**) as shown in Fig. 10. Herein, we suggest that 7-(4-mba)dppz can have a potential application for the cation sensor material such as divalent Ni^{2+} and Cu^{2+} metal ions.[21] While, mononuclear metal complex changed to dinuclear metal complex through self-assemblization by hydrogen bond in solution system.

As shown in Fig. 11 (complex **31**), these undergo association ($K_A > 5000$ $dm^{-3}mol^{-1}$) by hydrogen bonding between the complementary cytosine(C)/guanine(G) groups, and photoinduced energy transfer (from Ru center to Os center) occurs within Ru-C···G-Os associated pair.[22]

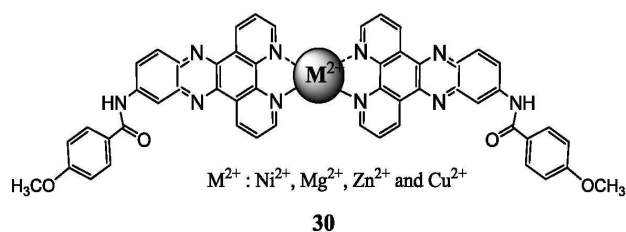**Fig 10.** The complex structure of [M^{2+}] : [7-(4-mba)dppz] = 1 : 2
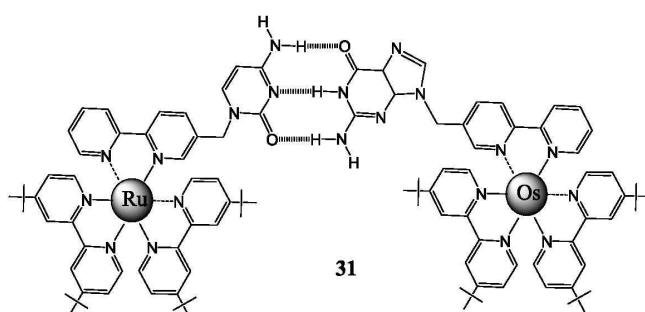

Fig 11. Dinuclear metal complex by self-assemblization.

CONCLUSION

To build up effective energy/electron transfer systems, it is necessary to tune structural and electronic properties of the connector units between the donor and the acceptor units. The introduced bond such as amide bond and imine bond has been proven to be effective as the connecting bond for energy or electron transfer systems Thus, variety of acceptor units could easily be attached through the connected bond, and the other resultant connected unit as well as azo unit and hydrogen bonding unit was shown to serve as the effective connector in the energy/electron system. In addition, by introducing benzoyl group to the dppz unit, dinuclear metal complexes having the extended л-conjugation system could be easily prepared by one-step reaction, and those complexes gave a novel synthetic strategy for the efficient energy/electron transfer in the molecular system.

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