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New Self-Assembly Luminescent Molecular Triangle and Square Rhenium(I) Complexes

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The design and study of well-arranged metal-containing macrocycles is one of the major current research areas in modern supramolecular chemistry.[1] Apart from their particular structural features, supramolecular species formed by self-assembly of transition metals introduce many special functional properties such as luminescence,[2] redox activity,[3] and magnetism[4] into the structure. More recently, transition metal based molecular squares have been synthesized by utilizing self-assembly of preorganized metal centers and pyridine-based bridging ligands.[2,5] The 90° bonding angles between ligands in transition metal complexes provide an attractive feature for constructing macrocyclic structures. Since 1990, Fujita et al. and Stang et al. have reported many different molecular square complexes based on square planar Pd(II), Pt(II), and Cd(II) metal centers.[5] These squares usually bear highly positive charges, and thus they could be potential hosts for an electron-rich species,[5] perhaps with catalytic properties.[5c] However, there are only a few reported examples for self-assembly molecular squares based on an octahedral geometry at the metal center.[2,6]

Previously, Hupp et al.[2] prepared a series of luminescent molecular squares with the general formula $[ClRe(CO)_3(\mu\text{-}L)]_4$, and some of these have been proved to be useful as molecular sensors for volatile molecules based on the square cavity size and changes of luminescence intensity.[2] Polynuclear Re(I) diimine complexes are receiving considerable attention as candidates for incorporation into photochemical molecular devices because of their well-known photophysical and redox properties.[7] However, we have reasoned that increasing the overall length of the bridging ligand may induce the formation of a new triangular structure; such species have been suggested to exist in an equilibrium mixture with the corresponding molecular square in solution from an assembly of $Pd(en)(NO_3)_2$ (en = ethylenediamine) and bis(4-pyridyl)benzene[5e] or $Pd(en)(NO_3)_2$ and *trans*-1,2-bis(4-pyridyl)ethylene.[8] Surprisingly, none of the self-assembly transition metal based triangular molecules with an octahedral geometry have been isolated before. Thus, we set out a project to investigate the possibility of preparing and isolating Re(I)-based self-assembly molecular triangles and their possible application as molecular receptors. We report herein the preparation of luminescent rhenium(I)-based self-assembly molecular triangle and square complexes (see Scheme 1) and associated photophysical data.

The self-assembly complex **1** was prepared by refluxing equimolar $ClRe(CO)_5$ and 1,4-dipyridylbutadiyne (DPB)[9] in a 1:1 THF/toluene mixture for 48 h with 92% isolated yield. The characterization of complex **1** was achieved by a variety of analytical techniques including infrared spectroscopy, NMR spectroscopy, FAB^+ mass spectrometry, and elemental analysis.[10] Infrared carbonyl stretching frequencies exhibit tricarbonyl stretching patterns in a facial arrangement.[11] Elemental analysis confirms the 1:1 stoichiometry between the Re atom and the bridging ligand. The ^1H NMR spectroscopic data show simply two sets of doublets originating from α and β protons in the pyridine rings, confirming the symmetric structure. FAB^+ mass spectral measurement for complex **1** yielded a peak at $m/z = 2002.4$ ($\mathbf{1} - Cl^-$). All these data support the formation of the square structure for complex **1** without any trace amount of a triangular structure.

Complex **2** was prepared similarly to complex **1** by refluxing $BrRe(CO)_5$ and 1,4-bis(4′-pyridylethynyl)-2,5-dihexyloxybenzene (BPDB)[12] in neat benzene with an isolated yield of 90%. When the reflux was performed in various ratios of toluene/THF mixture, only unidentified products were formed. Complex **2** exhibits both light and thermal decomposition in THF solution, and this may be the reason for the unsuccessful attempts at synthesis in THF. All the spectroscopic (NMR, IR) and elemental analysis data[13] are again concordant with a 1:1 stoichiometry between the Re atom and the bridging ligand. However, the mass spectrum yielded a peak at 2494.2 ($M + H^+$) which corresponds to the parent ion of the trimeric structure, and no peaks corresponding to square or higher order oligomers were found in the spectrum up to *m*/*z*

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(10) Complex **1**: IR (DMF, ν_{CO}): 2021 (s), 1928 (m), 1892 (m). ^1H NMR (360 MHz, DMSO-d_6): 8.73 (d, $J_{H-H} = 6.5$ Hz, 16 H, PyH_α), 7.77 (d, $J_{H-H} = 6.5$ Hz, 16 H, PyH_β). MS (FAB, *m*-NBA as matrix): $m/z = 2002.4$ ($M - Cl^-$) (calcd $m/z = 2003$ for $M - Cl^-$). Anal. Calcd: C, 40.02; H, 1.57; N, 5.49. Found: C, 39.86; H, 1.44; N, 5.61. We were unable to obtain an X-ray-quality single crystal due to the rapid solvent loss and collapse to amorphous material upon removal of the crystals from the mother liquor.

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(12) See Supporting Information for detailed procedure for synthesis of BPDB.

(13) Complex **2**: IR (DMF, ν_{CO}): 2027 (s), 1928 (m), 1893 (m). ^1H NMR (360 MHz, $CDCl_3$): 8.77 (d, $J_{H-H} = 6.6$ Hz, 12 H, PyH_α), 7.34 (d, $J_{H-H} = 6.5$ Hz, 12 H, PyH_β), 7.00 (s, 6 H, Ph), 4.01 (t, $J_{H-H} = 6.5$ Hz, 12 H, $-OCH_2C_5H_{11}$), 1.81 (t, $J_{H-H} = 6.6$ Hz, 12 H, $-OCH_2CH_2C_4H_9$), 1.50−1.33 (m, 36 H, $-OC_2H_4C_3H_6CH_3$), 0.87 (m, 18 H, $-OC_5H_{10}CH_3$). MS (FAB, *m*-NBA as matrix): $m/z = 2494.2$ ($M + H^+$) (calcd $m/z = 2493$), 2412.1 ($M - Br^-$) (calcd $m/z = 2412$). Anal. Calcd: C, 50.60; H, 4.34; N, 3.37. Found: C, 50.11; H, 4.79; N, 3.03. The introduction of the long alkyl chains into the bridging ligand largely increases the solubility of compound **2** in most moderately polar organic solvents. However, all attempts to grow single crystals of **2** from a variety of solvents or solvent combinations were still unsuccessful.

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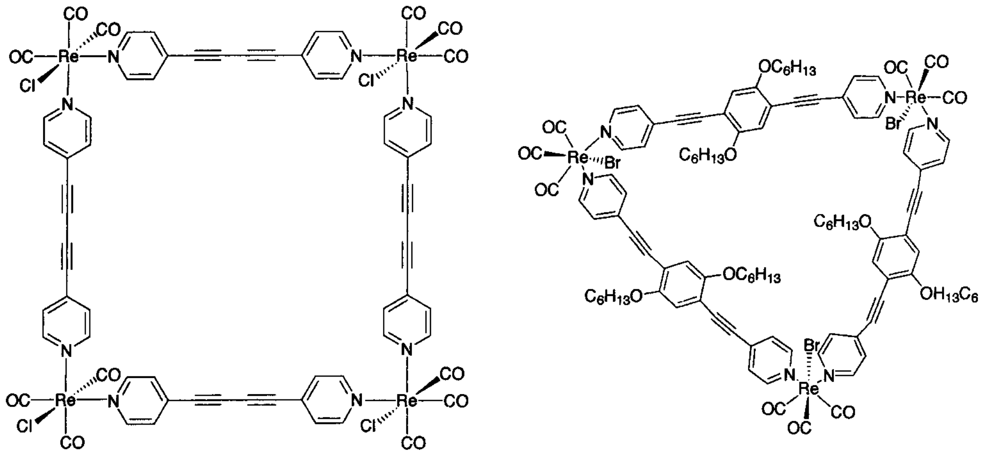
Scheme 1



Complex **1** Complex **2**

Table 1. Electronic Absorption and Luminescence Data for Square and Triangular Re(I) Complexes at 293 K

complex	solvent	$\lambda_{\pi-\pi^*}$, nm (ϵ, M^{-1} cm^{-1})	λ_{MLCT}, nm (ϵ, M^{-1} cm^{-1})	λ_{em}, nm	τ, ns	Φ_{em}
1[a]	THF	322 (151 000)	360[d] (160 000)	635	38.8	8.5×10^{-4}
2[b]	DCE[c]	329 (118 200)	406[d] (145 400)	476, 499	0.36	0.032

[a] $\lambda_{ex} = 400$ nm. [b] $\lambda_{ex} = 340$ nm. [c] 1,2-Dichloroethane. [d] Overlapping MLCT and $\pi-\pi^*$ bands.

= 3300. The isotopic distribution pattern of the parent ion agrees well with the calculated composition for the trimeric structure.

It has been suggested that the driving force for the self-assembly process is under thermodynamic control.[14] The most thermodynamically stable product will form from self-assembly of a labile metal center with a bridging ligand. On the other hand, the kinetic product will form in the self-assembly process with the inert metal center. From the thermodynamic point of view, the cyclic product will be more favorable in terms of enthalpy and disfavorable in terms of entropy.[2c] The formation of the molecular triangle as the most thermodynamically stable product indicates that the entropy effects play an important role during the self-assembly process because the square structure is more stable in terms of enthalpy effects, whereas entropy effects favor the triangular structure.[5e,14] Fujita et al. have observed a concentration dependent equilibrium between the molecular square and triangle in the self-assembly process between (en)Pd(NO_3)$_2$ and DPB.[5e] However, we did not isolate any trace amount of the triangular structure from the assembly of ClRe(CO)$_5$ and DPB. The lack of a triangular structure is likely due to the poor solubility of **1** in THF/toluene mixtures and immediate precipitation from solution once the square is formed.[15] The relatively larger BPDB ligand seems to make the entropy effects dominant over the enthalpy effects. To our best knowledge, complex **2** represents the first isolated self-assembly molecular triangle based on an octahedral metal center.[16] Moreover, the larger strain that exists in the triangular structure may be responsible for the increased thermal and photochemical decomposition of **2** in THF solution.

Table 1 summarizes the electronic absorption, emission, and lifetime data for complexes **1** and **2**. The electronic absorption spectra of both complexes exhibit two bands that are assigned as ligand-localized $\pi-\pi^*$ and metal-to-ligand charge transfer (MLCT) transitions. Both complexes **1** and **2** are luminescent in room temperature solution, although the emission apparently originates from excited states of differing orbital parentage. The emission from **1** is assigned to arise from the lowest ^{3}MLCT state on the basis of the emission band structure, long-wavelength maximum, relatively long lifetime, and calculated radiative rate constant ($k_r = 2.2 \times 10^5$ s^{-1}).[2a,11] Complex **2** exhibits dual emission with $\sim$1000 cm^{-1} spacing in 1,2-dichloroethane, and the intense emission bands at relatively high energy and the short lifetime suggest that the emission originates from $\pi-\pi^*$ excited states. The low-temperature (77 K) emission spectrum displays more distinct structure with bands at 463, 488, 520, and 549 nm (1188 cm^{-1} average spacing). We have found that the dual emission spectrum is not dependent on the excitation wavelength in the 340−400 nm range and that there is a single exponential decay from these two bands. These observations illustrate that the dual emission bands are actually vibronic structure from the $\pi-\pi^*$ state. Work on the detailed photophysical and photochemical properties as well as their possible host−guest interactions and sensor applications is in progress.

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Supporting Information Available: The procedure describing the preparation of the bridging ligand (BPDB), experimental details of the photophysical measurements, FAB$^+$ mass spectral data obtained for **1** and **2**, and a table listing of the mass fragment assignments for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Generally, we observe that the complexes with more metal centers have lower solubility; so it seems reasonable that the square complex with four metal components displays lower solubility than the triangular complex with three metal components.

(16) Preliminary ^{1}H NMR results from assembling BrRe(CO)$_5$ and bridging ligand 2,5-bis(4-pyridylethynyl)thiophene showed that the isolated product comprises both triangular and square structures with a 1:4 (triangle:square) ratio.