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Self-Assembly Molecular Squares with Metal Complexes as Bridging Ligands

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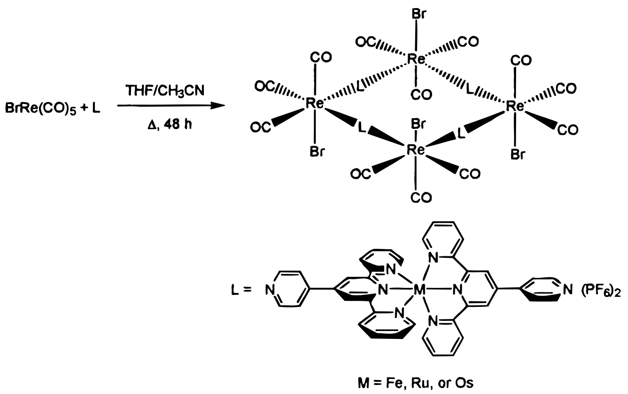
Polynuclear transition metal complexes containing multichromophoric units, such as metal polypyridyl complexes, are of considerable current interest.[1] Much attention has be paid to the synthesis of multicomponent systems that exhibit photoinduced intercomponent electron and/or energy-transfer processes and to their potential applications for photonic and electronic devices.[2] Systems incorporating Re(I)-, Ru(II)-, and Os(II)-based polypyridyl chromophores are the most commonly studied because of their favorable redox and spectroscopic characteristics.[1−3]

Polynuclear metal complexes are usually synthesized through tedious procedures to covalently link the individual components,[4] whereas the self-assembly process provides an efficient way for the spontaneous generation of multicomponent structures.[5] Various square complexes have been prepared via the self-assembly process over the past decade.[6] The majority of molecular squares that have been assembled are based on the square planar metal centers involving Pd(II) or Pt(II) and linear bidentate ligands such as 4,4′-bipyridine. Self-assembly square complexes incorporating other geometric metal centers are less common, however.[7] In addition, only a few examples have utilized metal complexes as bridging ligands.[8] In this communication, we combine the concepts of self-assembly and "complexes as ligands" and report the preparation of a series of molecular squares with the general molecular formula [*fac*-Br(CO)$_3$Re(μ-(pyterpy)$_2$M)]$_4$(PF$_6$)$_8$, where pyterpy is 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine and M = Fe, Ru, or Os. The spectroscopic properties and a preliminary anion binding study of these novel octanuclear molecular squares are also presented.

Scheme 1



Self-assembly square complexes **1**−**3** were prepared in quantitative yield by reaction between BrRe(CO)$_5$ and the metal-complex bridging ligands in refluxing CH$_3$CN/THF mixture (Scheme 1). A variety of analytical methods were employed to characterize the square structures,[9,10] and all obtained data confirm the 1:1 stoichiometry between the Re metal and the metal-complex bridging ligand. Direct evidence proving that complexes **1**−**3** are square structures has been determined from electrospray ionization (ESI) mass spectra.[11] Additionally, we have obtained a high-resolution ESI mass spectrum for complex **2** utilizing the Fourier transform ion cyclotron resonance (FTICR) technique. Figure 1 illustrates the ESI-FTICR mass spectrum as well as the calculated and experimental isotopic distribution for complex **2** based on [**2**−2PF$_6^-$]$^{2+}$, and the good agreement between the calculated and experimental isotopic pattern clearly confirms the square structure.[13] Attempts to obtain X-ray quality crystals were unsuccessful. Although it was possible to grow very small crystals from slow diffusion of ether into acetonitrile solution, we found that they underwent solvent loss readily and collapsed to form amorphous solids.[8a]

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(9) See Supporting Information for characterization data of complexes **1**−**3**.

(10) Four possible diastereomers with respect to the relative positions of CO and Br$^-$ may exist in our systems. Here, we do not imply any preferential isomer, which will form during the self-assembly process.

(11) Electrospray ionization mass spectrometry (ESI-MS) has been successfully used for detection of supramolecular species in solution.[12] The efficient ionization process and the multiple-charging phenomenon inherent in ESI mass spectra have provided high sensitivities and the observation of high molecular weight species within a limited mass-to-charge ratio observation window. On gentle ionization, even highly charged intact species can be observed without undergoing fragmentation.[8,12a.]

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(13) Several papers have suggested the coexistence of molecular triangle and square structures in solution and their physical data (IR, NMR, and elemental analysis) could be very similar.[7a,14] However, the lack of detection of a molecular weight that corresponds to either the molecular triangle or other higher order structures and the clean NMR spectra confirm that the square complexes are the only products.

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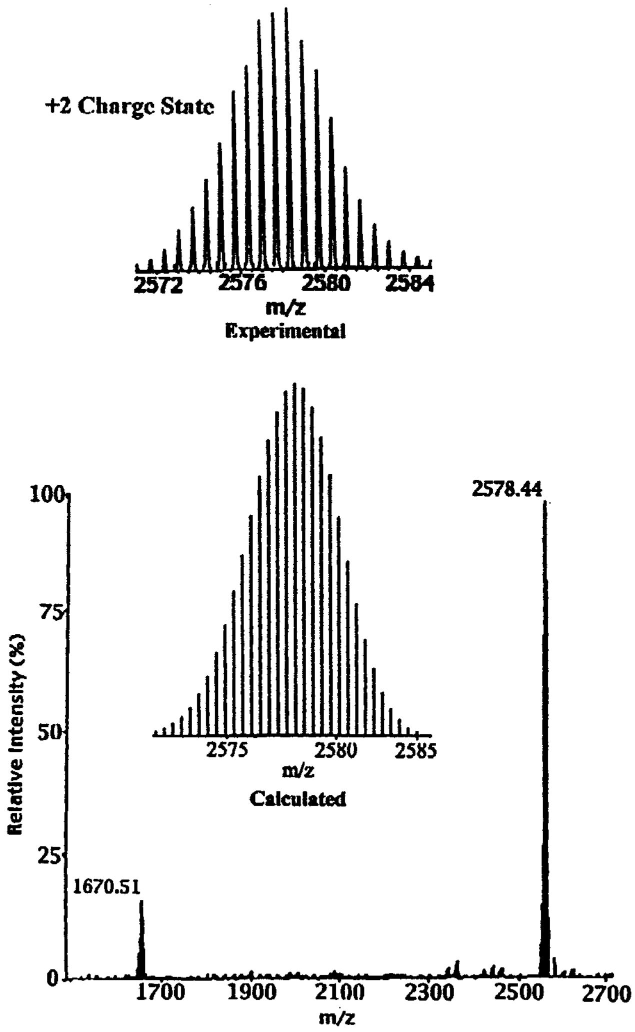

Figure 1. ESI-FTICR mass spectrum of complex **2**.

Table 1. Electronic Absorption and Emission Spectra at 293 K

complex	λ_{max}, nm ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})	λ_{em}, nm
1[a]	281 (279), 333 (200), 345 (192), 377 (107), 588 (147)	*b*
2[a]	279 (278), 320 (175), 332 (159), 498 (133)	*b*
3[c]	275 (281), 283 (299), 318 (262), 402 (80.5), 490 (198), 670 (50.3)	748

[a] DMSO solution. [b] No luminescence detected. [c] CH_3CN solution.

Electronic absorption and luminescence data recorded from the square complexes **1**−**3** are summarized in Table 1. All three complexes display strong visible absorptions in the region 400−600 nm, which are assigned as metal (Fe, Ru, or Os)-to-ligand (pyterpy) charge transfer (MLCT) bands.[15] Complex **3** exhibits an additional weak band at 676 nm that is assigned to an Os-based ^{3}MLCT (Os-^{3}MLCT) band.[15,16] For each complex, the bands centered between 279 and 377 nm are assigned as pyterpy-based $\pi-\pi^*$ bands and the Re-based MLCT band. Complex **3** is highly luminescent in room-temperature deoxygenated solution, while complexes **1** and **2** do not have any detectable luminescence under identical experimental conditions. The lack of luminescence at room temperature from complexes **1** and **2** is attributed to the existence of metal-centered (MC) states lying in proximity to the MLCT states. The distortion from perfect octahedral structure due to the C_{2v} symmetry in M(pyterpy)$_2$ (M = Fe, Ru) results in a relatively weak ligand field at the metal, and thus, the MC states are at low energy.[17] The MLCT excited states appear to be deactivated through these low-lying nonemissive MC states via an efficient nonradiative decay pathway. In contrast, the emission intensity and position of complex **3** are similar to those of the free metal-complex ligand and the emission is also independent of the excitation wavelength. Here, the energy transfer from higher energy states (Re-MLCT or $\pi-\pi^*$) to the lowest Os-^{3}MLCT state is relatively efficient, and consequently, luminescence is observed.

The highly positive-charged square complexes **1**−**3** are potential host materials for anions.[18] The luminescence features of **3** provide a way other than ^{1}H NMR spectroscopy to study the host−guest chemistry. A preliminary binding study between complex **3** and BF_4^- anions was carried out in CH_3CN solution. The luminescence of **3** was observed to increase with increasing BF_4^- anion concentration, although there was no change in either the emission position or band shape. The binding mechanism is unclear at this stage, but we believe it is related to the greater electrostatic stability imparted by the BF_4^- anion compared to the PF_6^- counteranions associated with complex **3**. We have found there is no significant effect of adding excess PF_6^- anions on the luminescence of complex **3**. Work on elucidating the detailed inorganic anion binding mechanism as well as investigating aromatic anion binding is in progress.

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Supporting Information Available: Characterization data including IR, ^{1}H NMR, ^{13}C NMR, elemental analysis, and ESI mass spectral data for complexes **1**−**3**, and absorption and luminescence spectra of complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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