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Self-Assembly of Luminescent Molecular Squares Featuring Octahedral Rhenium Corners

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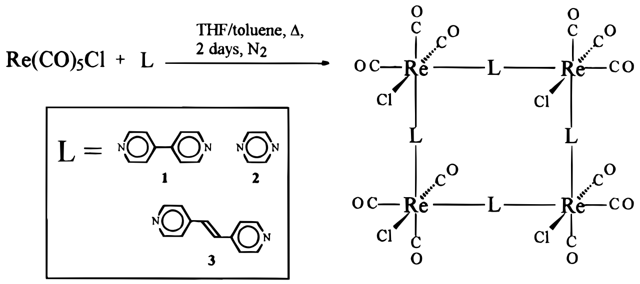
The self-assembly of rigid inorganic cyclophanes comprising cis bridging metal centers connected by aromatic edges has emerged as a promising new area within the realm of host−guest chemistry.[1−5] By utilizing the power and simplicity of molecular self-assembly which enables components to arrange themselves into square host cavities, chemists have synthesized a large number of new species with recognition capabilities. In nearly all previous examples of square self-assemblies, Pd^{II} or Pt^{II} materials with leaving groups cis to one another have served in some capacity to drive the process. We report herein the extension of the chemistry of self-assembled[6] molecular squares to include compounds incorporating solely octahedral metal centers (**1**−**3**).[7,8] It should be noted that the synthetic methods used to construct the 4,4′-bipyridine square, **1**, have been generalized with the synthesis of pyrazine (**2**) and 1,2-bis(4-pyridyl)ethylene (**3**) molecular squares. Squares **1** and **2** luminesce at room temperature, making them potentially useful as small-molecule sensors; unfortunately, the excited state for square **3** decays exclusively via nonradiative pathways.

The approach used for the assembly of these inorganic cyclophanes is depicted in Scheme 1.[9] Yields in excess of 95% are obtained with the method shown. A variety of analytical techniques has been used to characterize these new compounds including FAB^+ mass spectrometry, NMR spectroscopy, and X-ray crystallography; all of the studies indicate that molecular squares are formed exclusively (i.e. with no higher order oligomers or catenanes).

Scheme 1



X-ray-quality crystals of squares **1** and **2** were grown by first solubilizing the samples in acetone and then layering with *n*-hexanes.[10] Exclusion of solvent from the small pyrazine square cavity in **2** (Figure 1) afforded a more highly ordered structure than that of **1** (see Supporting Information). Nevertheless, the CO/Cl^- trans ligand pairs for both were disordered.[11] The structural data additionally reveal for **2** a slight distortion from a strictly square cavity geometry (angles of 85.6° rather than 90°). In any case, the ability to tune cavity sizes over such a broad range is apparently unique to this system; previous attempts to synthesize small pyrazine-containing squares via the Pd(1,3-bis(diphenylphosphino)propane)$(CF_3SO_3)_2$ were unsuccessful because of the steric demands of the diphenylphosphine groups.[2a]

NMR spectroscopic studies of **2** reveal a set of two singlets of equal integration at 8.999 and 8.963 ppm, respectively. This splitting of the nominally equivalent pyrazine protons is attributed to a subtle difference in the environment surrounding each. From the X-ray crystal structure, the rings of this square are canted at an angle of about 41° to the normal of the square plane. The tilting places half of the protons inside the square framwork with the other half necessarily lying outside the square. The protons inside the framework are located above the neighboring pyrazine rings, where they are expected to experience a ring current effect and, therefore, be shifted upfield. Note that this interpretation implies that the canted configuration is unchanging on the NMR time scale. An alternative interpretation is that the splitting reflects equal populations of isomers (or portions of isomers) with chlorides “trans” and chlorides “cis” to the pyrazine bridges.

The electronic absorption spectra of all three squares exhibit two bands in the UV and visible regions that are assigned respectively as bridging-ligand-localized $\pi-\pi^*$ and metal-to-(bridging) ligand charge transfer (MLCT) transitions (Table 1). These transitions are common to nearly all complexes in the

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(3) For a pair of early reports, see: (a) Kalb, W. C.; Demidowicz, Z.; Speckmann, D. M.; Knobler, C.; Teller, R. G.; Hawthorne, M. F. *Inorg. Chem.* **1982**, *21*, 4027. (b) Stricklen, P. M.; Volcko, E. J.; Verkade, J. G. *Inorg. Chem.* **1983**, *105*, 2494.

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(6) In some contexts the term “self-assembly” has been reserved for structures generated via weak intermolecular interactions. Here we employ the term in a broader sense as a descriptor for the one-step construction of relatively high symmetry *covalent* assemblies in high overall yield.

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(8) We are aware of one prior report on solely octahedral systems: a series of $P(OCH_3)_3P$-bridged squares.[3b]

(9) For example, **1** was synthesized by combining 100 mg (0.276 mmol) of $Re(CO)_5Cl$ and 43.1mg (0.276 mmol) of 4,4′-bipyridine in 100 mL of 3:1 THF−toluene. The reaction solution was then heated with stirring at 60 °C for 36−48 h, whereupon a bright yellow solid formed. After cooling, the solid was collected on a glass frit, washed with hexanes, and dried under vacuum. Typically, no further purification was needed. Compounds **2** and **3** were synthesized in a similar fashion. Elemental analysis, FT-IR, and ^1H NMR data (Supporting Information) were consistent with the formation of 1:1 Re:ligand compounds. Conclusive evidence for square formation as compared to other random macrocycles or oligomers was obtained from FAB^+ mass spectrometry and X-ray crystallography.

(10) X-ray-quality crystals of **2** were grown out of the crude reaction material from an attempted synthesis of a molecular rectangle containing pyrazine and 4,4′-bipyridine edges. The material obtained in this way was otherwise identical to the noncrystalline compound obtained from $Re(CO)_5Cl$ and pyrazine (only).

(11) Note that, with respect to the positions of the CO/Cl^- trans ligand pairs, four distinct isomeric forms can be envisioned for each square; no claims are made regarding the isomeric composition of these samples.

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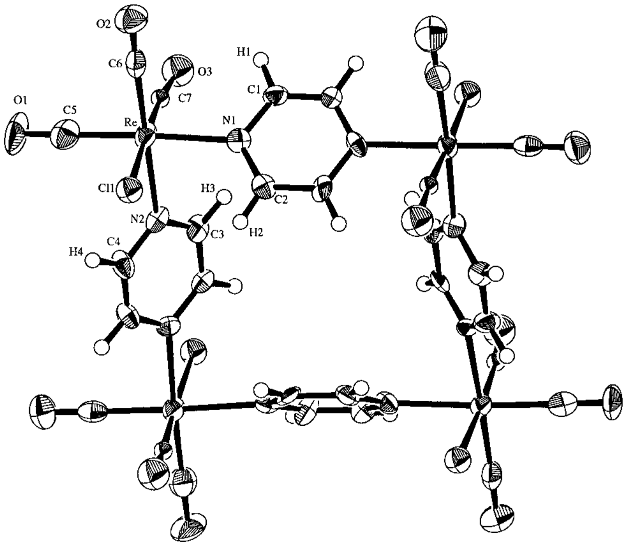

Figure 1. Single-crystal X-ray structure of **2**.

Table 1. Electronic Absorption and Luminescence Data[a]

	$\lambda_{\pi-\pi^*}$, nm	λ_{MLCT}, nm	λ_{em},[b] nm	τ, ns
1	248	348	632	134
Re(CO)$_3$(bpy)$_2$Cl	248	314	585	1670
2	274	396	682	54
Re(CO)$_3$(pz)$_2$Cl	264	320	584	318
3	294	358		

[a] All studies were performed in Ar-saturated CH$_2$Cl$_2$. [b] Emission maxima of corrected luminescence spectra.

rhenium tricarbonyl polypyridyl family. The MLCT transition is of particular significance in that it results in the creation of a Re^{II}–L$^{\bullet-}$ excited state which can, in principle, relax radiatively (i.e. luminesce) in the visible region of the spectrum. Squares **1** and **2** do exhibit luminescent properties at room temperature; however, square **3** does not detectably luminesce under these conditions. The absence of luminescence may possibly be associated with enhanced nonradiative decay via torsional motion about the ethylene bond.[12]

Time-resolved luminescence studies of the two photoactive squares have been conducted at room temperature in methylene chloride purged with argon gas. As shown in Table 1, emissive excited state lifetimes (τ) are significantly shorter for the squares than for the corresponding monomeric "corner" complexes, Re(CO)$_3$(L)$_2$Cl. One possible interpretation of the shortened lifetimes is that excited states in squares are quenched by further charge transfer to proximal chromophores. Indeed, previous work on dimeric rhenium polypyridyl complexes has yielded evidence for intramolecular quenching effects.[13] Nevertheless, alternative explanations such as enhanced Franck–Condon overlaps (enhanced nonradiative decay kinetics) for transitions involving the squares cannot be ruled out at present.

In summary, a new series of molecular square transition-metal complexes has been obtained via a simple self-assembly method. These luminescent squares are unique in that they contain corners exclusively composed of octahedral rhenium metal centers. In addition to incorporation of other interesting bridge elements such as metalated and free-base porphyrins and amino acids, current work is focused on replacing the axial ligands in these squares to allow them to be attached to surfaces. Finally, the luminescence characteristics of the squares make them candidates for sensing applications based on recognition and inclusion of appropriate guest molecules.[14] The recognition chemistry of related luminescent squares is currently being studied.

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Supporting Information Available: Tables of elemental analyses and FAB$^+$ mass spectral, ^{1}H NMR, and IR data for **1**–**3**, text presenting X-ray experimental details for **1**, tables of atomic coordinates, bond lengths, bond angles, and thermal parameters for **1** and **2**, and figures showing the single-crystal X-ray structure of **1** and a packing diagram for **2** (13 pages). Ordering information is given on any given masthead page.

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