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Luminescent Squares and Rings Based on Metal-to-Ligand Charge Transfer Excited States

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Rigid metallomacrocycles have been of interest during the past decade due to their potential use in host−guest, inclusion, and molecular recognition chemistry.[1−15] The reports by Slone et al.[11,12] of the first luminescent molecular squares suggests that Re(I) chemistry has great potential in these areas, especially with regard to using their molecular sizes and shapes for sensing applications. The previous Communication[16] in this issue reports the preparation of linear oligomers based on luminescent *cis*-Re(I) dicarbonyl units[17] and bridging diphosphines. Remarkably, during these reactions cyclic diphosphine-bridged oligomers also are produced. In this Communication, we report their preparations and structural characterization. The complexes are the first examples of squares and rings of Re(I)−2,2-bipyridine-based MLCT excited states that emit in solution.

Two types of preparations give rise to metallomacrocycles of differing nuclearity. One preparation[18] involves reacting equimolar quantities of *fac*-Re(bpy)$(CO)_3$OTf and P-P in *o*-dichlorobenzene (*o*-DCB) (OTf is the trifluoromethanesulfonate anion, and P-P is a bridging diphosphine, e.g., *trans*-1,2-bis(diphenylphosphino)ethylene, t-dppene, or 1,3-bis(diphenylphosphino)propane, dppp)). Remarkably, the resulting product is a tetrameric complex with *trans*-Re(I) dicarbonyl bis-diphosphine units as corners. Although we have no X-ray crystallographic structural data yet, modeling indicates that the metal sites form a loose square motif. These structures will be termed "petite" squares. Another preparation[19] involves reacting *cis*-*trans*-$[Re(CO)_2(P\text{-}P)_2(bpy)]$OTf[17] with $Re(CO)_5Cl$ in *o*-DCB producing two isomeric octametallic complexes possessing Re(I) dicarbonyl *cis*-bis-diphosphine units and either *fac*- or *mer*-$Re(CO)_3Cl$ links. Modeling suggests that such large structures are best viewed as rings due to the conformational flexibility of the diphosphine bridges. These will be termed "grand" rings. In each case the reaction times were between 4 and 18 h, with yields after purification ranging from 75% to 90%.

Elemental analysis data establishes the basic repeating units in the petite squares and the grand rings to be $[Re(bpy)(CO)_2(P\text{-}P)](OTf)$ and $[Re_2(bpy)(CO)_5(P\text{-}P)_2Cl](OTf)$, respectively. Table 1 shows physical data for the four complexes we have isolated, two squares and two rings, in addition to the comparator *cis*-*trans*-$[Re(bpy)(CO)_2(P\text{-}P)_2](OTf)$. Fast atom bombardment (FAB) mass spectrometry data is convincing in support of the overall structural assignments, i.e., the degree of polymerization and the cyclic nature of the oligomers. FAB-MS for complex **1**, which is assigned the overall formulation $[Re(bpy)(CO)_2(P\text{-}P)(OTf)]_4$, shows the "parent" complex as a +1 cation (i.e., the square backbone minus one OTf counterion) at a *m*/*z* of 3627.9. In addition, the theoretical and the observed isotopic distributions for the parent are nearly identical. Some of the more interesting fragments derived from the parent arise from either a symmetric split or the loss of a corner (see Figure 1). FAB-MS for complex **4**, which is assigned the overall formulation $\{[Re_2(bpy)(CO)_5(P\text{-}P)_2Cl](OTf)\}_4$, gives the first recognizable fragment at 6323.7, which corresponds to the +1 "parent" ion minus one OTf and four carbon monoxide ligands. Other diagnostic fragments are found at 5376.6, 4703.9, and 3364.6, which correspond to seven, six, and five metal-containing fragments, respectively. In fact, 13 major fragments are observed, all of which are related to each other by either loss of $Re(CO)_2Cl$, t-dppene, or $[Re(bpy)(CO)_2(t\text{-}dppene)]$OTf aggregates. Similar data is found for complex **3**, except that some fragments containing $Re(CO)_3$ units are found, perhaps reflecting the greater stability of *fac* versus *mer* geometries under the FAB-MS conditions.

A combination of ^1H, ^{13}C, and ^{31}P NMR spectroscopies are of particular help in revealing the geometry around the Re(I) centers ($CH(D)_3CN$ in most cases). ^{31}P NMR spectroscopy on the petite squares shows a single resonance, and that of the grand rings shows two. The shift positions indicate coordination to the Re center in all cases. For the petite squares, the apparent high symmetry that is inferred from the ^{31}P NMR data remains unchanged upon lowering the temperature to −50 °C in CH_2Cl_2. Proton NMR spectroscopy of the petite squares shows four types of bpy protons, three types of phenyl protons, and, in the case of complex **1**, a single type of vinylic proton. The grand rings, however, have complex aromatic regions consistent with two types

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(18) Preparation of [*trans*-*cis*-$Re(CO)_2$(t-dppene)(bpy)$]_4(OTf)_4$ (**1**): *fac*-Re(bpy)$(CO)_3$(OTf) (512 mg, 0.890 mmol) and t-dppene (358 mg, 0.903 mmol) were placed in a 50 mL round-bottom flask containing approximately 15 mL of *o*-dichlorobenzene. The reaction mixture was purged with nitrogen for 20 min and refluxed with magnetic stirring for 12 h, after which the hot *o*-dichlorobenzene was decanted, leaving an orange residue, which was washed four times with 5 mL portions of hot *o*-dichlorobenzene. The residue was dissolved in dichloromethane and reprecipitated by dropping into a stirring mixture of 2:1 diethyl ether: hexanes. The resulting orange-yellow solid was collected, washed with diethyl ether, and air-dried (716 mg, 85% yield). Anal. Calcd for $Re_4C_{156}H_{120}N_8O_{20}P_8S_4F_{12}$: C, 49.63; H, 3.20; N, 2.97. Found: C, 49.43; H, 3.16; N, 2.85.
(19) Preparation of **3**: *cis*-Re$(CO)_2$(bpy)(t-dppene)$_2$(OTf) (**6**) (210 mg, 0.157 mmol) and $Re(CO)_5Cl$ (58 mg, 0.160 mmol) were placed in a 50 mL round-bottom flask containing approximately 25 mL of toluene and purged with nitrogen for 20 min. The reaction mixture was then refluxed with magnetic stirring for 4 h, after which the hot toluene was decanted off, leaving a yellow-orange residue. Reprecipitation was achieved as in footnote 18, resulting in a yellow solid (230 mg, 90% yield). Anal. Calcd for $Re_8C_{272}H_{208}N_8O_{32}P_{16}S_4F_{12}Cl_4$: C, 49.62; H, 3.18; N, 1.70. Found: C, 49.70; H, 3.23; N, 1.68.

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Table 1. Spectral and Photophysical Data for the Complexes[a,b]

complex	IR frequencies (cm^{-1})[c]	^{31}P shifts (ppm)[d]	λ_{abs} (nm)[c]	λ_{em} (nm)[c]	ϕ[c,e]	τ (ns)[f]
(**1**) [*trans-cis*-Re(CO)$_2$(bpy)(t-dppene)]$_4$$^{4+}$	1942, 1866	+18.8	404	615	0.027	485
(**2**) [*trans-cis*-Re(CO)$_2$(bpy)(dppp)]$_4$$^{4+}$	1937, 1866	+16.6	414	631	0.011	208
(**3**) {[Re(CO)$_3$Cl][Re(CO)$_2$(bpy)(t-dppene)]$_2$}$_4$$^{4+}$	2035, 1950, 1943, 1906, 1873	+0.8, +18.1	410	624	0.019	288
(**4**) {[Re(CO)$_3$Cl][Re(CO)$_2$(bpy)(t-dppene)]$_2$}$_4$$^{4+}$	2024 (w), 1956, 1943, 1910, 1874	+5.3, +17.2	410	624	0.020	259
(**5**) *cis-trans*-Re(CO)$_2$(t-dppene)$_2$(bpy)$^+$	1942, 1873	−5.7, +16.6	420	637	0.014	191

[a] All complexes are triflate (OTf) salts. [b] Abbreviations: t-dppene is *trans*-1,2-bis(diphenylphosphino)ethylene, dppp is 1,3-bis(diphenylphosphino)propane, and bpy is 2,2′-bipyridine. [c] Data recorded in CH$_2$Cl$_2$ solution. [d] Data recorded in CD$_3$CN solution versus 85% H$_3$PO$_4$ as external standard. [e] N$_2$ saturated, versus Re(bpy)(CO)$_3$(py)(OTf) as in ref 17. [f] N$_2$ saturated performed on an Edinburgh LP900S1 time-resolved absorption/emission spectrometer.

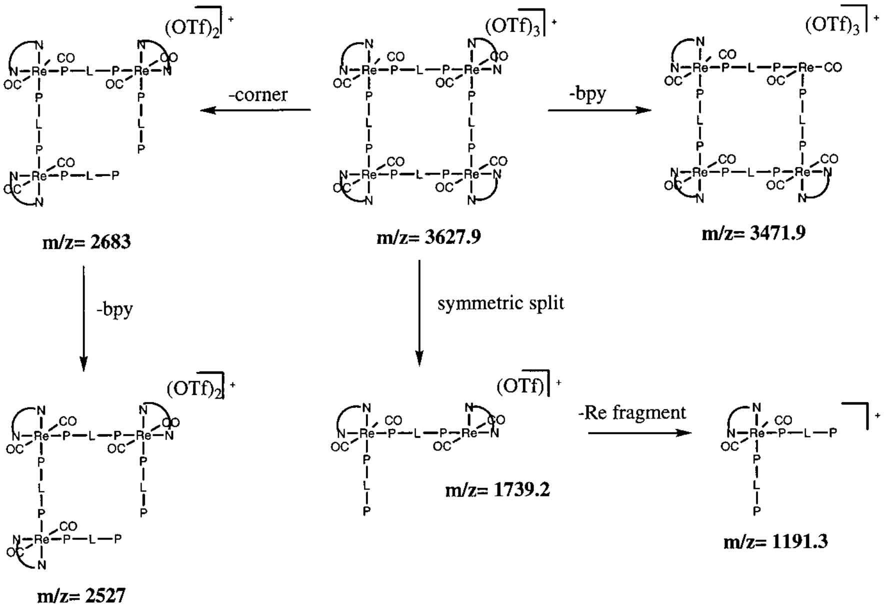

Figure 1. Positive ion FAB-MS fragmentation pattern for [*trans-cis*-Re(CO)$_2$(bpy)(t-dppene)]$_4$(OTf)$_4$ (**1**) in a 3-NBA matrix. Diagnostic fragments are shown.

of t-dppene bridges. Finally, ^{13}C NMR spectral data provide crucial evidence for the symmetry around the metal; e.g., complex **1** possesses a single CO resonance at +202.5, complex **3**, three resonances (+202.7, +191.0, and +190.2), and complex **4**, three resonances (+202.7, +192.7, and +190.1).

For the petite squares, the structure most consistent with all of the NMR spectroscopic data is one with *trans-cis*-Re(CO)$_2$(P-P)$_2$(bpy)$^+$ repeating units. Although a *cis-trans* structure is possible, modeling suggests it is highly unlikely. IR spectroscopy of both petite squares shows two absorptions of nearly equal intensity, which is consistent with effective D_{4h} symmetry. Attempts to observe the Raman allowed modes were fruitless due to intense solid state emission.

The structures of the isomeric grand rings are equivocal; however, attempts to grow crystals of suitable quality for X-ray crystallographic analysis are underway. The best tentative assignment for the nature of the coordination spheres for complex **4** is based on alternating *trans-cis*-Re(CO)$_2$(P-P)$_2$(bpy)$^+$ and *mer-trans*-Re(CO)$_3$(P-P)$_2$Cl moieties. For complex **3** the structure is probably based on alternating *trans-cis*-Re(CO)$_2$(P-P)$_2$(bpy)$^+$ and *fac-cis*-Re(CO)$_3$(P-P)$_2$Cl entities. IR spectroscopy also provides some support for these assignments, since the former exhibits a *fac* and the latter a *mer* pattern[20−24] (see Table 1). Apparently, the mechanism of formation of the grand rings involves formation of the *fac* followed by the *mer* isomer. Thus, complex **3** undergoes thermal isomerization in the solid state when heated beyond 4 h, creating an isomeric distribution of *fac* and *mer* geometries. After 24 h the *fac* to *mer* transformation is complete, as evidenced by IR and ^{31}P NMR spectroscopies, giving complex **4**. The *fac* to *mer* transformation is most evident in the IR spectrum by loss of the highest frequency mode and the appearance of a very weak mode assigned to a *mer* configuration. The transformation is also seen in ^{31}P NMR spectroscopy by the downfield shift of the tricarbonyl-bound phosphorus.

For all of the complexes based on the t-dppene bridge, the MLCT absorption (380−450 nm) and emission maxima (610−650 nm) fall in a narrow range. The quantum yields and lifetimes are relatively large when compared to the classical facial Re(I) tricarbonyls of similar energy gap[25] as has been recently demonstrated for *cis*-Re(CO)$_2$-containing monomers.[17] When **1**, **3**, and **4** are compared to the monomer **5**, it is found that the quantum yields and lifetimes are increased by approximately a factor of 2, while the emission energy is essentially unchanged. Future studies will be directed toward understanding these photophysical differences and to applications in molecular host−guest chemistry.

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