

Luminescent Rhenium/Palladium Square Complex Exhibiting Excited State Intramolecular Electron Transfer Reactivity and Molecular Anion Sensing Characteristics

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Rigid macrocycles based on *cis* bridging ligation of transition metals represent an unusual,^{1–4} and largely new,⁵ class of compounds having tremendous promise in host–guest, inclusion, and molecular recognition chemistry. Most of the available systems are (1) derived from Pt(II) or Pd(II) triflate species, (2) tetranuclear with respect to metal content, and therefore, (3) arranged in square or box-like geometries, with metal atoms defining the corners. We report a simple, but potentially very useful, variant and extension of this theme: incorporation of visible-light-addressable, luminescent metal–ligand components within a square assembly. Induction of photoluminescent characteristics is particularly attractive in the context of eventual molecular sensing applications because it suggests an alternative to ¹H NMR spectroscopy for detection of guest inclusion. Induction of luminescence also opens up the possibility of electronic excited state reactivity and possible manipulation of reactivity by encapsulated guests.

The light-emitting square complex, **1**, was prepared by combining the chromophore *fac*-Re(CO)₃Cl(4,4'-bpy)₂ (**2**)⁶ (105 mg, 0.170 mmol) (4,4'-bpy = 4,4'-bipyridine) with Pd(dppp)-(triflate)₂^{1d} (139 mg, 0.170 mmol) (dppp = 1,3-(diphenylphosphino)propane) in 50 mL of dry CH₂Cl₂. After 12 h of stirring, the pale yellow product was collected as a powder on a glass frit, washed with methylene chloride, and dried under vacuum. The yield was 83%. Elemental analysis data are consistent with the formation of either **1** or a larger assembly with 1:1 Re: Pd stoichiometry.⁷ FAB⁺ mass spectral measurements (*m*-NBA) yielded intense peaks at *m/z* = 2871.7 (2871.2 expected for **1**·H⁺), 2721.0 (**1** – triflate) and 2564.9 (**1** – triflate – 4,4'-bpy), thereby establishing the tetranuclear metal content of the compound. No peaks for compounds of higher mass (e.g., hexanuclear or octanuclear complexes) were found. FT-IR and ¹H NMR measurements (supporting information) yielded additional data supportive of molecular square formation.⁸

Figure 1 shows that the lowest energy transition in the electronic absorption spectrum of **2** is shifted substantially red by formation of the square. The shift is similar to that observed upon ligand protonation in **2**⁶ and is consistent with assignment

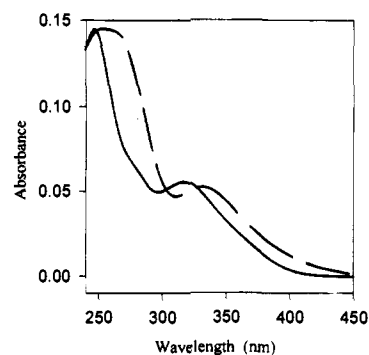
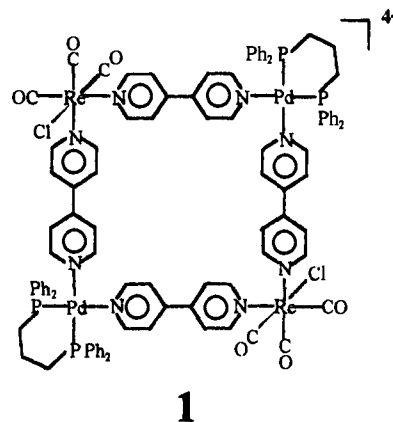


Figure 1. Electronic absorption spectra for $1.01 \times 10^{-6} \text{ M}^{-1}$ **1** (---) and $3.43 \times 10^{-6} \text{ M}^{-1}$ **2** (—) in CH₂Cl₂ as solvent.



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of the feature as a metal-to-ligand charge transfer (MLCT) transition. Thus both H⁺ and Pd(II) should lower the MLCT excited state by electrostatically stabilizing a negative charge in the acceptor (π^* 4,4'-bpy) orbital.

Figure 2 shows that square formation also induces a significant red shift (ca. 1100 cm⁻¹) in emission from the nominally triplet MLCT excited state, while decreasing by ca. 25-fold the emission intensity. Time-resolved luminescence measurements (deoxygenated acetone) demonstrate that the intensity loss is associated with an attenuation of the excited state lifetime: $\tau(\mathbf{2}) = 645 \text{ ns}$; $\tau(\mathbf{1}) = 17 \text{ ns}$. The degree of attenuation clearly is too large to be accommodated by energy gap effects,⁹ instead it is attributed to quenching by the Pd(II) fragments. Bimolecular studies (**2** with added Pd(dppp)(pyridine)₂²⁺ (**3**)) confirm that efficient Pd-based quenching is possible ($k_q = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). The absence of absorption/emission spectral overlap for **3** with either **1** or **2**, however, rules out Förster energy transfer as the quenching mechanism.

The available electrochemical and luminescence data offer insight into the viability of alternative electron transfer (ET) quenching pathways. The potential for oxidation of photo-excited **1** is estimated as ca. -0.9 V based on the difference between the potential for ground state Re(I) (square) oxidation (+1.37 V; reversible wave) and the 0–0 emission energy (~2.24 eV).¹⁰ The corresponding reductive electrochemistry of **1** is complicated. **3**, however, exhibits a well-defined two-electron wave at -0.56 V vs sce and therefore offers an upper limit for the potential of the Pd(II/I) couple. Thus the combined potential data are energetically consistent with an oxidative quenching mechanism¹¹ (i.e., coordinated bipyridyl anion to palladium ET), with $k_{\text{ET}} = 6 \times 10^7 \text{ s}^{-1}$ (based on the availability of two

(9) For related monomeric rhenium complexes (Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952) luminescence lifetimes are dominated by nonradiative decay kinetics ($\tau \approx 1/k_{\text{nr}}$), where k_{nr} increases with decreasing E_{00} (the "energy gap law"). On the basis of the reported monomer behavior, an 1100 cm⁻¹ decrease in E_{00} should yield a ca. 5-fold increase in k_{nr} .

(1) (a) Fujita, M.; Yakazi, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645. (b) Fujita, M.; Yakazi, J.; Ogura, K. *Tetrahedron Lett.* **1991**, *32*, 5589. (c) Fujita, M.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574. (d) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 4981.

(2) (a) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. (b) Stang, P. J.; Whiteford, J. A. *Organometallics* **1994**, *13*, 3776. (c) Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667. (d) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

(3) Rauter, H.; Hillgeris, E. C.; Erxleben, A.; Lippert, B. *J. Am. Chem. Soc.* **1994**, *116*, 616.

(4) Drain, C. M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2313. (5) Nevertheless, at least one early report exists: Stricklen, P. M.; Volcko, E. J.; Verkade, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 2494.

(6) Wrighton, M. S.; Giordano, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 2888.

(7) Calcd for C₁₀₄H₈₄Re₂Pd₂Cl₂F₁₂N₈O₁₈P₄S₄·2CH₂Cl₂: C, 41.88; H, 2.92; N, 3.69; S, 4.22. Found: C, 41.77; H, 2.83; N, 3.82; S, 4.19. ¹H NMR of **1** in acetone-*d*₆ confirms the presence of CH₂Cl₂.

(8) Although the available experimental results are silent on this point, **1** is almost certainly obtained as a mixture of two isomers featuring chloro ligands either on the same side or on opposite sides of the plane containing the four metal centers.

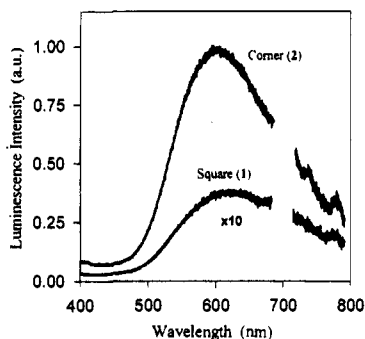


Figure 2. Instrument response corrected emission spectra (note differences in scale) for **1** and **2** in deoxygenated acetone as solvent. For both samples, the absorbance at the excitation wavelength (350 nm) was 0.1.

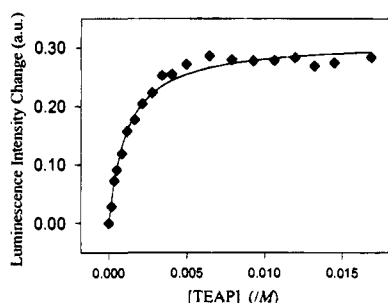


Figure 3. Relative emission intensity ($\lambda_{\text{ex}} = 420$ nm; $\lambda_{\text{em}} = 625$ nm; stray-light-corrected; average of four experiments) for **1** in acetone as a function of added tetraethylammonium perchlorate (TEAP) concentration. $[\mathbf{1}] = 5 \times 10^{-5}$ M. Line shown is a best fit.

quencher per photoexcited square). An alternative reductive quenching pathway can be discounted on the basis of the absence of a signal for the oxidation of **3** below the solvent limit.

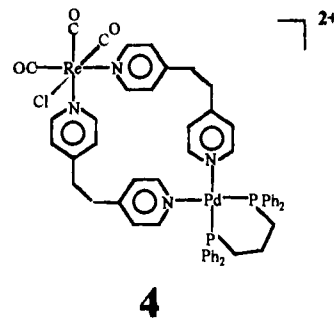
As indicated in Figure 3, emission from the square is enhanced by added tetraethylammonium perchlorate, presumably via ClO_4^- binding in the tetracationic host cavity. A fit of the concentration-dependent luminescence intensity changes yields a guest–host association constant of 900 M^{-1} . (A control experiment with the neutral luminophore, **2**, yields no change in emission intensity with added electrolyte.) The absence of an emission line shape or energy change in the ion-binding experiment (spectra not shown) implies that the guest affects the luminescence efficiency *indirectly*, e.g., by altering the quenching energetics. Indeed, anion encapsulation should preferentially stabilize the oxidized form of the quencher, thereby decreasing the exothermicity of the oxidative quenching reaction and diminishing the quenching rate constant.^{12,13} Time-

(10) E_{00} was extracted from the corrected emission spectrum by assuming that the spectrum is effectively defined by two vibrational modes ($\nu_1 = 1350 \text{ cm}^{-1}$, $S_1 = 1.03$, $\nu_2 = 400 \text{ cm}^{-1}$, $S_2 = 3.0$; S_i is the Huang–Rhys parameter (related to mode displacement); parameters equated with those reported by Caspar (Ph.D. Thesis, University of North Carolina, 1982) for *fac*- $\text{Re}(\text{CO})_3\text{Cl}(2,2'\text{-bpy})$, a solvent reorganization energy (1100 cm^{-1} , also for *fac*- $\text{Re}(\text{CO})\text{Cl}(2,2'\text{-bpy})$: Worl, L. A.; Duesing, R.; Chen, P.; Della Ciana, L.; Meyer, T. *J. Chem. Soc., Dalton Trans.* **1991**, 849), and an empirical (adjustable) “damping” parameter. The analysis entailed a simulation of the spectrum via a time-dependent analysis that views the solvent as both a source of line broadening and a Franck–Condon active mode (see: Myers, A. B. *Chem. Phys.* **1994**, 180, 215). As used here, the damping parameter functions as a nonspecific correction for errors associated with application of literature vibrational and solvent parameters to our system.

(11) See, for example: Fox, M. A.; Wang, P. *Inorg. Chem.* **1995**, 34, 36.

resolved experiments reveal a lifetime increase (up to 21 ns) in the presence of ClO_4^- , consistent with an (admittedly speculative) emission enhancement mechanism involving attenuation of Pd(II) quenching kinetics.¹⁴

Finally, an attempt to extend the synthetic chemistry by replacing 4,4'-bpy with bis(pyridyl)ethane (BPA) as the bridging ligand yielded a compound (**4**) that analyzed correctly for a molecular square,¹⁵ but proved by FAB^+ MS to be a dinuclear metal complex.¹⁶ The formation of macrocyclic dinuclear metal complexes has also been noted by Fujita et al. in their studies with flexible bridging ligands.¹ Curiously, compound **4**, unlike **1**, is undetectably luminescent at room temperature in both acetone and CH_2Cl_2 . Attempts to induce luminescence by perchlorate binding were unsuccessful.



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Supporting Information Available: ^1H , ^{31}P , and ^{19}F NMR and IR data for **1** and **4** (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(12) For related examples based on *cationic* guest inhibition of *reductive* luminescence quenching processes, see: (a) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, 113, 7470. (b) Shen, Y.; Sullivan, B. P. *Inorg. Chem.*, in press.

(13) Although “encapsulation” would appear, from simple electrostatic considerations, to be the most attractive mode of binding, we cannot rigorously exclude other possibilities such as ion pairing to the exterior of the square.

(14) In contrast, in CH_2Cl_2 as solvent somewhat more complicated behavior was encountered: In the presence of excess perchlorate a luminescence intensity *decrease* was observed (ca. 50%) and evidence for association with multiple perchlorate ions was found. Time-resolved measurements ($\tau(\mathbf{2}) = 990$ ns; $\tau(\mathbf{1}) = 20$ ns; $\tau(\mathbf{1} \cdot n\text{ClO}_4^-) = 11$ ns) showed that the decrease was associated with an increase in the rate of intramolecular quenching. The physical basis for the rate increase is unclear. Conceivably, however, it may represent a differential electrostatic effect associated with displacement of triflate counterions already present in or near the cavity of **1** in this low-dielectric solvent.

(15) Calculated for $\text{C}_{112}\text{H}_{100}\text{Re}_2\text{Pd}_2\text{Cl}_2\text{F}_{12}\text{N}_8\text{O}_{18}\text{P}_4\text{S}_4 \cdot \text{CH}_2\text{Cl}_2$ or $\text{C}_{56}\text{H}_{50}\text{RePdClF}_6\text{N}_4\text{O}_9\text{P}_2\text{S}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 44.25; H, 3.35; N, 3.65. Found: C, 43.85; H, 3.38; N, 3.71.

(16) MS m/z (relative intensity; assignment) 2833.7 (3; M – triflate), 2158.9 (4; M – triflate – { $\text{Re}(\text{CO})_3(\text{BPA})_2\text{Cl}$ }); 1860.9 (4; M – 2 triflate – { $\text{Re}(\text{CO})_3(\text{BPA})_2\text{Cl}$ }), 1341.0 (85; 0.5M – triflate), 1156.9 (100; 0.5M – triflate – 4,4'-bpy). M = BPA-bridged tetranuclear metal complex. While indicative of at least trace amounts of tetranuclear metal complex formation, the mass spectral data for **4** are most readily interpreted in terms of predominant generation of the dinuclear complex. Attempts to remove the tetranuclear component via repetitive recrystallization were unsuccessful. In view of the known lability of the Pd–N(pyridine) bond, however, it is conceivable that dinuclear and tetranuclear species (either the desired square complex or catenated dinuclear pairs) exist in equilibrium. (See, for example: Fujita, M; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, 367, 720.)