

Highly Luminescing Rhenium(I) Heterocyclic Ligand Tetracarbonyl Complexes

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The photophysical properties and crystal structure of $[\text{Re}(\text{bpm})(\text{CO})_4](\text{BF}_4)$ (bpm = 2,2'-bipyrimidine) are described: it is revealed that the Re–C(CO) bond distances to the CO ligands *trans* to each other are longer (2.03 Å) than to the CO ligands *trans* to bpm (1.93 Å), and that the cation luminesces strongly in acetonitrile (ϕ_f 0.050, λ_{em} 543 nm, λ_{ox} 355 nm, τ_0 390 ns) at room temperature and undergoes reductive quenching to generate powerful organic and inorganic oxidizing agents.

Our work involves the design of photocatalysts capable of charge transfer either within the same molecular framework or to substrates external to the photochromophore.¹ Most recently our attention has focused on rhenium(I) tricarbonyl complexes of the general formula $[(\text{L}-\text{L})\text{Re}(\text{CO})_3\text{Cl}]$, where L–L is a diimine ligand such as 2,2'-bipyrimidine (bpm).² These complexes have low emissive quantum yields ($\phi_f \leq 10^{-3}$), short excited-state lifetimes ($\tau_0 \leq 50$ ns), and low energy emission maxima ($\lambda_{\text{em}} \geq 600$ nm). We sought to alter these photophysical properties *via* synthetic control and have found a route to prepare the tetracarbonyl analogues whose excited-state properties are dramatically different. We report here a new class of previously unreported luminophores with high emission energies, fairly long lifetimes, and excited states that behave as powerful oxidants.

The complex $[\text{Re}(\text{bpm})(\text{CO})_4](\text{CF}_3\text{SO}_3)$ was prepared according to Scheme 1. $\text{Re}(\text{CO})_5\text{Cl}$ (0.28 mmol) and $\text{Ag}(\text{CF}_3\text{SO}_3)$ (0.27 mmol) were stirred in CH_2Cl_2 (20 ml) for 15 h. The AgCl was removed by filtration and bpm (0.51 mmol) previously dissolved in CH_2Cl_2 (10 ml) was added to the filtrate. After stirring for 5 h, the solvent volume was reduced by a half and hexanes were added to precipitate the product.

Suitable crystals of the BF_4^- salt were grown from CH_2Cl_2 for X-ray analysis (Figure 1).[†] The average Re–N(bpm) bond distance was 2.16 Å and the average Re–C(CO) bond distance for the CO groups *trans* to bpm was 1.93 Å. However, the Re–C(CO) bond distance of the two CO groups *trans* to each other was 2.03 Å.

$[\text{Re}(\text{bpm})(\text{CO})_4](\text{CF}_3\text{SO}_3)$ exhibits four CO stretching vibrations located at 2129, 2029, 2009, and 1974 cm^{-1} (Nujol mull). Typical vibrations of tricarbonyl complexes generally fall in the 2000–1700 cm^{-1} range.³ Thus, the vibration at 2129 cm^{-1} most likely arises from the presence of four CO ligands. In acetonitrile containing tetrabutylammonium hexafluorophosphate (TBAH; 0.1 M) as electrolyte, cyclic voltammetry

from +1.9 to –1.9 V vs. a standard sodium calomel electrode (SSCE) revealed no oxidations, one reversible reduction with $E_{1/2} -0.87$ V (ΔE_p 75 mV, sweep rate 200 mV/s, i_{pc}/i_{pa} 1), and an irreversible reduction with $E_p -1.88$ V. The reversible reduction is ligand centred as illustrated in equation (1). The irreversible reduction is most likely associated with the reduction of the rhenium centre as suggested for the tricarbonyl complexes.⁴

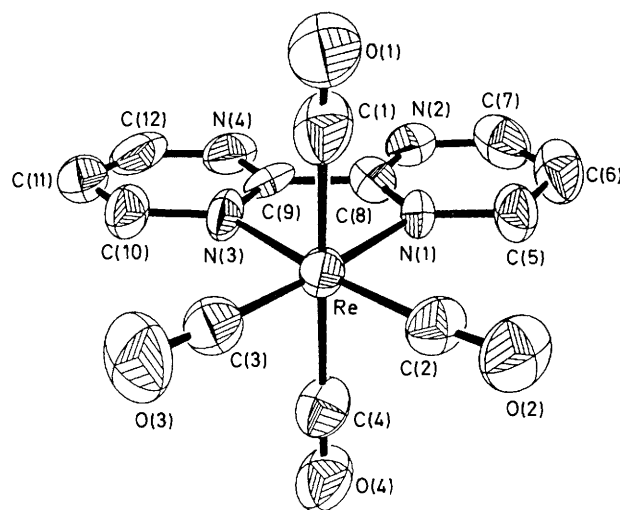


Figure 1. An ORTEP diagram of the $[\text{Re}(\text{bpm})(\text{CO})_4]^+$ cation.

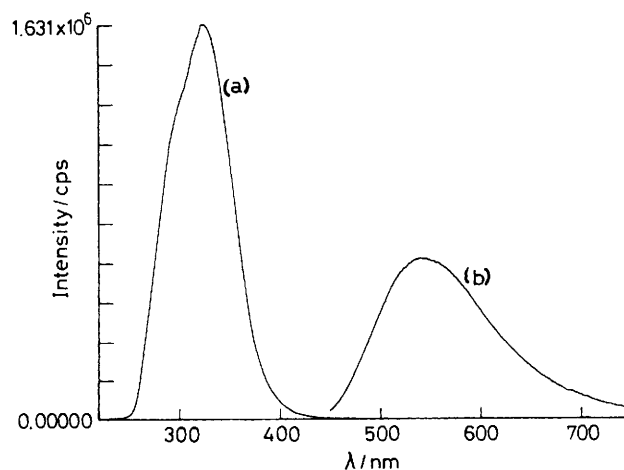
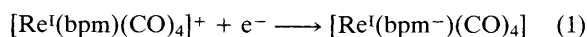


Figure 2. (a) Excitation spectrum of the $[\text{Re}(\text{bpm})(\text{CO})_4]^+$ cation in acetonitrile, λ_{em} 543 nm. (b) Emission spectrum of the $[\text{Re}(\text{bpm})(\text{CO})_4]^+$ cation in acetonitrile, λ_{ex} 355 nm.



Scheme 1. Preparation of $[\text{Re}(\text{bpm})(\text{CO})_4](\text{O}_3\text{SCF}_3)$. Reagents and conditions: i. $\text{Ag}(\text{O}_3\text{SCF}_3)$, CH_2Cl_2 , Ar, room temp., 15 h; ii, bpm, Ar, room temp., 6 h.

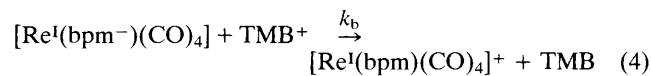
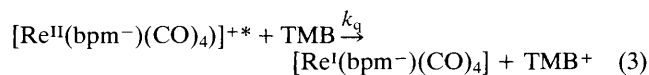
[†] Crystal data for $[\text{Re}(\text{C}_8\text{H}_6\text{N}_4)(\text{CO})_4](\text{BF}_4)$: $M = 543.2$, monoclinic, space group $P2_1/n$, $a = 6.846(2)$, $b = 13.287(3)$, $c = 17.606(4)$ Å, $\beta = 95.58(2)^\circ$, $U = 1594(6)$ Å³, $Z = 4$, $D_c = 2.274$ Mg m⁻³, $F(000) = 1016$, integrated reflections diffractometrically with an incident-beam graphite monochromator and Mo- K_α ($\lambda = 0.71073$ Å) radiation, $\mu(\text{Mo}-K_\alpha) = 7.831$ mm⁻¹. The structure was solved directly with the program SHELXTL PLUS. Least-squares refinement with 1802 non-zero weighted observations led to a final discrepancy index $R_w = 0.0639$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



The $[\text{Re}(\text{bpm})(\text{CO})_4]^+$ cation absorption maxima are located at 319 nm (ϵ $3.2 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and at 246 nm (ϵ $3.2 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), and it emits at 543 nm when excited at 355 nm at room temperature in acetonitrile. The emission manifold is structureless [Figure 2(b)] even down to 77 K, which is consistent with emission from a triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) state.⁵ The excitation maximum is located at 325 nm as illustrated in Figure 2(a). The emission quantum yield ϕ_r 0.050 relative to rhodamine b and τ_0 390 ns. The striking features are the high energy luminescence and the long excited-state lifetime. The lifetime is over one order of magnitude greater than found in $\text{Re}(\text{bpm})(\text{CO})_3\text{Cl}^{2,4}$ suggesting that substitution of the strong field CO ligand for Cl^- decreases the nonradiative decay channel and enhances the radiative decay route according to the energy gap law.⁶

The redox potential of the $[\text{Re}(\text{bpm})(\text{CO})_4]^{+*/0}$ couple [estimated to be 1.43 V by summing the energy (eV) of the emission energy maximum and the potential(V) for the first reduction] suggested that the excited state species would be a powerful oxidant. Experimentally, reductive quenching was verified in acetonitrile [equations (2) and (3)] with the electron donor 1,3,5-trimethoxybenzene (TMB) which has a comparable redox potential ($\text{TMB}^{+/0}$ 1.49 V).⁷ Stern-Volmer behaviour was followed with K_{SV} $1277 \text{ mol}^{-1} \text{ dm}^3$ and k_q $3.2 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. Laser flash photolysis provided spectroscopic evidence for TMB^+ (λ_{max} 600 nm⁸, $\epsilon \sim 4220 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). Back electron transfer for the process illustrated in equation (4) was observed at 600 nm with an estimated rate constant k_b $2.2 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ consistent with the large driving force (ΔG° 2.3 V) for the reaction.⁹

‡ The ϵ_{600} value for TMB^+ was estimated from a paper by R. Scheerer and M. Grätzel, *J. Am. Chem. Soc.*, 1977, **99**, 865, where excess TMB was used to quench the excited state of duroquinone. The calculation assumed 100% conversion to TMB^+ . Hence $\epsilon \sim 4220 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$.



We have further evidence for dynamic quenching by Cl^- . Both luminescence and lifetime measurements follow Stern-Volmer behaviour and have similar Stern-Volmer constants of 3228 and 3135 $\text{mol}^{-1} \text{ dm}^3$, respectively. Whether Cl^- quenching occurs by electron transfer or another mechanism is currently under investigation. We are also investigating a series of rhenium tetracarbonyl complexes containing other diimine ligands such as 2,2'-bipyridine.

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