Long-Lived, Highly Luminescent Rhenium(I) Complexes as Molecular Probes: Intra- and Intermolecular Excited-State Interactions

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Abstract: A series of isonitrile complexes of the form *fac*-LRe(CO)$_3$CNR$^+$, where L is an α-diimine and R = *t*-Bu or *n*-alkyl, have been synthesized and characterized. These complexes can have extraordinarily high quantum yields (>0.7) and long excited-state lifetimes (>100 μs) in fluid solutions at room temperature. The lowest excited state (charge transfer or ligand localized) can be controlled by varying either L or the temperature. Intramolecular foldback can affect the luminescence properties. These complexes are *bihydrophobic* because they have two spacially separated hydrophobic binding sites (i.e. L and R). By suitably engineering the complex, one can control which group will bind to hydrophobic targets such as cyclodextrins. Since the luminescence is strongly localized in the α-diimine portion of the complex, the orientation of the metal complex in the binding site profoundly affects the luminescence and quenching properties that can be used to differentiate between the two binding modes. Since the systems have a near degeneracy of the lowest charge-transfer and ligand triplet state, the luminescence properties can depend strongly on temperature. A three-state model involving the lowest MLCT and $\pi-\pi^*$ states as well as higher energy d–d excited states must be evoked to explain the temperature dependencies of the luminescence. This model is used to assign the ordering and positions of the lowest MLCT and $^3\pi-\pi^*$ states as well as their relationship to the lowest deactivating d–d state.

Introduction

Luminescent transition metal complexes can be used as photosensitizers in such areas as solar energy conversion,[1] electron-transfer studies,[2] chemi- and electroluminescent systems,[3,4] binding dynamics of heterogeneous media,[5] and probes of macromolecular structure.[6] Ru^{II}(L)$_3^{2+}$ complexes (L = 2,2'-bipyridine, 1,10-phenanthroline, or substituted derivatives) have been the most frequently used probes in these applications due to strong visible absorption, high photochemical stability, efficient luminescence, and relatively long-lived metal to ligand charge transfer (MLCT) excited states.[7]

Furthermore, the emitting-state energies and excited-state redox properties of the sensitizers can be very sensitive to variations in the metal, coordinating ligands, and solvent. Solvent and substituents have been used to control the relative positions of different excited states and "tune" photophysical and photochemical properties.[8–10] Many of these sensitizers exhibit a wide variety of energetically accessible charge-transfer (CT), ligand field (LF), and intraligand (IL) excited states. These excited states have different orbital parentage and, thus, quite different excited-state characteristics. Since the photophysical properties of the metal complexes are determined predominantly by the lowest energy excited states,[11] the rational design of new and more useful photosensitizers and probes necessitates an intimate understanding of their excited-state energetics and dynamics.

The majority of work and models for photophysics and photochemistry have been based on sensitizers having lowest lying MLCT states, predominantly Ru(bpy)$_3^{2+}$ (bpy = 2,2'-bipyridine) and related sensitizers. Recently, Os(II),[12] Ir(III),[13] Mo(0), W(0),[14] and Re(I)[15,16] complexes have been studied with increasing

(1) (a) *Energy Resources through Photochemistry and Catalysis*; Grätzel, M., Ed.; Academic Press: New York, 1983. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (c) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

(2) (a) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2858. (b) Lin, C.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97.

(3) (a) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582. (b) Martin, J. E.; Hunt, E. J.; Adamson, A. W.; Gafney, H.; Halpern, J. *J. Am. Chem. Soc.* **1972**, *94*, 9283. (c) Lytle, F. E.; Hercules, D. M. *Photochem. Photobiol.* **1971**, *13*, 123.

(4) (a) Buttry, D. A.; Anson, F. A. *J. Am. Chem. Soc.* **1982**, *104*, 4824. (b) White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6891. (c) D. Bolletta, F.; Balzani, V. *J. Am. Chem. Soc.* **1982**, *104*, 4250. (d) Vogler, A.; El-Sayed, L.; Jones, R. G.; Namnath, J.; Adamson, A. W. *Inorg. Chim. Acta* **1981**, *53*, L35. (e) Kunkely, H.; Merz, A.; Vogler, A. *J. Am. Chem. Soc.* **1983**, *105*, 7241. (f) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.

(5) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*, Academic Press: New York, 1987.

(6) (a) Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5518. (b) Barton, J. K.; Lolis, E. *J. Am. Chem. Soc.* **1985**, *107*, 708. (c) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2172. (d) Barton, J. K.; Basik, L. A.; Danishefsky, A.; Alexandrescu, A. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 1961.

(7) (a) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834 and references therein. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193 and references therein.

(8) (a) Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3184. (b) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213. (c) Ford, P. C. *Rev. Chem. Intermed.* **1979**, *2*, 267.

(9) (a) Pankuch, B. J.; Lackey, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2061. (b) Pankuch, B. J.; Lackey, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2068.

(10) (a) Sutin, N.; Creutz, C. In *Inorganic and Organometallic Chemistry*; Wrighton, M. S., Ed.; Advances in Chemistry 168; American Chemical Society: Washington, DC, 1978; p 1. (b) Creutz, C.; Chou, M.; Netzel, T. L.; Okimura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(11) (a) Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14. (b) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 7262.

(12) (a) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755. (b) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (c) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

(13) (a) Watts, R. J.; Brown, M. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 6029. (b) Watts, R. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 674.

(14) (a) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711. (b) Connor, J. A.; Overton, C.; El Murr, N. *J. Organomet. Chem.* **1984**, *277*, 277. (c) Connor, J. A.; Overton, C. *Inorg. Chim. Acta* **1982**, *65*, L1. (d) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 3385. (e) Wrighton, M. *Chem. Rev.* **1972**, *74*, 401.

(15) (a) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.

Rhenium(I) Complexes as Molecular Probes

J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8231

interest. Some of these systems exhibit even more desirable excited-state properties than the Ru(II) ones.

The additional complexity of multiple luminescences has been observed for a number of transition metal compounds with α-diimine ligands. DeArmond and co-workers originally reported dual ligand localized phosphorescences from heterochelated Rh^{3+} complexes.[17] Watts *et al.* observed multiple CT emissions from Ir^{3+} sensitizers.[13] Wrighton *et al.* have seen dual low-temperature emissions for a number of Re(I) carbonyl compounds.[16] McMillin and co-workers have reported mixed CT and IL emissions at 77 K from tetrahedral Cu(I) complexes.[18] Lees has reported dual MLCT emissions at room temperature for W(0) and Mo(0) carbonyl complexes.[19] Indeed, in low-temperature rigid glasses, multiple emissions may be the rule rather than the exception.

We recently embarked on a detailed study of Re(I) photosensitizers[20] of the form

$$[(bpy)Re(CO)_3NC(CH_2)_nCH_3]^+, \quad n = 0-17$$

Our initial goal was to design cationic complexes that would anchor to cationic micelles. We predicted that for large enough n's the hydrophobic interactions would overcome electrostatic repulsions. This worked well, and for $n \geq 5$, strong binding to cationic cetyltrimethylammonium bromide (CTAB) micelles was observed.

However, we also discovered the remarkable fact that, even in pure solvents, the electronically passive alkyl chain of the nitrile appeared to dramatically perturb the emissions.[20] These changes were highly dependent on the alkyl chain length and resulted from an intramolecular foldback of the chain onto the bpy ligand. This foldback perturbed the solvent environment around the excited portion of the complex and altered the excited-state properties. As we will show, impurities with spectacular luminescence properties were responsible for some of the observed effects.

The preliminary studies indicate that these types of complexes show a remarkable emission sensitivity to local environment. Given the current interest in metal complexes serving as molecular probes and environmental reporters, we have expanded on our studies to determine the subtle factors affecting the environmental sensitivity of these complexes.

Experimental Section

Materials. $Re(CO)_5Cl$ (Pressure Chemical Co.) and α-diimines (GFS Chemical Co.) were used as received. *t*-BuNC was used as received from Aldrich Chemical Co. Other isonitriles were synthesized using literature methods.[21]

High-purity solvents (acetonitrile, methanol, CH_2Cl_2, and toluene) were from Burdick-Jackson Laboratories or Fisher Scientific. All other inorganic salts and solvents were reagent grade. Neutral alumina (Fisher) was used for chromatography. α- and β-cyclodextrins (α-CD and β-CD) were purchased from Sigma Chemical Co. Deionized water was redistilled from alkaline $KMnO_4$.

Syntheses. $LRe(CO)_3Cl$ were prepared as previously described.[15b,16a] Yields were quantitative, and the product was used without purification.

The $LRe(CO)_3NC(CH_2)_nCH_3^+$ were synthesized as reported earlier.[20] The $[LRe(CO)_3NCR](ClO_4)$ were prepared from $ReL(CO)_3$(triflate)[22] by reaction with the isonitrile.[22] Reactions were carried out at room temperature in the dark and generally took several days. Workup was similar to that used for the nitrile. During synthesis and workup, alcohols and water had to be scrupulously excluded, or else intractable mixtures without any isonitrile resulted. Microanalyses were all satisfactory. By NMR and IR, all *n*-alkyl isonitriles were shown to be free of nitriles, and all of the nitrile complexes were free of isonitriles.

Equipment and Procedures. Absorption spectra were obtained using Hewlett-Packard 8450A spectrophotometers. NMR and IR spectra were measured as reported earlier. Corrected emission spectra were obtained as described earlier.[20] Spectra at 298 K typically used 325-nm excitation. The solvent used was CH_2Cl_2. Deoxygenation did not affect the emission band shape or position. Low-temperature (77 K) emissions were in DMF–CH_2Cl_2 (9:2, v/v) glasses. Spectra were collected using excitation at 275–410 nm.

As a probe of emission heterogeneity, we used the excitation spectra method described earlier.[23] For a sample, two uncorrected excitation spectra were measured with different emission wavelengths (λ_1 and λ_2). $R(\lambda)$ is calculated as

$$R(\lambda) = E_1(\lambda)/E_2(\lambda) \tag{1}$$

where the E's are the emission intensities while exciting at λ and monitoring at two different wavelengths λ_1 and λ_2. Since the sample absorbance and excitation intensities are the same at each excitation wavelength, R is related to the relative contributions of different emission components. If there is no ground-state heterogeneity or the equilibration in the excited state is rapid relative to the sample decay times, $R(\lambda)$ is wavelength independent. If there are multiple ground species that fail to equilibrate in their excited states, $R(\lambda)$ varies with λ.

This procedure can be used without either low-temperature absorption spectra or calibrating the excitation output. It compensates for solvent absorption, is insensitive to solution absorbance, and works with fractured glasses.

Excited-state lifetimes (τ's) were measured using a pulsed N_2 laser (337 nm) nanosecond decay time system.[20] Measurements at 298 K were taken using a thermostated cell holder[24], and 77 k measurements were taken using a liquid nitrogen dewar.

Single exponential, multiexponential, or nonexponential luminescence decay curves were observed. All decays were fit by nonlinear least squares[25] to one or a sum of two or three exponentials using a simplex or Marquardt algorithm:

$$I(t) = \sum K_i \exp(-t/\tau_i), \quad i = 1, 2, \text{ or } 3 \tag{2}$$

where $I(t)$ is the luminescence intensity at time t, and the K's and τ's are the preexponential weighting factors and the excited-state lifetimes, respectively. The subscripts denote the components. At room temperature all decays were single exponentials while at 77 K the samples required two or three exponentials for good fits. Decays were typically fit over a factor of 50–100 changes in amplitude with 250–800 points.

For multiple exponential decays we reduce the decays to a single quantity, the preexponential weighted mean lifetime,

$$\tau_M = \sum K_i\tau_i/\sum K_i \tag{3}$$

where the actual decays may be more complex than a sum of a few exponentials; this reduces the lifetime information to a single representative value.

Luminescence quantum yields, Φ_{em}, in deoxygenated CH_2Cl_2 or acetonitrile were measured using the Parker–Rees method.[26] The quantum yield standard was deoxygenated aqueous $[Ru(bpy)_3]Cl_2$ (Φ_{em} = 0.042 at 25 °C),[27] and refractive index corrections were applied.[27]

(16) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Luong, J. C.; Faltynak, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1597. (c) Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2257. (d) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415. (e) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *100*, 2888.

(17) Halper, W.; DeArmond, M. K. *J. Lumin.* **1972**, *5*, 225.

(18) (a) Buckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 5846. (b) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906. (c) Casadonte, D. J. Jr.; McMillin, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 331.

(19) (a) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 572. (b) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 1354.

(20) (a) Reitz, G. A.; Dressick, W. J.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 5344. (b) Reitz, G. A.; Demas, J. N.; DeGraff, B. A.; Stephens, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 5051.

(21) Angelici, R. J.; Quick, M. H.; Kraus, G. A.; Plummer, D. T. *Inorg. Chem.* **1982**, *21*, 2178.

(22) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1244.

(23) Sacksteder, L.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1989**, *28*, 1787.

(24) Buell, S. L.; Demas, J. N. *Anal. Chem.* **1982**, *54*, 1214.

(25) (a) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431. (b) Daniels, R. W. *An Introduction to Numerical Methods and Optimization Techniques*; North Holland, Inc.: New York, 1978. (c) Demas, J. N.; Demas, S. E. *Interfacing and Scientific Computing on Personal Computers*; Allyn & Bacon: New York, 1990.

(26) (a) Parker, C. A.; Rees, W. T. *Analyst* **1962**, *87*, 83. (b) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(27) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

Table I. Absorption and NMR Data for ReL(CO)$_3$CNR$^+$ Complexes

no.	complex	abs λ_{max} (ϵ) (nm)	NMR data (δ vs TMS)
1	[Re(3,4,7,8-Me$_4$phen)(CO)$_3$(CN-t-Bu)]CF$_3$SO$_3$	234 (31 500), 250 (35 400), 278 (35 600), 320 (12 700), 366 (3400)	8.99 (s), 8.43 (s), 2.93 (s), 2.70 (s), 1.24 (s)
2	[Re(3,4,7,8-Me$_4$phen)(CO)$_3$(CN(CH$_2$)$_3$CH$_3$)]CF$_3$SO$_3$	234 (33 600), 254 (38 300), 280 (38 918), 316 (14 500), 348 (5200), 364 (3100)	9.00 (s), 8.32 (s), 3.53 (t), 2.90 (s), 2.66 (s), 1.17 (m), 0.79 (t)
3	[Re(3,4,7,8-Me$_4$phen)(CO)$_3$(CN(CH$_2$)$_7$CH$_3$]CF$_3$SO$_3$	236 (29 400), 250 (33 500), 280 (34 000), 316 (13 100), 368 (3000)	8.98 (s), 8.30 (s), 3.52 (t), 2.85 (s), 2.66 (s), 1.20 (s), 0.87 (t)
4	[Re(3,4,7,8-Me$_4$phen)(CO)$_3$(CN(CH$_2$)$_{11}$CH$_3$)]CF$_3$SO$_3$	236 (29 400), 250 (34 600), 280 (35 000), 324 (11 100), 364 (2650)	9.00 (s), 8.32 (s), 3.53 (t), 2.90 (s), 2.66 (s), 1.1–1.4 (m), 0.87 (t)
5	[Re(4,7-Me$_2$phen)(CO)$_3$(CN-t-Bu)]CF$_3$SO$_3$	234 (38 100), 254 (36 000), 274 (40 700), 318 (12 700), 364 (5600)	9.16 (d), 8.45 (s), 7.84 (d), 3.07 (s), 1.24 (s)
6	[Re(4,7-Me$_2$phen)(CO)$_3$(CN(CH$_2$)$_3$CH$_3$)]CF$_3$SO$_3$	234 (32 800), 252 (30 200), 274 (34 400), 318 (10 600), 346 (6100), 362 (4600)	9.14 (d), 8.33 (s), 7.80 (d), 3.52 (t), 3.02 (s), 1.18 (m), 0.80 (t)
7	[Re(4,7-Me$_2$phen)(CO)$_3$(CN(CH$_2$)$_{11}$CH$_3$)]CF$_3$SO$_3$	234 (33 600), 252 (30 600), 274 (35 300), 320 (10 100), 362 (4000)	9.14 (d), 8.35 (s), 7.79 (d), 3.02 (s), 1.1–1.3 (m), 0.89 (t)
8	[Re(4-Mephen)(CO)$_3$(CN-t-Bu)]CF$_3$SO$_3$	234 (24 500), 252 (24 600), 274 (27 700), 318 (7900), 360 (3470)	9.33 (d), 9.18 (d), 9.00 (d), 8.41 (s), 8.10 (q), 8.10 (q), 7.88 (d), 3.06 (s), 1.23 (s)
9	[Re(5-Mephen)(CO)$_3$(CN-t-Bu)]CF$_3$SO$_3$	236 (37 500), 252 (22 500), 280 (31 200), 324 (7600), 374 (3500)	9.36 (d), 9.24 (d), 8.98 (d), 8.84 (d), 8.15 (q), 8.13 (s), 8.03 (q), 2.98 (s), 1.22 (s)
10	[Re(phen)(CO)$_3$(CN-t-Bu)]CF$_3$SO$_3$	232 (28 300), 252 (22 000), 274 (24 900), 320 (6500), 364 (2900)	9.35 (d), 8.96 (d), 8.35 (s), 8.11 (q), 1.25 (s)
11	[Re(5-Clphen)(CO)$_3$(CN-t-Bu)]CF$_3$SO$_3$	236 (32 000), 256 (21 900), 280 (26 900), 324 (7000), 370 (3400)	9.44 (d), 9.35 (d), 9.13 (d), 8.91 (d), 8.43 (s), 8.17 (m), 1.27 (s)
12	[Re(4,7-Ph$_2$phen)(CO)$_3$(CN-t-Bu)]CF$_3$SO$_3$	236 (29 400), 256 (24 300), 292 (36 300), 330 (18 300), 386 (7000)	9.41 (d), 8.21 (s), 7.97 (d), 7.55–7.75 (m), 1.34 (s)
13	[Re(bpy)(CO)$_3$(CN-t-Bu)]CF$_3$SO$_3$	250 (21 300), 318 (13 600), 308 (11 600), 338 (4300)	9.11 (d), 8.91 (d), 8.39 (t), 7.64 (t), 1.30 (s)

Radiative (k_r) and nonradiative (k_{nr}) decay rate constants for the emissions were obtained from Φ_{em} and the observed lifetime, τ_{obs}:

$$\tau_{obs} = (k_r + k_{nr})^{-1} \qquad (4)$$

$$\Phi_{em} = k_r \tau_{obs} \qquad (5)$$

In eq 5 it is explicitly assumed that the emitting state is formed with unit efficiency. This condition is known to be fulfilled for the related MLCT excited states of Ru(II) and Os(II) α-diimine complex type sensitizers,[11b,28] and we assume the same is true for the Re(I) complexes. We also calculate an intrinsic lifetime, $\tau_{intrinsic}$, which is the lifetime that would be measured in the absence of nonradiative decay.

$$\tau_{intrinsic} = 1/k_r \qquad (6)$$

To obtain sensitizer–cyclodextrin equilibrium binding constants, titration curves of τ versus [CD] were carried out as described earlier.[20,29] Measurements were made in either deaerated (nitrogen purged) or oxygen-saturated (bubbled with pure oxygen) solutions. The τ versus [CD] data were fit by a simplex nonlinear least squares routine.[25]

Stern–Volmer (K_{SV}'s) and bimolecular oxygen quenching rate constants (k_q's) for sensitizers in pure solvent and aqueous CD solutions were obtained from the slopes of plots of τ_0/τ versus [O$_2$].

$$\tau_0/\tau = 1 + k_q\tau_0[O_2] = 1 + K_{SV}[O_2] \qquad (7)$$

τ_0 and τ are the photosensitizer lifetimes in the absence and presence of O$_2$, respectively. Literature values for the O$_2$ solubilities were used.[30] Oxygen solubility in the CD solutions was assumed to be the same as that for water.

Temperature Dependence Studies. Lifetimes in deoxygenated ethanol were measured as a function of temperature. Samples were cooled with dry ice ethanol slurry or water. The temperature of the sample was measured immediately above the excited region with an Omega platinum resistance thermometer monitored with a digital voltmeter. Temperatures were read from a calibration table of resistance that was accurate to better than 0.5 °C.

Results

Characterization. The nitrile complexes have been assigned as facial isomers.[16d] All of the isonitriles were prepared by an even milder route, and we conclude that all are facial isomers.

(28) (a) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, *18*, 3177. (b) Taylor, D. G.; Demas, J. N. *J. Chem. Phys.* **1979**, *71*, 1032.

(29) Cline, J. I., III; Dressick, W. J.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1985**, *89*, 94.

(30) *IUPAC Solubility Data Series, Volume 7, Oxygen and Ozone*; Battino, R., Ed.; Pergamon Press: Great Britain, 1981.

The solid Re(I) complexes are thermally and photochemically relatively inert and are soluble in most organic solvents except alkanes. The complexes all show low levels of solution photo-degradation. Once isolated, they are amazingly robust in alcohol or aqueous solutions and will persist without significant decomposition for days in the dark. This result is quite unexpected since introducing alcohol at any stage in the synthesis or purification completely destroys the complexes.

Spectra. Absorption and NMR spectra of the isonitrile complexes are summarized in Table I. The spectral maxima of the low-energy absorption band around 340–370 nm and the more intense higher energy absorption at about 275 nm are the characteristic MLCT and π–π^* absorptions, respectively. These are so characteristic that no spectra are reproduced. For coordinated RCH$_2$NC complexes, the methylene NMR resonance at 3.54 ppm is characteristic of an isonitrile. There is no evidence for the characteristic methylene resonance of RCH$_2$CN at 2.45 ppm in the isonitrile complexes. Thus, our synthesis of the isonitriles produces pure isonitriles. Furthermore, IR supported the assignments of pure isonitrile and nitrile complexes. The characteristic NC stretch of the isonitrile is present at about 2230 cm^{-1} in all isonitriles while the characteristic 2300 cm^{-1} CN nitrile stretch is absent. Similarly, our nitrile complexes were free of isonitrile CN stretch.

Luminescence Data. Room temperature emission spectra for a number of the complexes are shown in Figure 1. The 5-Mephen (phen = 1,10-phenanthroline) was essentially identical to the 4-Mephen complex and is not duplicated. Figure 2 shows 77 K emission spectra for several complexes.

Room temperature luminescence quantum yields (Φ_{em} at 298 K), k_q's for oxygen quenching, radiative and nonradiative rate constants, and intrinsic lifetimes are summarized in Tables II and III for CH$_2$Cl$_2$ and acetonitrile, respectively. Table II also includes the 77 K emission results and lifetimes. At 77 K the data were fit well by a double-exponential decay. We present both a τ_M and the results of the double-exponential fit.

Figures 3 and 4 show representative β-cyclodextrin titration curves for Me$_2$phen/n=11 and phen/t-Bu in both deaerated (A) and oxygen-bubbled (B) solutions. For the oxygenated fits for the Me$_2$phen/n=11 complex (Figure 3), fits to a single and dual (vide infra) binding models are shown.
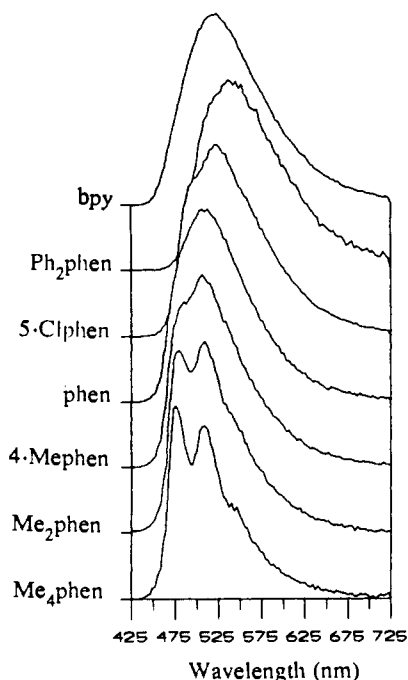
Rhenium(I) Complexes as Molecular Probes

J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8233

Figure 1. Room temperature emission spectra of $LRe(CO)_3(CN-t-Bu)^+$ in CH_2Cl_2.

For phen/t-Bu in oxygenated solutions (Figure 4B), the data are presented in two ways. The data for curve 1 were derived by fitting the decay curves to a single lifetime. The best fit to this curve uses a 1:1 CD binding model with a rapid exchange. The fit is excellent for $K_{eq} = 226$ M^{-1}. However, this value is in poor agreement with the nitrogen-purged sample in Figure 4A (720 M^{-1}) and is well outside experimental error. Thus, we need to reconcile this discrepancy.

The origin of these discrepancies can be traced to the assumption of a rapid exchange of free and included complex. Close inspection of the oxygenated luminescence decay curves shows that they are not well represented by a single-exponential decay but require a biexponential fit. Although the two decay times are difficult to resolve accurately, they appear to have values close to that of the uncomplexed τ and the limiting τ at infinite cyclodextrin concentration. The accurate resolution of multiexponential decay is a problem well-known for its difficulty.

To circumvent the inaccuracies of complete decay time resolution with two unknown lifetimes and two preexponential factors, we exploited the fact that we know one of the lifetimes and can make an accurate estimate of the other. The uncomplexed lifetime is directly measured, and the lifetime of the complexed form is the limiting lifetime extrapolated to infinite [CD] from the single-exponential fit. Thus, fitting our decays becomes the much more accurate exercise in fitting only two preexponential factors with known lifetimes. The double-exponential fits to the luminescence decays were all acceptable.

The "double-exponential" fit in Figure 4B (part 2) shows τ_M versus [CD]; fitting of this data gives excellent fits to the titration data. More importantly, however, the K_{eq} is 660 M^{-1}, which matches that for the deaerated solution. Thus, the failure to get matching K_{eq}'s for deoxygenated and oxygenated solutions is a failure of the rapid exchange model. In other words, the exchange time is slow compared to the decay time. This effect is so pronounced that, even with a purely analog oscilloscope with poorer resolution than our digital oscilloscope, the failure to obtain satisfactory agreement between oxygenated and deoxygenated samples would serve as a clear warning of the failure of the slow exchange model.

Why must the double exponential fitting procedure be invoked for some, but not all, data? There are several reasons. For longer lived samples without oxygen quenching, exchange can become
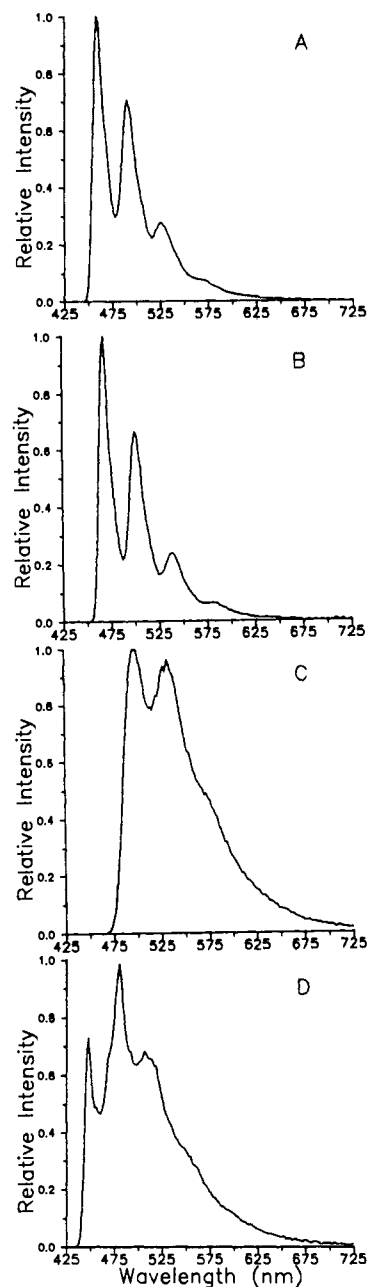

Figure 2. Low-temperature emission spectra of $LRe(CO)_3(CN-t-Bu)^+$ in 9:2 DMF/CH_2Cl_2. (A) L = phen. (B) L = Me_4phen. (C) L = Ph_2phen. (D) L = bpy.

competitive with, or dominate over, the decay rates; the assumption of a single average lifetime then holds, and multiexponential fits are not required. Secondly, for other systems the differences between the bound and unbound forms are relatively small. From earlier simulations, we reported that as long as the lifetimes were within less than a factor of 2 of each other, the same equilibrium constants were obtained in fitting regardless of whether exchange was rapid or slow. This is fortuitous as in these cases it allowed a typically analog instrument to provide satisfactory results even though it would give no warning of nonexponential decays.

Figure 3 for the Me_2phen/n=11 complex shows another interesting complication. The dashed line is the best fit for a single binding site. While the agreement is reasonable for the oxygenated data, the fit shows some obvious discrepancies for the deoxygenated case. In particular, while the very lowest concentration data is fit well, there is a curvature to the fit that is not well described by a single binding site. However, this complex has a potential binding site at the hydrophobic Me_2phen as well as at the alkyl chain, which we have shown earlier has a high

Table II. Luminescence Properties of $ReL(CO)_3CNR^+$ Complexes

no.	τ_0(298 K) (μs)	$10^{-8}k_q$ (M^{-1} s^{-1})	Φ	$10^{-4}k_r$ (s^{-1})	$10^{-4}k_{nr}$ (s^{-1})	$\tau_{intrinsic}$ (μs)	em λ_{max} (77 K) (nm)	τ(77 K)^a (ms)
1	120.7	2.7	0.47	0.39	0.44	260	468	0.52 (59% 0.29, 41% 0.85)
2	120.3	2.4	0.41	0.34	0.49	290	468	0.53 (56% 0.26, 44% 0.88)
3	139.9	2.4	0.40	0.29	0.43	350	468	0.36 (55% 0.56, 45% 0.11)
4	135.1	2.5	0.39	0.29	0.45	350	468	0.33 (94% 0.29, 6% 0.90)
5	70.5	2.3	0.48	0.68	0.74	150	466	0.55 (51% 0.81, 49% 0.29)
6	63.3	2.1	0.56	0.89	0.70	110	466	0.62 (55% 0.32, 45% 0.98)
7	68.9	2.1	0.53	0.77	0.68	130	466	0.35 (92% 0.30, 8% 0.92)
8	23.8	2.3	0.68	2.86	1.34	35	462	0.29 (58% 0.14, 42% 0.51)
9	28.7	3.1	0.69	2.39	1.09	42	466	0.33 (61% 0.15, 39% 0.61)
10	10.6	1.8	0.77	7.22	2.19	14	458	0.13 (63% 0.06, 37% 0.26)
11	19.2	2.3	0.75	3.90	1.30	26	474	0.37 (60% 0.67, 40% 0.67)
12	44.4	3.4	0.60	1.35	0.90	74	496	0.12 (66% 0.07, 34% 0.21)
13	1.97	2.1	0.59	30.1	20.7	3	448	0.013 66% 0.008, 34% 0.023)

^{a} Multiexponential. Weighted average.

Table III. Luminescence Properties of $ReL(CO)_3CNR^+$ Complexes in MeCN

no.	τ_0(298 K) (μs)	$10^{-9}k_q$ (M^{-1} s^{-1})	Φ	$10^{-4}k_r$ (s^{-1})	$10^{-4}k_{nr}$ (s^{-1})	$\tau_{intrinsic}$ (μs)
1	74.6	1.2	0.22	0.30	1.04	330
5	60.1	1.0	0.37	0.61	1.05	160
8	20.2	1.2	0.46	2.25	2.69	44
10	7.4	1.4	0.49	6.57	6.94	15
12	38.3	1.0	0.40	1.05	1.56	95
13	1.1	2.4	0.23	20.6	69.2	5

affinity for CD.[20] The solid lines represent the best two binding site models with the same fitting parameters used in both figures. The improved agreement suggests that both the Me₂phen and the $n = 11$ isonitrile can bind similarly to CD.

For the Ph₂phen/BuNC in the presence of CD we did observe small luminescence rises in the decay curves. These rise times were much shorter than the main decays and showed complex dependencies on [CD]. These rise times are not present in the absence of CD, and instrumental artifacts have been precluded as their source. The rise times grow longer as the temperature is lowered. We are still trying to model them, but they clearly arise from some type of reequilibration of the excited species. This fast reequilibration has no effect on the remainder of our fittings, which are all based on the slower steady–state decay regions.

Temperature Dependence Studies. For several representative complexes the variations in excited-state lifetimes as a function of temperature are shown in Figure 5. The solid lines are the theoretical fits using the model described below.

Discussion

We had earlier[20] attributed the large chain length dependence of the luminescence decay times of $Re(bpy)(CO)_3NC(CH_2)_nCH_3^+$ complexes to an intramolecular foldback of the alkyl chain onto the excited α-diimine portion of the molecule. We have traced the large effect to increasing amounts of isonitrile complexes in the products. The unexpected chemistry that produces isonitriles with nitrile starting materials turned out to be irreproducible, and we have been unable to reproduce the original mixtures. All of our current syntheses produce only nitriles from nitrile starting material.
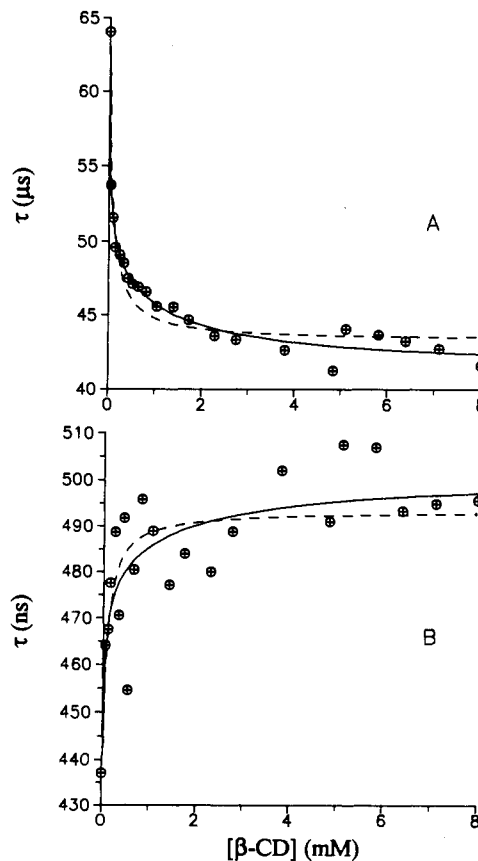

Figure 3. β-Cyclodextrin titration for Me₂phenRe(CO)₃CN(CH₂)₁₁CH₃)⁺. (A) N₂ saturated. (B) Oxygen saturated. (- - -) best fit, single binding. (—) best fit, double binding.

We find that with isonitrile-free nitrile complexes there is still a chain length dependence on τ; however, the effect is much more muted than observed earlier. The lifetime only increases by about 10% compared to the ≈50% observed earlier. The level of effect is similar to our later results with $OsL_2(CO)NC(CH_2)_nCH_3^{2+}$, which were free of any isonitrile contaminants. This places our effects more in line with those observed in Cu and Zn 1,10-phenanthroline complexes coordinated with alkyl carboxylic
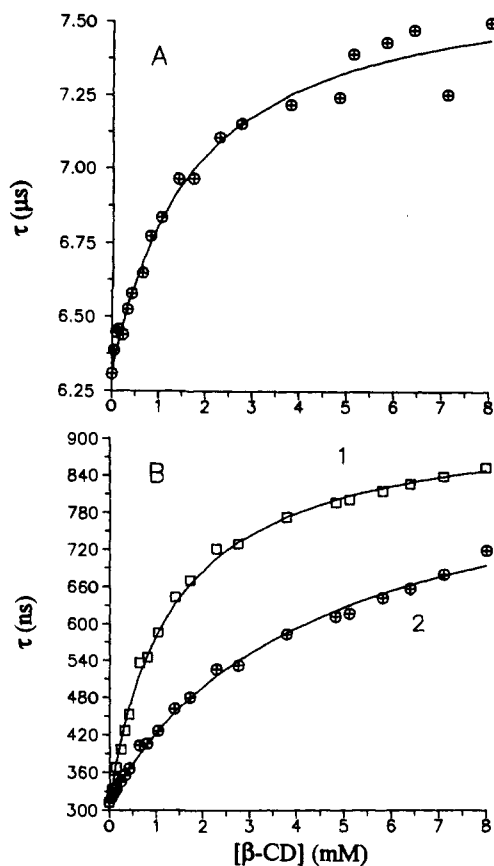
Rhenium(I) Complexes as Molecular Probes

J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8235

Figure 4. β-Cyclodextrin titration for phenRe(CO)$_3$NC(t-Bu)$^+$. (A) N$_2$ saturated, K_{eq} = 720 M^{-1}. (B) Oxygen saturated, K_{eq} = 226 M^{-1}. (1) Single exponential lifetime fit. (2) Double exponential lifetime fit to τ_M. The solid lines are the best fits.

acids.[31] With increasing n the alkyl chain spent more time folded over the exposed phen face. Even for relatively long chains, however, the percentage of folded or closed form did not greatly exceed 40%. Our earlier CD binding studies were not affected by the presence of isonitrile contaminants.

It was, however, the obviously much higher quantum yields and longer lifetimes for the isonitrile impurities that led us to study isonitrile complexes. These complexes have turned out to have extraordinary high luminescence quantum yields and long lifetimes in fluid solution. Some of the yields approach 80%, and some of the excited-state lifetimes are greater than 130 μs at room temperature, although not with quite such high yields. These characteristics make the complexes very attractive from the standpoint of sensors and molecular probes. Particularly in bioprobes, rotational probes with such long lifetimes typically have miserable luminescence quantum yields.

Absorption Spectra. The absorption bands at about 250 and 320 nm can be clearly ascribed to ligand-localized π–π^* transitions. This assignment is based on the striking similarity in energy, extinction coefficient, and band shape to the transitions observed in the free ligand. This result is similar to that for analogous bpy and phen complexes.[32]

The intense transitions at about 275 and 330–360 nm are clearly different from the ligand transitions. We assign these bands to CT transitions. These bands do not occur in the spectra of the uncoordinated phen ligands or the Re(CO)$_5$Cl starting material. They are clearly CT in nature.

(31) (a) Sigel, H.; Malini-Balakrishnan, R.; Haring, U. K. *J. Am. Chem. Soc.* **1985**, *107*, 5137. (b) Malini-Balakrishnan, R.; Scheller, K. H.; Haring, U. K.; Tribolet, R.; Sigel, H. *Inorg. Chem.* **1985**, *24*, 2067. (c) Sigel, H.; Fischer, B. E.; Farkas, E. *Inorg. Chem.* **1983**, *22*, 925. (d) Sigel, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *6*, 389.

(32) (a) Carstens, D. W. H. Ph.D. Dissertation, University of New Mexico, 1968. (b) Yamasaki, K. *Bull. Chem. Soc. Jpn.* **1937**, *12*, 390. (c) Sone, K.; Krumholz, P.; Stammreich, H. *J. Am. Chem. Soc.* **1955**, *77*, 777.
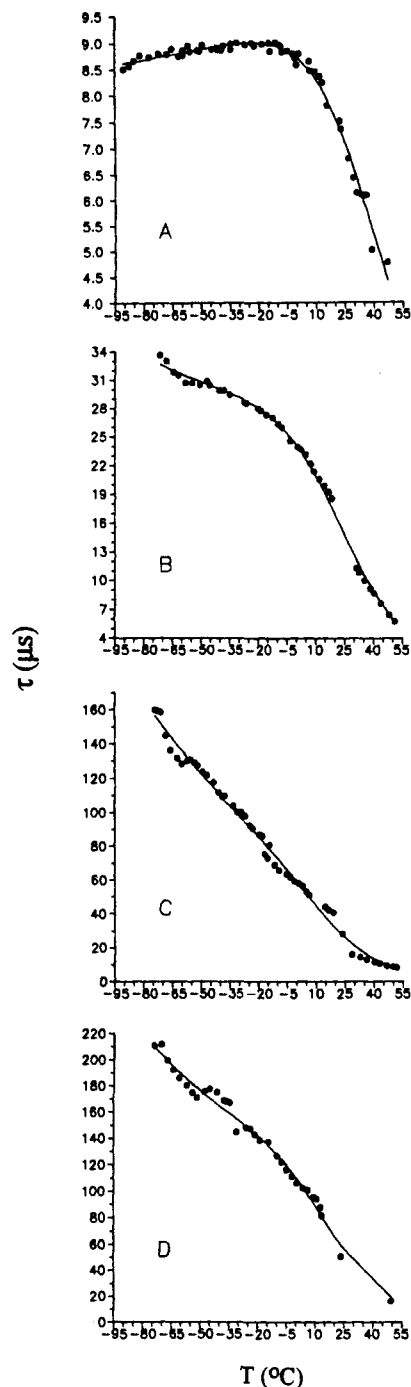

T (°C)

Figure 5. Temperature dependence studies for the luminescence lifetime of LRe(CO)$_3$(CN-t-Bu)$^+$. (A) L = phen. (B) L = 4-Mephen. (C) L = Me$_2$phen. (D) L = Me$_4$phen. The solid lines are the best fits using the three-state model of Figure 6.

We assign the low-energy band as an MLCT transition, as it is too low in energy to be metal to carbonyl.[20] The low-energy band in the analogous n = 0 phen complex has been previously assigned to an MLCT absorption.[16d]

We also assign the higher energy 275-nm transitions to a metal to ligand CT transition. While not definitive, analogous pairs of MLCT transitions are well-known in the visible and near-UV spectra of W(0) and Mo(0) α-diimine systems.

Room Temperature Emission Data. Tables II and III show the radiative and radiationless decay rate constants at room temperature. The luminescence quantum yields are remarkably high for room temperature solutions of species with such long excited-state lifetimes.

We assume that all of the emissions originate from the lowest π–π^* or MLCT states. This would make the emissions originate

from a formal triplet state. This makes the emissions spin forbidden and, thus, ligand or MLCT phosphorescences.

For labeling convenience we use singlet and triplet notations for the CT states. In fact, spin–orbit coupling is very large in the CT states, and S is not a good quantum number. The CT states are best described as spin–orbit states. Indeed, the emitting CT state of Ru(bpy)$_3^{2+}$ can function very efficiently as both singlet and triplet sensitizers.[33] In the current context, we use a singlet notation to denote an allowed transition with a high extinction coefficient and a triplet notation for the less strongly absorbing transition that gives rise to the emission.

At room temperature the emission spectra show a clear progression from broad structureless MLCT to highly structured π–π^* phosphorescences on going from bpy to phen to Mephen to Me$_2$phen to Me$_4$phen. The Me$_4$phen complex shows an almost completely π–π^* phosphorescence. The trend in π–π^* character revealed in the emission spectra is paralleled by the changes in $\tau_{Intrinsic}$ with the Me$_2$phen and Me$_4$phen complexes being well over 100 μs, which is characteristic of a π–π^* emission, but not of an MLCT one. The Ph$_2$phen complex shows no evidence for π–π^* emission, but the ligand is quite different from any of the passively substituted phen ligands.

The intramolecular chain foldback appears to be operative for the Me$_4$phen complexes. The t-BuNC and CH$_3$(CH$_2$)$_3$NC complexes cannot experience significant foldback while the n = 7 and n = 11 isonitriles can. There is a clear increase in lifetime and intrinsic lifetime for the longer chains along with a decrease in quantum yield. For the Me$_2$phen complexes the effect is muted. Since increasing foldback should shift the lowest MLCT state to higher energy, we would expect the intrinsic lifetime to increase as the amount of π–π^* character in the emitting state increases. The presence of the foldback effect is a consequence of the close proximity of the lowest MLCT and π–π^* states ($\approx$330 cm^{-1}, *vide infra*). Small changes in the energy of the MLCT state relative to the π–π^* state can significantly affect their relative populations and, thus, the emission properties.

A parallel effect is not seen for the Me$_2$phen complexes. However, in this case the π–π^* and MLCT states are further apart (640 cm^{-1}) compared to the Me$_4$phen complexes, and foldback has a correspondingly smaller effect on the emission properties.

There is a negative correlation between observed room temperature lifetime and quantum yield. Shorter lived species with more MLCT character have higher yields. Increasing MLCT character increases k_r; it also increases k_{nr}, but not as rapidly. Thus, the net effect is an enhanced yield for shorter lived, more MLCT-like emission. The complexes with lowest π–π^* states have such long lifetimes that they are more efficiently deactivated by radiationless processes. However, the effect is not as severe as one might expect because, while the lifetimes vary by a factor of 14 for the phen complexes, the quantum yields vary by only a factor of 2.

For this class of molecules there appears to be little effect due to varying the solvent from CH$_2$Cl$_2$ to acetonitrile. The yields, lifetimes, and intrinsic lifetimes vary little. Where the yields are lower in acetonitrile, it is principally k_{nr} that is increasing to reduce the lifetime.

Low-Temperature Emission Data. The emissions at 77 K (Figure 2) exhibit a spectacular change in character as L varies. All of the complexes show increased π–π^* character at 77 K versus room temperature as evidenced by the increase in structure. Except for the bpy complex, all of the complexes have a lifetime component that clearly falls in the range expected for a heavy atom perturbed or MLCT mixed π–π^* phosphorescence (>100 μs).

The bpy complex clearly shows a highly structured π–π^* phosphorescence riding on a more intense underlying broad,

(33) Mandal, K.; Pearson, T. D. L.; Krug, W. P.; Demas, J. N. *J. Am. Chem. Soc.* 1983, *105*, 701.

structureless MLCT emission. From the known structure of the bpy π–π^* phosphorescence, we estimate that >80% of the total emission is MLCT in character, although the resolved lifetimes of 8 and 23 μs are more consistent with only an MLCT emission. The absence of a long-lived π–π^* component may arise from our inability to resolve a very long-lived component in the presence of intense short-lived components or may be due to mixing of MLCT character into a π–π^* state to make it more allowed. This is not surprising as earlier results have shown that bpy has the greatest tendency to give MLCT emissions relative to π–π^* phosphorescences.[20]

The R values are flat for excitation from 270 to 380 nm. Thus, regardless of excitation wavelength only one basic excited state is present. This result is in marked contrast to a variety of other ReL(CO)$_3$X species studied earlier.[23]

However, the decay data do indicate an inhomogeneous population of emitters. In view of the well-known ability of a sum of two exponentials to mimic a variety of distribution functions, we do not suggest that the two decay times of Table II represent two discrete sites. However, even if the data are represented by a distribution, there must be components at least as short as the shortest fit τ and as long as the longest fit τ. It is clear that at low temperatures all of the complexes except 13 have significant emission components in the 0.11–0.80-ms range. These values are clearly associated with π–π^* phosphorescences. These significant ligand contributions to the emission are also seen by the highly structured emissions that bear a striking resemblance to the L π–π^* phosphorescences.

Oxygen Quenching Constants. Within either acetonitrile or CH$_2$Cl$_2$ there is little variation in k_q for all the complexes. However, there is about a factor of 5 difference in rate constant on going from CH$_2$Cl$_2$ to acetonitrile. All quenching is well below the diffusion-controlled limit. Since in CH$_2$Cl$_2$ we are certainly varying the emitting states from MLCT to IL ($\tau_{Intrinsic}$ spans 3–350 μs), it is clear that the quenching constant does not depend on the orbital parentage of the excited state. That the rates are below the diffusion limit may arise in part because of steric consideration; excitation is localized on one portion of the molecule, and collisions with only that part will quench.

Steric effect cannot account for the large solvent variations, however. Since the viscosity of acetonitrile and CH$_2$Cl$_2$ are nearly the same, the variation in quenching constants is not likely to be a consequence of changes in the diffusion coefficients. Apparently something about the microstructure of the encounter complex such as orientation or duration assists energy transfer in acetonitrile. We suggest that the order of the acetonitrile may make departure of an O$_2$ slower and may increase the chances of a successful quenching encounter.

Temperature Dependence Studies. The widely used model for the temperature dependence of excited states of transition metal complexes invokes a temperature-activated decay from the emitting state through an upper d–d excited state. We have attempted to fit our decay data with this two-state model. While it can give reasonable fits, the fitting parameters such as ΔE do not vary in a physically reasonable fashion; ΔE decreases from over 4000 cm^{-1} to less than 2000 cm^{-1} on going from phen to Me$_4$phen. Given the relatively small change in state energies and the similar expected crystal field strength of the ligands, this is not realistic. In addition, different rate constants do not vary in a realistic fashion.

However, we had predicted that the two-state d–d model would fail in these systems. All our molecules have the added complexity of two emissive states (e.g. MLCT and $^3\pi$–π^*) relatively close to each other in addition to the upper deactivating d–d state. Thus, we invoke a three-state model (Figure 6). This model assumes that the two lowest lying states, 0 and 1, are potentially emissive. The total rates of decay to the ground state (radiative and nonradiative) for the two states are k_0 and k_1, respectively. These two states are the triplet MLCT and a $^3\pi$–π^*. In addition, each state is deactivated to the ground state via radiationless

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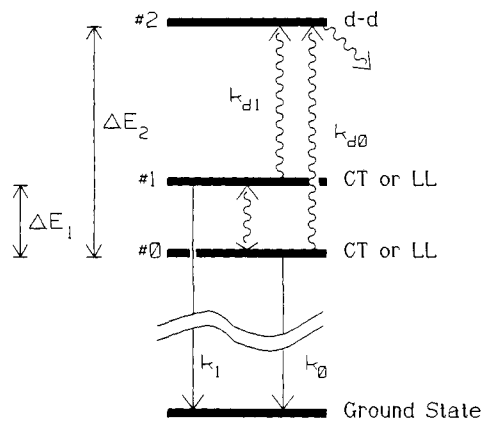
J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8237

Figure 6. Three-state model used in fitting temperature dependences of the excited-state lifetimes.

Table IV. Fitting Parameters of versus T Data[a]

L	ΔE_1 (cm^{-1})	ΔE_2 (cm^{-1})	$10^{-3}k_0$ (s^{-1})	$10^{-3}k_1$ (s^{-1})
phen	390	3800	121	2.39
4-Mephen	130	3800	3.06	99.2
Me$_2$phen	640	3900	3.64	283
Me$_4$phen	330	4100	1.37	41.8

[a] $k_{p0} + k_{p1} = 4 \times 10^{12}$ (fixed).

decay through an upper d–d state. We assume that the d–d state is so efficiently deactivated that once reached the molecule can only deactivate. Also, the rates for reaching the d–d state obey an Arrhenius activation equation.

$$k_{d0} = k_{p0} \exp(-\Delta E_1/kT) \quad (8a)$$

$$k_{d1} = k_{p1} \exp(-\Delta E_2 \cdot \Delta E_1)/kT) \quad (8b)$$

where k_{pi} is the preexponential factor associated with deactivation through the d–d state from the MLCT and $^3\pi$–π^* states, and the ΔE's are the energy gaps in Figure 6. If decay from state 0 and state 1 obeys this equation and the two lowest states are in thermal equilibrium with each other, then the observed lifetime is

$$\tau_{obs} = \frac{1}{k_{obs}} = \frac{1 + e^{-\Delta E_1/kT}}{k_0 + k_1 e^{-\Delta E_1/kT} + (k_{p0} + k_{p1})e^{-\Delta E_2/kT}} \quad (9)$$

where the rate constants are as shown in Figure 6 and eq 8. No assumption is made in eq 9 concerning which state is lowest in the molecule.

The best fits are shown as the solid lines in Figure 5, and the fitting parameters are shown in Table IV. For free floating fits to eq 9, the best fit $k_{p0} + k_{p1}$'s were nearly constant at 2–6 × 10^{12} s^{-1}. To minimize the number of fitting parameters, we assumed an average value of 4 × 10^{12} s^{-1} for all fits.

The data reveal a number of interesting trends. The most remarkable feature of the data is the reversal of the magnitudes of k_0 and k_1 on going from phen to the other three complexes. The rate constant for direct decay to the ground-state decay of state 0 for the phen complex corresponds to a lifetime of 8.3 μs, while for the remaining complexes state 0 has a reciprocal decay rate of 300–700 μs. The first corresponds to a typical value for an MLCT emission while the others are for an IL $^3\pi$–π^* state. On the basis of these rate constants we assign the lowest and emitting state of phen to an MLCT state; for the remaining complexes, the lowest state is a $^3\pi$–π^* one. On going from phen to the other complexes the MLCT and $^3\pi$–π^* states invert. That is, altering L allows one to invert the ordering of the lowest states and exert major control on the decay kinetics.

This ability to locate the ordering of the two lowest states is quite useful as it is not readily apparent from the emission spectra what the order is. From the emission spectra of Figure 1, you might conclude that the 4-Mephen had a lowest MLCT emission
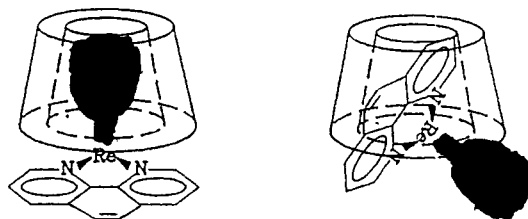

Figure 7. Schematic representation of a bihydrophobic complex and the two ways of binding with CD.

since it has only a hint of π–π^* emission. The Me$_2$phen complex looks like it is still predominantly MLCT in character. Only the Me$_4$phen complex has an emission, which indicates that the lowest state is $^3\pi$–π^*.

In fact, the visual assessment of the relative contributions of the different states to the *emission* is correct. However, since k_1 is about 50–100 times larger for the MLCT state than for the $^3\pi$–π^* state, the major contribution to the emission can arise from the MLCT state even when it is not the lowest state; the higher rate constant compensates for the lower population of the thermally populated upper state.

The energy of the d–d state above the lowest emitting level is essentially constant at 4000 cm^{-1}. This is reasonable as the changes in energy for the MLCT and $^3\pi$–π^* states with variations in L are not large, and the crystal field strength of all the ligands should be similar. Thus, the d–d state energy should not change very much. Finally, the variation in the position of the MLCT relative to the lower $^3\pi$–π^* mirrors the tendency of the ligands to exhibit MLCT versus IL emissions.

An alternative model to the one in Figure 6 assumes that all three states are in thermal equilibrium. This can fit our data, but the necessary rate constants are chemically unreasonable. Furthermore, at the temperatures involved it seems unlikely that the d–d state would not be essentially instantaneously deactivated once reached. For these reasons, we favor the model in Figure 6.

Cyclodextrin Binding. The CD binding studies reveal a number of features relevant to the area of molecular recognition. The majority of our complexes possess two structurally dissimilar regions: the α-diimine and the alkyl portion of the isonitrile. Earlier we showed that the hydrophobic alkyl chains could form inclusion complexes with CD and significantly affect luminescence properties. However, in this earlier work L was bpy, which is quite hydrophilic with apparently little propensity for forming CD inclusion complexes. The complexes studied here all have a much more hydrophobic phen or substituted phen. Thus, in the current work we have a class of complexes that are *bihydrophobic* and can bind at two different regions. We expect a concomitantly large difference in the luminescence properties of the inclusion complexes depending on binding mode. Figure 7 is a schematic representation of such a bihydrophobic complex and the two potential binding modes. The dark area represents a prototype hydrophobic region.

Functionally, we found two different types of behavior, which we refer to as class I and class II:

I. The complexes showed small red shifts on addition of CD, oxygen-quenching constants were not greatly different for the bound and the unbound complex, and the lifetime decreased on addition of CD in a deaerated solution, but increased in an oxygenated solution.

II. The complexes showed small blue shifts on addition of CD, oxygen-quenching constants were much smaller for the bound than for the unbound complex, and the lifetime increased on addition of CD in both oxygenated and deaerated solutions.

Table V summarizes the results as well as the K_{eq}'s for the systems studied. All of these results can be explained on the basis of diimine chromophore (L) and/or hydrocarbon side chain (R) binding as shown in Figure 7. In Table V we assign two binding modes. "Diimine" is an L binding mode while "hydro-

Table V. Excited-State β-Cyclodextrin Binding Properties of Selected Re(I) Isonitrile Complexes

complex	binding constant K_{eq} (M^{-1})	emission shift (aerated H$_2$O)	$10^{-9}k_q$ (M^{-1} s^{-1}) unbound	bound	type of binding
bpy/t-BuNC	390	blue	2.6	1.1	diimine
phen/t-BuNC	690	blue	1.9	0.7	diimine
Me$_2$phen/t-BuNC	160	blue	1.9	0.6	diimine
Me$_2$phen/n=3	360	none	1.7	0.6	hydrocarbon
Me$_2$phen/n=11	8800	red	1.8	1.6	hydrocarbon
Phe$_2$phen/t-BuNC	1000	red	1.6	1.3	phenyl

carbon" or "phenyl binding" is the other case. The Me$_2$phen/n=3 complex is an interesting mixture of class I and II behavior. The oxygen-quenching constant is class I, but there is no spectral shift and the shapes of the CD titration curves are class II.

The spectral shifts are easily accounted for since blue shifts are generally an indication of binding of a luminescence species in a more hydrophobic environment. Since the emission is localized in the ReL portion of the complex, L binding will place the emitting portion of the complex in a more hydrophobic environment and yield a blue shift. A red shift results when the hydrophobic tail is peeled from L and decreases the hydrophobic environment around L. For the Me$_2$phen/n=3 complex, the tail is too short to actively fold back onto L and CD binding has no effect on the polarity around the emitting portion, thus, the absence of any spectral shift for this molecule. The Ph$_2$phen/t-BuNC complex is a special case.

In the presence of oxygen the lifetimes all increase with increasing [CD]. We attribute this to an increased shielding of the excited state from oxygen quenching by the bulky CD versus the more penetrable alkyl group. This result is consistent with that observed for the Re(bpy)(CO)$_3$NCR$^+$ and Ru(Ph$_2$phen)-phen$_2{}^{2+}$ complexes.

For L binders, the decrease in the O$_2$-quenching constant is much greater than for R binders. This arises since L binding nearly completely hides the excited portion of the complex from the oxygen quencher, while R binding leaves the excited and easily quenched portion of the molecule exposed to the bulk solution.

In the absence of oxygen, the L binders show an increasing lifetime with [CD] while the R binders show a decrease. We attribute this to shielding of the excited ReL portion of the complex from water quenching in the L-binding case. For R binding the hydroxyl groups of the open face of the CD are pressed against the excited L. We have shown earlier that the OH's of CD are better quenchers of some metal complexes than water.[29] Thus, R binding reduces the excited-state lifetime in the absence of O$_2$.

Geometric control of binding is shown for different sized L's. Phen is an almost perfect fit for the CD cavity. However, the steric interference of the methyl on the Me$_2$phen reduces the depth of penetration into the cavity and lowers the number of favorable inclusion conformers with a concomitant decrease in K_{eq}. Molecular models very clearly show this reduced interaction, and K_{eq} is lower by about a factor of 4 on going from phen to Me$_2$phen even though Me$_2$phen is more hydrophobic than phen and on this basis should bind better.

It is clear that the strongest binding is exerted by long alkyl chains (e.g. Me$_2$phen/n=11) where the alkyl chain can conform to the interior of the cavity for optimum water displacement. Again, increasing binding with increasing n was observed earlier for Re(bpy)(CO)$_3$NCR$^+$ complexes.[20]

An interesting question arises with the Me$_2$phen/n=11 complex. Since there are two possible binding sites, is there evidence for dual binding? The answer appears to be yes. Close inspection of the fits using a single binding model gives good fits to the data at low [CD], but there is a clear deviation at higher values, especially for the deoxygenated data. The titration curve is too rounded and does not break crisply enough. The solid lines, which give much better fits in Figure 3, are the two-component fits. The K_{eq}'s in this case are 30 000 and 700 M^{-1}. The lower of the two is not greatly different than that for binding of CD to Me$_2$phen directly. Thus, we suggest that double binding is observable, with the higher of the two K_{eq}'s for R binding and the lower for L binding.

We return now to the Me$_2$phen/n=3 complex, where the behavior shows elements of both class I and II behavior. On the basis of the binding of Me$_2$phen/t-Bu, we conclude that Me$_2$phen can bind in the Me$_2$phen/n=3 complex. However, the apparent binding constant is about a factor of 2 larger for the n=3 complex, indicating an additional binding mode. We suggest two possibilities. First, we could have dual binding, as shown for the Me$_2$phen/n=11 case, but with binding constants too close to resolve. Alternatively, molecular models suggest a composite binding with Me$_2$phen partly in the cavity, but with the flexible n-Bu group folding down into the hydrophobic pocket. Both possibilities can give substantial oxygen shielding and reduced spectral shift. We tend to favor the second possibility because the tightly confined n-Bu group can give good oxygen shielding even though Me$_2$phen is not so deeply enclosed in the CD.

The Ph$_2$phen complex is certainly binding via the phenyl group. This is similar to what we saw in binding of CD to a series of phenyl-substituted ligands on RuL$_2$L' complexes.[29] Comparison of the Ph$_2$phen/t-Bu with the Me$_2$phen/t-Bu complexes indicates that the phenyl group aids binding. Even though the steric bulk of the phenyl group reduces overall penetration of the phen, its increased hydrophobicity enhances overall binding.

Thus, by proper control of L and R one can direct the binding mode and its strength in the formation of inclusion complexes. Similar considerations clearly can be used to design binders for specific types of structural features on target substrates for molecular probes and site specific cleavers.

Conclusions

We have demonstrated that ReL(CO)$_3$CNR$^+$ complexes have very favorable properties such as extremely high quantum yields and exceptionally long fluid solution lifetimes. In addition, the complexes lend themselves to a variety of structural variations that permit designing systems with specific binding properties (both orientation and magnitude) for molecular probes. The near degeneracy of the lowest MLCT and $^3\pi-\pi^*$ states coupled with the ability to change their ordering by modest structural variations makes them remarkably interesting systems for probing excited-state dynamics and equilibration in the low-lying photophysically and photochemically important excited states of metal complexes.

Even though the intramolecular shielding effect of the alkyl chain is muted, a number of exciting possibilities exist for using the alkyl chain as an anchor point for forming inclusion or intercalation complexes. Use of optically active groups will permit chiral recognition. In effect, we have a very versatile chromophore with stereochemical and hydrophobic hooks for forming complexes.

Supplementary Material Available: The derivation of eq 9, carbon–hydrogen–nitrogen analyses for the complexes, and a detailed sample synthesis (3 pages). Ordering information is given on any current masthead page.