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Synthesis and Photophysical and Electrochemical Properties of New Halotricarbonyl(polypyridine)rhenium(I) Complexes

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The complexes $\mathrm{Re(LL)(CO)_3Cl}$ [LL = 4,4′-bis(dimethylamino)-2,2′-bipyridine (DMA-bpy), 4,4′-dinitro-2,2′-bipyridine (NI-bpy), 4,4′-dicarboxy-2,2′-bipyridine (CA-bpy), 4,4′-bis(isopropoxycarbonyl)-2,2′-bipyridine (IPE-bpy), 4,4′-bis[*p*-(diethylamino)-α-styryl]-2,2′-bipyridine (DEAS-bpy), 4,4′-bis[2-[*p*-(diethylamino)phenyl]ethyl]-2,2′-bipyridine (DEAPE-bpy), sodium 2,2′-bipyridine-5-sulfonate (S-bpy), 2,9-dimethyl-1,10-phenanthroline (neocuproine), 1,4-diphenyl-2,3-dimethyl-1,4-diazabuta-1,3-diene (DPDAB)], $\mathrm{Re(terpy)(CO)_2Cl}$ (terpy = 2,2′:6′,2″-terpyridine), $\mathrm{[Re(CO)_3Cl]_2(bpym)}$ (bpym = 2,2′-bipyrimidine), and $\mathrm{[Re(CO)_3Br]_2(QP)}$ (QP = 5,5′,3″,5‴-tetramethyl-2,2′:6′,2″:6″,2‴-quaterpyridine) have been prepared. Most of the complexes feature luminescence emission. Their absorption spectra, emission spectra, luminescence lifetime, luminescence quantum yields, and redox potentials have been obtained. $\mathrm{Re(DMA\text{-}bpy)(CO)_3Cl}$ and $\mathrm{Re(DEAS\text{-}bpy)(CO)_3Cl}$ emit from ligand-centered (LC) excited states, whereas the other emitting complexes luminesce from metal-to-ligand charge-transfer (MLCT) states. $\mathrm{[Re(CO)_3Br]_2(QP)}$ appears to be the first binuclear Re–polypyridine–carbonyl complex which luminesces in fluid solution at room temperature. Correlations between electrochemical and spectroscopic properties are discussed.

Introduction

In the last few years the study of photophysics and photochemistry of ruthenium polypyridine complexes[1,2] has grown impressively, particularly in the ligth of the potential use of these complexes in photoinduced redox reactions. Much less attention has been focused on the family of Re(I)–polypyridine–carbonyl complexes[3] (Figure 1), in spite of the fact that such compounds feature properties very similar to those of the ruthenium complexes. In particular, these Re(I) compounds are d^6 complexes whose lowest excited state is often metal-to-ligand charge transfer (MLCT) in character and can luminesce at room temperature in fluid solution. It has been shown earlier that Re(I) complexes catalyze the efficient and selective photo- and electroreduction of $\mathrm{CO_2}$ to CO.[4-6] It has also been suggested that they may represent new materials possessing nonlinear optical properties.[7]

To extend the number of Re–carbonyl–polypyridine complexes available, we have synthesized a dozen of complexes in which the chromophoric polypyridine ligand varies, and we have carried out electrochemical and photophysical characterization of these new complexes. The formulas of the ligands are shown in Chart I. As could be expected, the use of different polypyridine ligands causes profound changes on the properties of such complexes, up to the point that in some case the lowest excited state is no longer of MLCT but rather of ligand-centered (LC) nature. We also report the first case (to our knowledge) of a binuclear Re–carbonyl–polypyridine complex that luminesces in fluid solution.

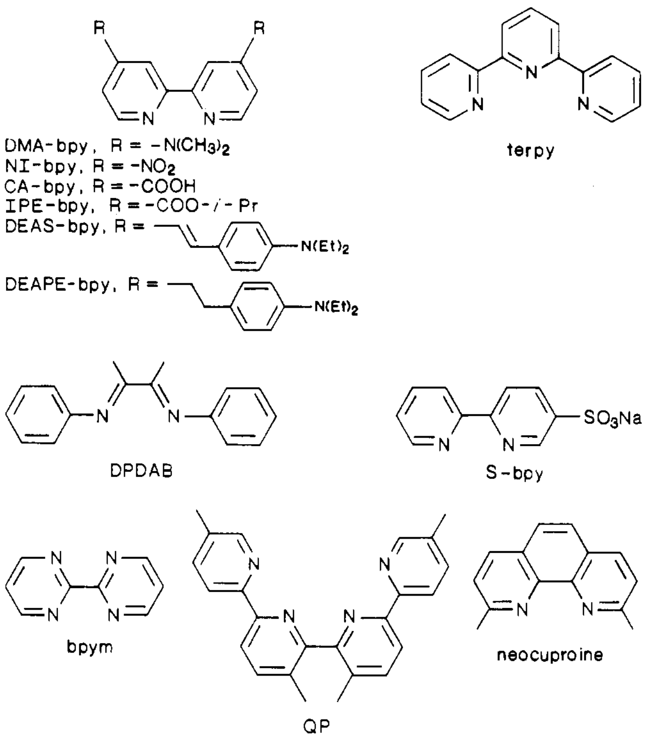
Experimental Section

Materials. All solvents for preparative experiments were of reagent grade. 2,9-Dimethyl-1,10-phenanthroline (neocuproine), 2,2′:6′,2″-terpyridine (terpy), and 2,2′-bipyrimidine (bpym) are commercially available. Solvents used for electrochemical studies were prepared from spectroquality solvents, which were dried over $\mathrm{P_2O_5}$ and KOH (DMF) or $\mathrm{CaH_2}$ ($\mathrm{CH_3CN}$) and subsequently distilled under reduced pressure. Supporting electrolytes for electrochemical measurements were tetrabutylammonium perchlorate (TBAP) in reduction and $\mathrm{KPF_6}$ in oxidation. Both salts were recrystallized prior to use. Solvents for spectroscopic experiments were of spectroquality grade.

Preparation of the Ligands. 4,4′-Bis(dimethylamino)-2,2′-bipyridine (DMA-bpy),[8] 4,4′-dinitro-2,2′-bipyridine (NI-bpy),[8,9] 4,4′-dicarboxy-2,2′-bipyridine (CA-bpy),[10] 4,4′-bis(isopropoxycarbonyl)-2,2′-bipyridine (IPE-bpy),[11] sodium 2,2′-bipyridine-5-sulfonate (S-bpy),[12] 1,4-diphenyl-2,3-dimethyl-1,4-diazabuta-1,3-diene (DPDAB),[13] and 5,5′,3″,5‴-tetramethyl-2,2′:6′,2″:6″,2‴-quaterpyridine (QP)[14] were synthesized by literature methods.

4,4′-Bis[2-hydroxy-2-[*p*-(diethylamino)phenyl]ethyl]-2,2′-bipyridine. *n*-Butyllithium (4.4 mL, 0.07 mol) was added to a solution of diisopropylamine (10 mL, 0.0715 mol) in dry tetrahydrofuran (20 mL) at 0 °C, under argon. The pale yellow solution was stirred at 0 °C for 20 min.

Chart I



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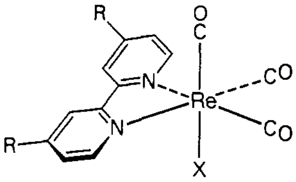

Figure 1. Structural formula of Re(polypyridine)$(CO)_3X$ complexes.

Then, a solution of 4,4′-dimethyl-2,2′-bipyridine (5 g, 0.027 mol) in dry THF (100 mL) was added dropwise. At this point the reaction mixture became dark orange-red. The turbid mixture was stirred at 0 °C for 75 min; then a solution of 4-(diethylamino)benzaldehyde (9.55 g, 0.054 mol) in dry THF (50 mL) was added over a 5-min period. The mixture was stirred at 0 °C for 75 min and then at room temperature for 5 h. The mixture was quenched with methanol (5 mL), whereupon the color changed from green to a clear yellow. Water (100 mL) was added, and the product was extracted into CH_2Cl_2 (3 × 100 mL). The organic layers were washed with water (100 mL) and brine (100 mL) and dried ($MgSO_4$). Evaporation of the solvent gave the crude product (14.9 g), which was crystallized from benzene to give the pure product as a pale yellow solid (9.0 g, 62%). The mother liquors were evaporated and column-chromatographed on alumina, activity II–III (200 g) with 10% $MeOH/CH_2Cl_2$, giving an additional 2 g of the desired diol as a major compound. Total yield of diol: 11 g, 76%. ^1H NMR spectrum in $CDCl_3$ solution (vs Me_4Si): δ 8.53 (d, 6, 6′), 8.28 (s, 3, 3′), 7.21 (d, Ar H), 7.13 (dd, 5, 5′), 6.65 (d, Ar H), 4.90 (t, C*H*OH), 3.25 (q, $CH_3C\mathit{H}_2$), 3.08 (m, $C\mathit{H}_2CHOH$), 1.95 (b s, O*H*), 1.13 (t, $C\mathit{H}_3CH_2$). Anal. Calcd: C, 75.80; H, 7.86; N, 10.40. Found: C, 75.66; H, 8.09; N, 10.51.

4,4′-Bis[*p*-(diethylamino)-*α*-styryl]-2,2′-bipyridine. A 10% aqueous H_2SO_4 solution (100 mL) was added to the diol (4.5 g, 8.36 × 10^{-3} mol), and the mixture was heated at 90 °C for 2 h to yield a purple solution. The mixture was cooled in an ice bath and neutralized with 1 N aqueous NaOH, to yield an orange-yellow precipitate. The product was extracted into CH_2Cl_2 (5 × 200 mL) (filtration had proved difficult in previous experiments), and the resulting solution was washed with brine (200 mL) and dried ($MgSO_4$). Evaporation of the solvent gave the product (trans form), which was found to be pure by ^1H NMR spectroscopy (4.20 g, 100%). The compound was recrystallized from CH_2Cl_2/MeOH. ^1H NMR spectrum in $CDCl_3$ solution: δ 8.59 (d, 6, 6′), 8.46 (s, 3, 3′), 7.42 (d, Ar H), 7.40 (d, C*H*=C*H*), 7.38 (dd, 5, 5′), 6.87 (d, C*H*=C*H*), 6.66 (d, Ar H), 3.38 (q, $C\mathit{H}_2CH_3$), 1.18 (t, $C\mathit{H}_3CH_2$). Anal. Calcd: C, 81.23; H, 7.62; N, 11.15. Found (compound + 0.5 H_2O): C, 79.80; H, 7.68; N, 10.95. λ_{max}($CHCl_3$ or CH_3CN) = 394 nm, ϵ = 53 200.

4,4′-Bis[2-[*p*-(diethylamino)phenyl]ethyl]-2,2′-bipyridine. The previous dialkene (0.25 g, 4.97 × 10^{-4} mol) and 10% palladium on charcoal (0.1 g) were suspended in a mixture of ethanol and acetic acid, 4:1 (25 mL). The flask was evacuated and flushed three times with hydrogen before the contents were allowed to stir under at atmosphere of hydrogen at 50 °C for 5.5 h. The red solution became colorless during this period. The reaction mixture was cooled, and the catalyst was filtered off and washed with water. The filtrate and the washings were neutralized with 1 M aqueous NaOH to yield a white precipitate. The product was extracted into CH_2Cl_2 (3 × 50 mL), the mixture was dried ($MgSO_4$), and the solvent was evaporated to give the off-white product (0.21 g, 83%). ^1H NMR spectroscopy showed the product to be pure. The compound was recrystallized from benzene. ^1H NMR spectrum in $CDCl_3$ solution: δ 8.54 (d, 6, 6′), 8.27 (s, 3, 3′), 7.10 (dd, 5, 5′), 7.04 (d, Ar H), 6.62 (d, Ar H), 3.31 (q, $C\mathit{H}_2CH_3$), 2.90 (m, $C\mathit{H}_2C\mathit{H}_2$), 1.12 (t, $C\mathit{H}_3CH_2$). λ_{max}($CHCl_3$) = 268 nm, ϵ = 37 200.

Preparation of the Re Complexes. The following general procedure has been used for the synthesis of the rhenium complexes. $Re(CO)_5Cl$[15] was dissolved in toluene at 60 °C under argon. One equivalent of the ligand was added to the clear solution, causing a color change (from pale yellow to deep red). A precipitate formed after 15–30 min. The mixture was stirred and heated at 80 °C for 15 h under argon. The mixture was cooled and filtered, and the product was washed three times with Et_2O. The complex was recrystallized from CH_2Cl_2 (or CH_3CN)/Et_2O and dried in vacuo to afford over 90% yield of pure compound.

Re(DMA-bpy)$(CO)_3$Cl (1). ^1H NMR (CD_2Cl_2): δ 8.43 (d, 6, 6′), 7.15 (d, 3, 3′), 6.58 (dd, 5, 5′), 3.16 (s, $C\mathit{H}_3N$). IR (KBr disk), ν_{CO}: 2010, 1900, 1870 cm^{-1}. Anal. Calcd: C, 37.26; H, 3.31; N, 10.22. Found: C, 37.02; H, 3.06; N, 10.37.

Re(NI-bpy)$(CO)_3$Cl (2). ^1H NMR (CD_3OD): δ, 9.57 (d, 6, 6′), 9.47 (d, 3, 3′), 8.50 (dd, 5, 5′). IR (KBr disk), ν_{CO}: 2030, 1935, 1900 cm^{-1}. Anal. Calcd: C, 28.29; H, 1.10; N, 10.15. Found: C, 28.07; H, 1.01; N, 9.96.

Re(CA-bpy)$(CO)_3$Cl (3). ^1H NMR (D_2O + OH): δ 9.24 (d, 6, 6′), 8.82 (s, 3, 3′), 8.01 (d, 5, 5′). IR (DMF), ν: 2020, 1920, 1900 cm^{-1} (carbonyl); 1620 cm^{-1} (carboxyl). Anal. Calcd: C, 37.08; H, 1.66;, N, 5.77. Found: C, 36.98; H, 1.47; N, 5.68.

Re(IPE-bpy)$(CO)_3$Cl (4). ^1H NMR ($CDCl_3$): δ 9.24 (d, 6, 6′), 8.86 (s, 3, 3′), 8.12 (d, 5, 5′), 5.43 [h, $C\mathit{H}(CH_3)_2$], 1.51 [d, $CH(C\mathit{H}_3)_2$]. IR (CH_2Cl_2), ν: 2025, 1928, 1905 cm^{-1} (carbonyl); 1730 cm^{-1} (ester). Anal. Calcd: C, 39.78; H, 3.18; N, 4.42. Found: C, 40.03; H, 2.99; N, 4.35.

Re(DEAS)$(CO)_3$Cl (5). ^1H NMR (CD_2Cl_2): δ 8.51 (d, 6, 6′), 8.15 (d, 3, 3′), 7.63 (d, Ar H), 7.40 (d, C*H*=C*H*), 6.95 (d, 5, 5′), 6.78 (d, Ar H), 6.65 (d, C*H*=C*H*), 3.46 (q, $C\mathit{H}_2CH_3$), 1.24 (t, $C\mathit{H}_3CH_2$). IR (KBr disk), ν_{CO}: 2015, 1915, 1895 cm^{-1}. Anal. Calcd: C, 53.77; H, 4.88; N, 6.77. Found (+H_2O): C, 53.72; H, 4.49; N, 6.53.

Re(DEAPE-bpy)$(CO)_3$Cl (6). ^1H NMR (CD_2Cl_2): δ 8.83 (d, 6, 6′), 7.81 (d, 3, 3′), 7.31 (dd, 5, 5′), 7.01 (d, Ar H), 6.62 (d, Ar H), 3.32 (q, $C\mathit{H}_2CH_3$), 2.88 (m, $C\mathit{H}_2C\mathit{H}_2Ar$), 1.11 (t, $C\mathit{H}_3CH_2$). IR (KBr disk), ν_{CO}: 2020, 1915, 1895 cm^{-1}. Anal. Calcd: C, 54.70; H, 5.21; N, 6.90. Found: C, 54.68; H, 5.31; N, 6.76.

Re(S-bpy)$(CO)_3$Cl (7). ^1H NMR (D_2O/+OH): δ 9.19 (d, 6), 8.81 (d, 6′), 8.52 (dd, 4), 8.00 (m, 3, 3′, 4′), 7.50 (td, 5′). IR (DMF), ν_{CO}: 2020, 1920, 1900 cm^{-1}. Anal. Calcd: C, 28.81; H, 1.49; N, 5.17. Found: C, 29.92; H, 2.08; N, 5.48.

Re(neocuproine)$(CO)_3$Cl (8). ^1H NMR (CD_2Cl_2): δ 8.39 (d, 4, 4′), 7.90 (s, 5, 6), 7.78 (d, 3, 3′), 3.31 (s, $C\mathit{H}_3$). IR (CH_2Cl_2), ν_{CO}: 2020, 1930, 1900 cm^{-1}. Anal. Calcd: C, 31.75; H, 2.66; N, 6.17. Found: C, 31.49; H, 2.80; N, 6.15.

Re(terpy)$(CO)_2$Cl (9). ^1H NMR (CD_2Cl_2): δ 9.07 (d, 1 H), 8.80 (d, 1 H), 8.30 (m, 2 H), 8.19 (t, 1 H), 8.12 (td, 1 H), 7.84 (td, 1 H), 7.81 (t, 2 H), 7.54 (m, 2 H). IR (CH_2Cl_2), ν_{CO}: 2020, 1925, 1900 cm^{-1}. Anal. Calcd: C, 40.11; H, 2.06; N, 7.80. Found: C, 40.10; H, 2.26; N, 7.87.

Re(DPDAB)$(CO)_3$Cl (10). ^1H NMR (CD_2Cl_2): δ, 7.55 (t of m, meta), 7.52 (d, ortho), 7.38 (tt, para), 2.30 (s, CH_3). IR (CH_2Cl_2), ν: 2025, 1935, 1905 (carbonyl); 1635 cm^{-1} (imine). Anal. Calcd: C, 42.10; H, 2.97; N, 5.17. Found: C, 42.03; H, 2.88; N, 5.02.

[Re$(CO)_3$Cl]$_2$(bpym), 18% Trans + 82% Cis Isomer Mixture (11). ^1H NMR (DMF-d_7): δ 9.84 (integration 1) and 9.77 (integration 5) (2 d, 4, 4′, 6, 6′), 8.35 and 8.28 (2 t, 5, 5′). IR (DMF) ν_{CO}: 2020, 1930, 1915 cm^{-1}. Anal. Calcd: C, 21.85; H, 0.79; N, 7.28. Found: C, 21.63; H, 1.02; N, 7.36.

[Re$(CO)_3$Br]$_2$(QP) (12). ^1H NMR (DMSO-d_6): δ, 8.92 (d, 2 H), 8.88 (s, 2 H), 8.80 (d, 2 H), 8.57 (d, 2 H), 8.26 (d, 2 H). IR (DMF), ν_{CO}: 2020, 1915, 1885 cm^{-1}. Anal. Calcd: C, 33.78; H, 2.08; N, 5.25. Found: C, 33.72; H, 2.14; N, 5.28.

Measurements. Electrochemical measurements were carried out on a classical three-electrode potentiostatic setup comprising a potentiostat, a pilot scanner, a current–potential converter (EDT-ECP 133), and an XY recorder (IFELEC IF 3802). The working electrode was a platinum rotating disk electrode (SOLEA Tacussel EDI type, area 3.14 mm^2) used without rotation for cyclic voltammetry. The reference electrode (saturated calomel electrode, SCE) was connected to the electrolysis cell by a bridge filled with the same solvent and supporting electrolyte as the solution.

^1H NMR spectra were recorded on a 200-MHz Bruker SY 200 spectrometer at 200.1 MHz with the solvent as an internal standard. IR spectra were carried out by using a Perkin-Elmer 597 spectrometer.

Absorption spectra were recorded with a Kontron Uvikon 860 spectrophotometer. The (uncorrected) emission spectra were obtained with a Perkin-Elmer 650-40 or a Perkin-Elmer LS-5 spectrofluorometer equipped with Hamamatsu R928 tubes. Emission lifetime measurements were carried out by using a JK System 2000 Neodymium YAG DPLY4 laser as excitation source (λ_{exc} = 355 nm) and a Tektronix 7612A digitizer, interfaced to a computer for decay data acquisition.

Emission quantum yields were measured at room temperature (20 °C) with the optically dilute method[16] calibrating the spectrofluorometer with a standard lamp. $Ru(bpy)_3^{2+}$ in aerated aqueous solution was used as a quantum yield standard, assuming a value of 0.028.[17]

When necessary, samples were degassed by bubbling nitrogen.

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Table I. Spectroscopic and Electrochemical Results for Re Complexes[a]

		293 K				77 K[b]		293 K	
no.	complex	λ_{abs}, nm	λ_{em}, nm	τ,[c] μs	Φ[c]	λ_{em}, nm	τ, μs	E_{red}, V	E_{ox},[d] V
1	Re(DMA-bpy)$(CO)_3$Cl	364	532	0.49	0.042	472	24	−1.75	+1.09[e]
2	Re(NI-bpy)$(CO)_3$Cl	442				640	0.98	−0.53, −0.98	+1.48
3	[Re(CA-bpy)$(CO)_3$Cl	360 sh	600	0.14	0.006	555	3.6	−1.47	+0.89[e]
4	Re(IPE-bpy)$(CO)_3$Cl	405				575	3.8	−0.99, −1.36	+0.87[e]
5	Re(DEAS-bpy)$(CO)_3$Cl	462	670	0.14	0.004	665	630	−1.27	+0.69
6	Re(DEAPE-bpy)$(CO)_3$Cl	362				530	2.8	−1.42	+0.69
7	Re(S-bpy)$(CO)_3$Cl	378	610	0.060	0.010	535	4.6	−1.33	+1.39
8	Re(neocuproine)$(CO)_3$Cl	380 sh	589	0.13	0.012	512	9.4	−1.47	+1.34
9	Re(terpy)$(CO)_2$Cl	375				530	3.4	−1.40	+1.19
10	Re(DPDAB)$(CO)_3$Cl	427						−0.97, −1.68	+1.00[e]
11	$[Re(CO)_3Cl]_2$(bpym)	465[d]						−0.51, −1.20	+1.48
12	$[Re(CO)_3Br]_2$(QP)	370 sh	583	0.096	0.016	520	7.0	−1.45	+0.98

[a] Data in DMF unless otherwise noted. [b] In DMF/CH_2Cl_2 (9:1 v/v). [c] In deaerated solution. [d] In acetonitrile. [e] Not reversible.

Results

In general, the complexes under investigation are thermall inert, and the absorption spectrum in solution shows no change in a couple of days. For Re(NI-bpy)$(CO)_3$Cl and Re(DEAS-bpy)$(CO)_3$Cl, on the contrary, a slight modification of the absorption spectrum indicated that some reaction had taken place within 24 h. To avoid such complications, all of the measurements were performed on freshly prepared samples. Table I summarizes data concerning absorption spectra (at 293 K), emission spectra (at 77 and 293 K), emission lifetimes (at 77 and 293 K), emission quantum yields (at 293 K), and redox potentials (at 293 K) for the examined complexes.

Figure 2 shows some examples of emission spectra at 293 and 77 K.

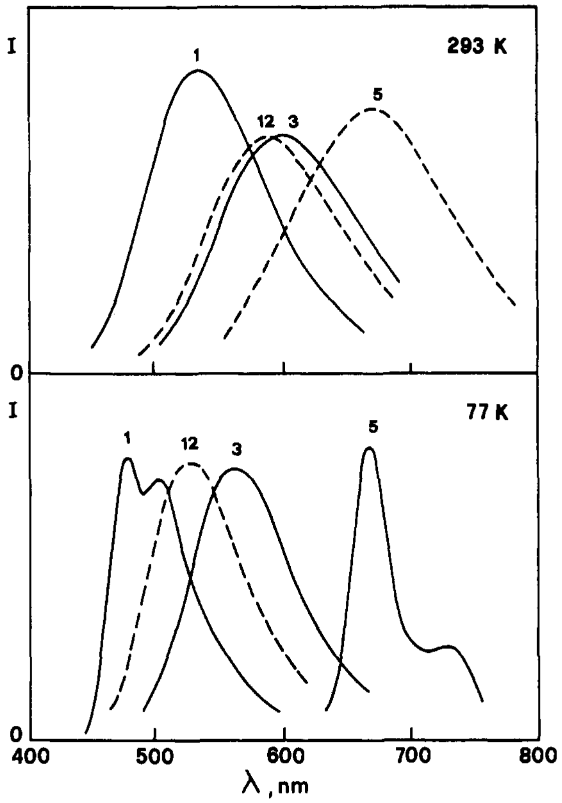

Figure 2. Emission spectra at 293 and 77 K of some of the complexes listed in Table I.

Discussion

Electrochemistry. Redox potentials for the complexes, measured by cyclic voltammetry, are presented in Table I. The complexes exhibit one or two reversible reduction waves in the 0 to −1.8 V range. The first reduction wave is a ligand-based reduction, and the second wave observed for complexes **2**, **4**, **10**, and **11** is due to reduction of Re(I) to Re(0).[18] Some of the complexes present a chemically irreversible oxidation wave for the Re(II)/Re(I) couple, as observed by other authors.[18] As expected, the redox potentials for the rhenium complexes depend on the nature of the ligand and on the bipyridine substituents. The largest effect is observed, on reduction, for the 4,4′-bis(isopropyoxycarbonyl)- and 4,4′-dinitro-2,2′-bipyridine ligands. In these cases the reduction of the coordinated ligand is easier by 1 V with respect to an unsubstituted bipyridine.

Spectroscopic Properties. The absorption spectra of the complexes under investigation are qualitatively similar to those already published[3,19-23] for similar Re complexes and can thus be interpreted in an analogous way. The lowest energy absorption band (or shoulder) listed in Table I is so assigned to a metal-to-ligand charge-transfer (MLCT) transition Re → π^*(LL). More intense bands of intraligand (IL) origin (not listed in Table I) are present in the UV region at higher energy. Ligand field (d–d) absorptions are known to be obscured by the more intense IL and MLCT transitions.[21] The absorption spectrum is clearly sensitive to the nature of the polypyridine ligand as required for a MLCT transition (vide infra correlations).

The fact that the lowest energy absorption band can be confidently assigned as MLCT in character does not necessarily mean that the lowest excited state is also of MLCT nature. Luminescence measurements are indeed very diagnostic (much more than the absorption spectrum) in assigning the proper label to the lowest lying excited state, and this is one of the reasons that photophysical properties of transition-metal complexes are so extensively studied. Most of the complexes listed in Table I luminesce at 77 K in frozen matrix, and many of them also luminesce in fluid solution at room temperature. For all of the emitting complexes listed in Table I, *with the exceptions of* ***1*** *and* ***5***, the emitting level can be labeled as MLCT in character according to usual considerations: (1) The position and shape of the emission band is consistent with that previously reported[3,19,21] for similar complexes assigned as MLCT emitters. Representative examples are reported in Figure 2 for complexes **3** and **12**. Note, particularly, the absence of any vibrational structure even at 77 K and the blue shift of the emission band obtained on going to 77 K. (2) A correlation can be found between the absorption and emission bands with the reduction potential of the complex (vide infra). (3) The time range (microseconds) of the 77 K emission is typical of MLCT states.

Complexes **1** and **5** have luminescence properties that are not understandable within the simple scheme of MLCT emission outlined above. In the case of Re–polypyridine–carbonyl com-

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plexes, the 77 K emission properties can be grouped mainly into three classes: (i) the emission band is featureless and has a lifetime in the range 1–50 μs; in this case the emission is considered to have a "pure" MLCT character;[19,21] (ii) the emission band is structured, has a lifetime in the range 250–500 μs, and is considered as having a mixed MLCT and LC character;[21] (iii) the emission band is again structured but can be resolved in two components, one short-lived (about 10 μs) and the other long-lived (50–1000 μs) originating from MLCT and LC states, respectively.[24,25] It is clear that all of the complexes discussed above fall into cases i, whereas **1** and **5** do not. The structured emission with a lifetime of 24 μs featured by **1** is somewhat puzzling, as any attempt to time resolve two components in the emission band has been unsuccessful (the LS-5 spectrofluorometer is equipped with a pulsed excitation lamp and can work in the "phosphorescence mode"). Moreover, the excitation spectrum of the complex matches its absorption spectrum, and the free ligand features at 77 K a phosphorescence emission centered around 480 nm, with a lifetime of 0.96 s. These facts indicate that the emission of **1** could confidently be assigned as LC in character at 77 K. On the other hand, the relatively short lifetime indicates that for the emitting level a mixed MLCT and LC character is more appropriate.

Attempts to resolve two components in the emission band at 77 K failed also for complex **5**. However, the very long lifetime, the structure of the emission band, and the observed phosphorescence emission of the free ligand at 656 nm in the same experimental conditions clearly indicate a LC orbital nature of the lowest excited state at 77 K. Unfortunately, the free ligands do not phosphorescence at room temperature, so that a direct comparison with the corresponding complex is no longer possible. Usually, rhenium–carbonyl–polypyridine complexes emitting from LC levels at 77 K become MLCT emitters in fluid solution. Indeed, it is known[21,26] that the position of MLCT states is sensitive to medium rigidity, so that with an increase in temperature the MLCT states are shifted to lower energy and become the lowest (emitting) levels. This is the origin of the red shift usually observed in the emission band of MLCT emitters on passing from rigid glass (low temperature) to fluid solution. This, however, is not the case for **5**. We note that the emission at 293 K, though very weak, shows only a very small red shift relative to the emission at 77 K. As other LC emitters feature similarly small shifts,[27,28] we suggest LC emission from **5** also at room temperature. Further support for this LC assignment comes from the value of the radiative rate constant, k_r, that can be calculated from the quantum yield and lifetime data obtained at room temperature. Indeed, one can note that for complex **5** $k_r = 2.8 \times 10^4$ s^{-1}, which is the smallest value among the listed complexes. To our knowledge, this is the first Re–carbonyl–polypyridine complex that features a LC emission at room temperature. Certainly, the fact that complex **5** is the lowest energy emitter listed in Table I contributes to placing the LC emitting level out of reach of the MLCT level that is moved down in energy as the temperature increases.

The last two entries in Table I present data for binuclear complexes. Photophysical investigations of polynuclear Re–polypyridine–carbonyl complexes have begun only very recently.[29] Complex **11** is insoluble in DMF, and was examined in acetonitrile, but no detectable emission has been evidenced. On the basis of the correlation between spectroscopic and electrochemical properties (vide infra), one could expect an emission around 640 nm at 77 K. The lack of emission at 77 K clearly indicates that radiative decay is not significant in this binuclear complex. These results are in agreement with those of Vogler and Kisslinger,[29] who did not detect any emission of **11** even in solid form at 4 K. On the contrary, complex **12** represents the first case of emitting polynuclear Re–carbonyl–polypyridine complex. Shape and position of the emission band and emission lifetime are clear indications of a MLCT emitting level. These results can be understood on the basis of what is known about photophysics of the analogous Ru polypyridine dinuclear complexes. As far as these Ru complexes are concerned, it has been shown that the key feature in determining the emissive properties of the molecule is the "communicative" ability of the ligand.[30–32] When the two metal centers bound are not strongly coupled via the bridging ligand, the complex is luminescent. This communicative ability of the ligand appears to be an intrinsic electronic property of the ligand. Factors such as flexibility or torsional capability of the ligand appear important, but not decisive.[31] In this sense the bpym ligand (which forces the two bridged atoms in the same plane) is known to allow communication between the two Ru atoms,[30] so that emission in $[\mathrm{Ru(bpy)_2}]_2\mathrm{(bpym)}^{4+}$ is observed only in solid at 15 K.[33] Photophysical studies on Ru dimers employing the QP ligand are not known, although the synthesis of $[\mathrm{Ru(bpy)_2}]_2\mathrm{(QP)}^{4+}$ has been reported.[14] It is known that the structure of the QP ligand forces the two connected bpy subunits into a twisted conformation around the central bond. Although, as said before, the torsional capability of the ligand does not seem a prerequisite to observe luminescence, certainly this can hinder communication between the two Re centers in $[\mathrm{Re(CO)_3Br}]_2\mathrm{QP}$.

Correlations between Spectroscopic and Electrochemical Properties. These correlations are extensively used for Ru(II)–,[34–38] Os(II)–,[39] and Re(I)–polypyridine complexes[40] and may be very useful as they offer the opportunity to obtain absorption and emission energies from electrochemical potentials, and vice versa. In MLCT emitters, as most of these complexes are, the basis for such correlations lies in the fact that the same metal-centered and ligand-centered orbitals that are involved in the MLCT transition are also involved in the oxidation and reduction processes.

As the MLCT excited state is produced by oxidizing the metal and reducing the ligand, the most significant correlation should be between the energy of the absorption and emission bands and $\Delta E_{1/2}$, that is the difference between the oxidation (at the metal) and the reduction (at the ligand) potential of the complex:

$$\Delta E_{1/2} = E_{\mathrm{ox}} - E_{\mathrm{red}}$$

Unfortunately, it is known[18,41,42] that Re–polypyridine–carbonyl complexes often feature irreversible oxidation processes. Moreover, in our case complex oxidation is often a ligand-centered process, so that we are forced to use only E_{red} instead of $\Delta E_{1/2}$. The correlation should however be significative, as in our case E_{ox} (at the metal) is not expected to vary much from one complex to another. Indeed it should be noted that the oxidation process obtained by MLCT excitation, involving removal of an electron

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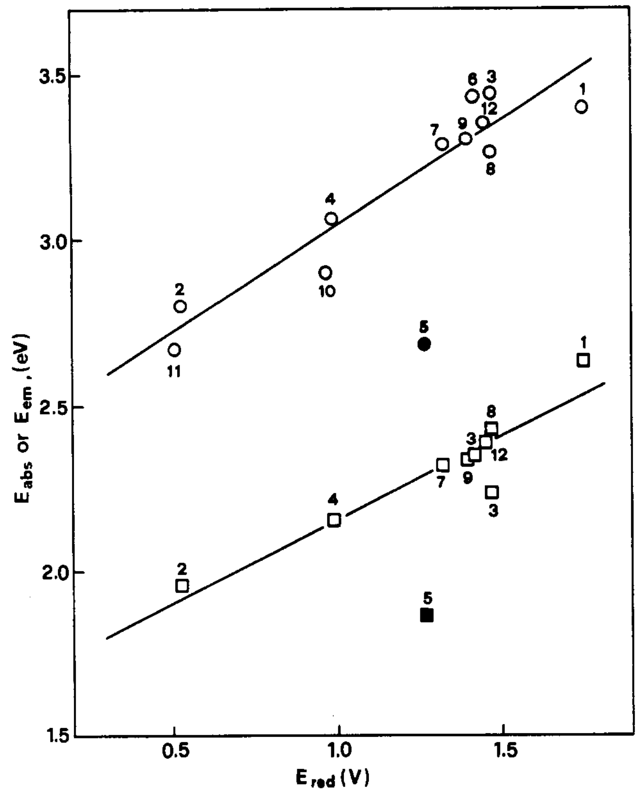

Figure 3. Correlations between the maxima of absorption at 293 K (○) or maxima of emission at 77 K (□) and the reduction potential for the complexes listed in Table I (see text).

from a metal-centered π_M orbital, should be relatively insensitive to the nature of the polypyridine ligands. Figure 3 shows the relationship between the reduction potential, E_{red}, and the lowest energy absorption band (or shoulder), E_{abs}, or the maximum of emission at 77 K, E_{em}, for the complexes listed in Table I. The analogous correlation involving E_{red} and the emission maximum at 293 K has not been considered because only a few points are available. With the exception of the point for complex **5**, a good correlation is found, in agreement with the MLCT assignment of the lowest energy transition in the Re(I) complexes examined.

The point corresponding to complex **5** is in any case out of correlation; this result further substantiates the LC assignment to the emission of **5** (vide supra). Moreover, one can note that the point for complex **5** is out of correlation also for the absorption; this seems to indicate that the lowest energy absorption feature of this complex is not of MLCT nature either, but rather LC. Complex **1**, on the other hand, appears "well-behaved", thus confirming that the LC contribution to the emitting level previously discussed (vide supra) is not substantial. Apparently, a MLCT level is present at the expected energy position but remains the lowest excited state, with only minor perturbation due to the vicinity of a LC level.

As a meaningful correlation can be drawn only for a family of homogeneous complexes, complex **5** has been ignored in calculating the linear least-squares fit (shown in Figure 3), which yielded

$$E_{abs} = -0.64E_{red} + 2.40 \qquad r = 0.95$$

$$E_{em} = -0.50E_{red} + 1.64 \qquad r = 0.93$$

where r is the correlation coefficient.

In principle, the slope of these least-squares lines is expected to be unity, and values close to unity have been observed as far as the absorption process is concerned.[38,40,43] In our case, however, the slope for the absorption process is far from unity. Possible reasons of such a difference could be the following: (1) E_{ox} is not considered in our correlations because of irreversibility problems, and this quantity may not be constant throughout the series of Re(I) complexes. (2) The complexes we are dealing with are *uncharged* species, and it may be expected that the polarity differences between ground and excited states induce different interactions with the solvent with respect to charged species. Similar effects have been observed for example in the photophysical behavior of $Ru(bpy)_2(CN)_2$ and $Ru(bpy)_2(i\text{-biq})^{2+}$ (i-biq = 3,3′-isobiquinoline).[44]

As far as the emission process is concerned, we obtain a smaller slope value with respect to absorption, as observed by other authors.[38,40] This decrease in slope can be attributed to the distortion of the excited state with respect to the ground state, and to interactions with the solvent.[39]

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