

# Intramolecular Photoinduced Electron Transfer in Multicomponent Rhenium(I) Donor–Acceptor Complexes

Raymond Ziessel,<sup>\*,†</sup> Alberto Juris,<sup>\*,‡</sup> and Margherita Venturi<sup>‡</sup>

Laboratoire de Chimie, d'Électronique et de Photonique Moléculaires UPRES-A 7008, Ecole Chimie, Polymères, Matériaux, 1 rue Blaise Pascal, BP 296F, 67008 Strasbourg Cédex, France, and Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy

Received May 26, 1998

The mononuclear [(DEAS-bpy)Re(CO)<sub>3</sub>(BPP)]<sup>+</sup>, [(DEAS-bpy)Re(CO)<sub>3</sub>(BPP-Me)]<sup>2+</sup>, and [(bpy)Re(CO)<sub>3</sub>(BPP)]<sup>+</sup> and the binuclear [(DEAS-bpy)Re(CO)<sub>3</sub>(μ-BPP)Re(CO)<sub>3</sub>(DEAS-bpy)]<sup>2+</sup> complexes have been prepared, and their electrochemical and photophysical properties have been investigated (DEAS-bpy = 4,4'-bis[*p*-(diethylamino)-α-styryl]-2,2'-bipyridine, BPP = 1,10-bis(4-pyridyl)-3,8-dimethyl-1,3,5,7,9-decapentaene, bpy = 2,2'-bipyridine). The electrochemical behavior of these complexes shows that reduction occurs first on the BPP ligand ( $E \approx -0.85$  V vs SCE) and then on the DEAS-bpy ligand ( $E \approx -1.30$  V). The site easier to oxidize is on the amines of the DEAS-bpy ligand ( $E \approx +0.70$  V); other oxidation processes occur at more positive potential on the ligands and on the metal center. The complexes containing both the DEAS-bpy and the BPP ligands phosphoresce in rigid matrix at 77 K from a <sup>3</sup>LC state of the DEAS-bpy ligand ( $\lambda_{\max} \approx 675$  nm,  $\tau > 350$  μs); no emission is observed at room temperature in fluid solution, where a long-lived ( $\tau \approx 4$  μs) species is observed through transient absorption measurements. By combining electrochemical and photophysical data, it is concluded that following light excitation a charge-separated state is formed, which is noticeably long-lived compared to that observed in other donor–acceptor complexes in homogeneous solution.

## Introduction

One of the most active research subjects being pursued worldwide concerns the design and construction of molecular-scale devices for information storage and transfer.<sup>1–7</sup> Many different approaches are being followed, but the overall goal, in all cases, involves establishment of the design features that permit logical signal generation upon external stimulation. Within this context intramolecular photoinduced redox separation in molecules containing an electron-transfer donor, an acceptor, a chromophore, and a chemical function allowing bonding to a macroscopic support is a very important target.

In the field of transition metal chemistry, polypyridyl complexes of Ru(II), Os(II), and Re(I) have been used extensively in the study of photoinduced charge-separation processes.<sup>8–16</sup> Among these compounds, the Re(I)–tricarbonyl complexes appear particularly interesting not only for their photophysical properties but also because it is challenging to synthesize species containing two different ligands connected to the same *fac*-Re<sup>I</sup>(CO)<sub>3</sub> core. Figure 1 shows formulas and

abbreviations of the ligands and of the complexes dealt with in this paper. We will focus on the characterization of the complexes [(DEAS-bpy)Re(BPP)]<sup>+</sup>, [(DEAS-bpy)Re(BPP-Me)]<sup>2+</sup>, and [(DEAS-bpy)<sub>2</sub>Re<sub>2</sub>(μ-BPP)]<sup>2+</sup>, containing the two DEAS-bpy and BPP ligands. As we will see, the DEAS-bpy ligand is an electron donor, whereas the BPP ligand is an electron acceptor. The simultaneous coordination of BPP and DEAS-bpy on the same metal center gives rise to very interesting donor–acceptor complexes, which form a long-lived charge-separated state following light excitation.<sup>17</sup> The understanding of the electrochemical and photophysical properties of such complexes requires the comparison with the behavior of the free ligands DEAS-bpy and BPP, and of the model [(DEAS-bpy)ReCl] and [(bpy)Re(BPP)]<sup>+</sup> complexes.

<sup>†</sup> Ecole Chimie, Polymères, Matériaux.

<sup>‡</sup> Università di Bologna.

- (1) *Molecular Electronics Devices*; Carter, F. L., Siatkowski, R. E., Wohltjen, H., Eds.; North-Holland: Amsterdam, 1988.
- (2) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991.
- (3) *Nanostructures based on Molecular Materials*; Göpel, W., Ziegler, C., Eds.; VCH: Weinheim, 1992.
- (4) Bard, A. *Integrated Chemical Systems*; J. Wiley: New York, 1994.
- (5) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
- (6) Denti, G.; Campagna, S.; Balzani, V. In *Mesomolecules: from Molecules to Materials*; Mendenhall, D., Greenberg, A., Liebman, J., Eds.; Chapman and Hall: New York, 1995; p 69.
- (7) Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707.

- (8) Seiler, M.; Dürr, H.; Willner, I.; Joselevich, E.; Doron, A.; Stoddart, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 3399.
- (9) Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786.
- (10) Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5481.
- (11) Mecklenburg, S. L.; McCafferty, D. G.; Schoonover, J. R.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 2974.
- (12) Collin, J.-P.; Harriman, A.; Heitz, V.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5679.
- (13) Opperman, K. A.; Mecklenburg, S. L.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 5295.
- (14) Kelly, L. A.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 13132.
- (15) Frank, M.; Nieger, M.; Vögtle, F.; Belsler, P.; von Zelewsky, A.; De Cola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L. *Inorg. Chim. Acta* **1996**, *242*, 281.
- (16) Kropf, M.; Joselevich, E.; Dürr, H.; Willner, I. *J. Am. Chem. Soc.* **1996**, *118*, 655.
- (17) Ziessel, R.; Juris, A.; Venturi, M. *J. Chem. Soc., Chem. Commun.* **1997**, 1593.

## Experimental Section

**General Methods.**  $^1\text{H}$  (200.1 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (50.3 MHz) NMR (Bruker SY-200 or AC 200) spectra were recorded at room temperature, unless otherwise specified, using perdeuterated solvents as internal standards:  $\delta$  (H) in ppm relative to residual protonated solvent in  $\text{CDCl}_3$  (7.26),  $\text{CD}_2\text{Cl}_2$  (5.32),  $\text{CD}_3\text{CN}$  (1.94);  $\delta$  (C) in ppm relative to  $\text{CDCl}_3$  (77.03),  $\text{CD}_2\text{Cl}_2$  (53.84),  $\text{CD}_3\text{CN}$  (118.26). Carbon signals were detected as singlets, and chemical shifts are quoted in ppm on the  $\delta$  scale with coupling constants expressed in hertz (Hz). Fast atomic bombardment (FAB, positive mode) mass spectra were recorded on a ZAB-HF-VB analytical apparatus in *m*-nitrobenzyl alcohol (*m*-NBA) matrixes using Ar atoms for the bombardment (8 keV), and electrospray mass spectra (ES-MS) were recorded on a Bio-Q analytical apparatus, in acetonitrile, using gramicidin as the internal standard. FT-IR spectra were recorded on a Bruker IFS 25 spectrometer with samples in KBr pellets or in solution with KBr cells. Melting points were obtained on a Büchi 535 capillary melting point apparatus in open-ended capillaries and were uncorrected. Elemental analysis was performed by Service de Microanalyse de l'Université Louis Pasteur de Strasbourg, France. Chromatography was carried out on alumina (Merck 90). Thin-layer chromatography (TLC) was carried out on Kieselgel 60 F<sub>254</sub> glass plates (Merck), visualization being by either a UV lamp, 5%  $\text{KMnO}_4$  solution in water, iodine vapor, 5% solution of phosphomolybdic acid in ethanol or cerium(IV) sulfate/ammonium molybdate(VI) tetrahydrate/ $\text{H}_2\text{SO}_4$  10% reagent followed by heating to ca. 150 °C on a hot plate.

Electrochemical experiments were carried out in argon-purged acetonitrile solution with a Princeton Applied Research 273 multipurpose instrument interfaced to a personal computer, using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The working electrode was a glassy carbon electrode (0.08 cm<sup>2</sup>, Amel); its surface was routinely polished with a 0.05  $\mu\text{m}$  alumina-water slurry on a felt surface immediately prior to use. The counter electrode was a Pt wire, and the reference electrode was a saturated calomel electrode (SCE) separated with a fine glass frit. The concentration of the examined compounds was usually  $5.0 \times 10^{-4}$  M; 0.05 M tetraethylammonium hexafluorophosphate was added as supporting electrolyte. Cyclic voltammograms were obtained at sweep rates of 20, 50, 200, 500, and 1000 mV s<sup>-1</sup>; DPV experiments were performed with a scan rate of 4 mV s<sup>-1</sup>, a pulse height of 10 mV, and a duration of 40 ms. For reversible processes the same halfwave potential values are obtained from the DPV peaks and from an average of the cathodic and anodic cyclic voltammetric peaks. For irreversible processes the reported values are those evaluated from the DPV peak. Both CV and DPV techniques have been used to measure the number of exchanged electrons in each redox process,<sup>18</sup> utilizing as reference compound  $[\text{Ru}(\text{bpy})_3]^{2+}$ , for which the oxidation and reduction processes are reversible and mono-electronic.<sup>19</sup> To establish the reversibility of a process, we used the criteria of (i) separation of 60 mV between cathodic and anodic peaks, (ii) close to unity ratio of the intensities of the cathodic and anodic currents, and (iii) constancy of the peak potential on changing sweep rate in the cyclic voltammograms.

Absorption spectra were recorded with a Shimadzu UV-260, a Perkin-Elmer  $\lambda 5$ , or a Perkin-Elmer  $\lambda 6$  spectrophotometer. Molar extinction coefficients were determined from absorbance measurements on at least two different concentrations of complex. Luminescence experiments were performed in dilute (ca.  $10^{-5}$  M) acetonitrile solutions at room temperature and in a 4:1 (v/v) methanol/ethanol rigid matrix at 77 K, by using a Perkin-Elmer LS-50 spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 photomultiplier. Luminescence maxima reported are uncorrected for photomultiplier response. Luminescence lifetimes were measured with an Edinburgh 199 single-photon counting apparatus (D<sub>2</sub> lamp, 310 nm, time resolution 0.5 ns). Excitation spectra were performed on all luminescent compounds, obtaining a good match with the respective absorption spectra. Luminescence quantum yields were measured with a Perkin-Elmer LS-50 spectrofluorimeter, following

the optical dilute method,<sup>20</sup> with  $[\text{Ru}(\text{bpy})_3]^{2+}$  in air-equilibrated aqueous solution as the quantum yield standard ( $\Phi = 0.028$ ).<sup>21</sup>

Transient absorption measurements were performed on samples degassed by freeze-pump-thaw cycles. Sample concentration was in the range  $3-10 \times 10^{-5}$  M. Excitation was performed using the 355 nm line of a JK System 2000 YAG-DPLY laser. The excitation beam was perpendicular to the analyzing path, which employed a PTI 150W Xe lamp. Spectra of transients were acquired at suitable delay times after pulse excitation with a EG&G PARC 1460 optical multichannel analyzer. Kinetic absorption measurements at selected wavelengths were accomplished using a Tektronix 466 storage oscilloscope (time resolution 10 ns). The obtained trace was digitized, and the kinetic analysis was performed with a personal computer.

Estimated errors are as follows: redox potentials,  $\pm 20$  mV; molar absorption coefficients, 10%;  $\lambda_{\text{max}}$ , 2 nm; excited state lifetimes, 10%; kinetic constants, 15%.

**Materials.** DEAS-bpy ligand,<sup>22</sup>  $[(\text{DEAS-bpy})\text{Re}(\text{CO})_3\text{Cl}]$ ,<sup>22</sup> BPP,<sup>23</sup> (BPP-Me<sub>2</sub>)<sup>24,23</sup> and  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ <sup>24-26</sup> were synthesized as described elsewhere.  $\text{AgCF}_3\text{SO}_3$  (Aldrich 17,643-5) and  $\text{CF}_3\text{SO}_3\text{Me}$  (Aldrich 16,428-3) are commercially available. All reactions were carried out under dry argon by using oven-dried (140 °C) Schlenk-tube glassware. Solvents, including deuterated solvents were dried over suitable reagents and freshly distilled under argon before use.

All of the rhenium(I) complexes described within this paper have a facial (*fac*) configuration of the three carbonyl ligands as inferred by IR and NMR spectroscopies.

**Characterization of BPP.**  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  8.49 (d,  $^3J = 6.0$  Hz, 4H), 7.30 (d,  $^3J = 6.0$  Hz, 4H), 7.10 + 6.55 (2d, AB system,  $^3J = 16.0$  Hz, 2+2H), 6.83 + 6.70 (2d, AB system,  $^3J = 5.0$  Hz, 2+2H), 2.06 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25 °C)  $\delta$  150.09 (CH), 144.87 (CH), 137.52 (CH), 136.09 (CC), 135.13 (CH), 131.13 (CH), 125.43 (CH), 120.65 (CH), 12.83 ( $\text{CH}_3\text{C}=\text{C}$ ). FAB<sup>+</sup> (*m*-NBA) 315.3 [M + H]<sup>+</sup>.

**Characterization of  $[(\text{DEAS-bpy})\text{Re}(\text{CO})_3\text{Cl}]$  Symbolized as  $[(\text{DEAS-bpy})\text{ReCl}]$ .**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25 °C)  $\delta$  196.96 + 193.38 (Re-CO), 155.89, 151.48, 148.93, 137.91, 129.96, 122.97, 119.19, 118.00, 112.29, 44.89 ( $\text{CH}_2\text{CH}_3$ ), 12.63 ( $\text{CH}_2\text{CH}_3$ ); FAB<sup>+</sup> (*m*-NBA) 809.2 [M + H]<sup>+</sup>, 781.2 [M + H - CO]<sup>+</sup>, 753.2 [M + H - 2CO]<sup>+</sup>, 718.4 [M + H - 2CO - Cl]<sup>+</sup>, 690.2 [M + H - 3CO - Cl]<sup>+</sup>.

**Synthesis of the New Rhenium(I) Complexes.  $[(\text{DEAS-bpy})\text{Re}(\text{BPP})(\text{CO})_3](\text{CF}_3\text{SO}_3)$  Symbolized as  $[(\text{DEAS-bpy})\text{Re}(\text{BPP})]^+$ .**  $\text{AgCF}_3\text{SO}_3$  (0.095 g, 0.37 mmol) was added as solid to a solution of  $[(\text{DEAS-bpy})\text{Re}(\text{CO})_3\text{Cl}]$  (0.150 g, 0.186 mmol) in dry acetone (50 mL). After the reaction mixture was refluxed under argon at 70 °C overnight, the suspension was filtered over Celite. The yellow solution was added dropwise to a solution of BPP (0.070 g, 0.223 mmol) in anhydrous ethanol (50 mL). At this point the color of the reaction mixture was deep-orange. The solution was stirred at 70 °C for 4 h, whereupon the color changed to deep-red. Evaporation of the solvent gave the crude product (0.225 g), which was chromatographed on alumina, activity II-III (110 g), with a gradient of 1-2% methanol in dichloromethane as eluant. The analytically pure  $[(\text{DEAS-bpy})\text{Re}(\text{BPP})(\text{CO})_3](\text{CF}_3\text{SO}_3)$  complex was obtained after recrystallization in dichloromethane/hexane (0.202 g, 88%):  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  8.82 (d,  $^3J = 5.8$  Hz, 2H), 8.46 (s, 4H), 7.98 (d,  $^3J = 5.9$  Hz, 2H), 7.56 (m, 10H), 7.12 (m, 8H), 6.68 (d,  $^3J = 5.8$  Hz, 4H), 6.46 (m, 4H), 3.42 (q,  $^3J = 6.8$  Hz, 8H,  $\text{CH}_2\text{CH}_3$ ), 2.13 (s, 3H,  $\text{CH}_3$ ), 1.98 (s, 3H,  $\text{CH}_3$ ), 1.18 (t,  $^3J = 6.8$  Hz, 12H,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  197.00 + 192.78 (Re-CO), 156.37, 152.23, 151.54, 150.16, 149.87, 141.83, 139.85, 138.31, 137.79, 135.26, 133.23, 131.19, 130.49, 126.29, 123.32, 122.49, 121.35, 121.09, 117.55, 112.86, 111.81, 44.89 ( $\text{CH}_2\text{CH}_3$ ), 12.79 ( $\text{CH}_2\text{CH}_3$ ), 12.71 ( $\text{CH}_3\text{C}=\text{C}$ ), 12.68 ( $\text{CH}_3\text{C}=\text{C}$ ); FAB<sup>+</sup> (*m*-

(20) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(21) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

(22) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007.

(23) Blanchard-Desce, M. Thèse de Doctorat, Université de Paris 6, 1989.

(24) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501.

(25) Zingales, F.; Graziani, M.; Faraone, F.; Belluco, U. *Inorg. Chim. Acta* **1967**, *1*, 172.

(26) Vitali, D.; Calderazzo, F. *Gazz. Chim. Ital.* **1972**, *102*, 587.

(18) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(19) De Armond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.

NBA) 1087.3 [M – OTf]<sup>+</sup>, 1059.3 [M – OTf – CO], 773.2 [M – OTf – BPP]; ES-MS (CH<sub>3</sub>CN) *m/z* 1087.2 [M – OTf]<sup>+</sup> calcd value 1087.3; IR (KBr pellet, cm<sup>-1</sup>)  $\nu_{CO}$  2025, 1925, 1907. Anal. Calcd for C<sub>60</sub>H<sub>50</sub>N<sub>6</sub>O<sub>6</sub>F<sub>3</sub>SRe (*M<sub>r</sub>* = 1236.446): C, 58.29; H, 4.89; N, 6.80. Found: C, 58.14; H, 4.76; N, 6.63.

**[(DEAS-bpy)Re(BPP-Me)(CO)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> Symbolized as [(DEAS-bpy)Re(BPP-Me)]<sup>2+</sup>.** CF<sub>3</sub>SO<sub>3</sub>Me (9.2  $\mu$ L, 0.081 mmol) was added to a solution of [(DEAS-bpy)Re(BPP)(CO)<sub>3</sub>]<sup>+</sup> (0.100 g, 0.081 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at 0 °C, under argon. The deep-red solution was stirred at 0 °C for 75 min, and then additional CF<sub>3</sub>SO<sub>3</sub>Me (9.2  $\mu$ L, 0.081 mmol) was added dropwise. The mixture was stirred overnight at room temperature and then quenched with water (5 mL). Evaporation of the solvent gave the crude product (0.120 g), which was chromatographed on alumina, activity II–III (100 g), with a gradient of 1–4% methanol in dichloromethane as eluant. The analytically pure [(DEAS-bpy)Re(BPP-Me)(CO)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> complex was obtained after recrystallization in dichloromethane/hexane (0.105 g, 93%): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  8.83 (d, <sup>3</sup>*J* = 5.6 Hz, 2H), 8.48 (s, 2H), 8.03 (d, <sup>3</sup>*J* = 5.6 Hz, 2H), 7.81 (s, 2H), 7.58 (m, 8H), 7.25 (d, <sup>3</sup>*J* = 5.2 Hz, 2H), 7.05 (m, 4H), 6.68 (m, 12H), 4.19 (s, 3H, py<sup>+</sup>–CH<sub>3</sub>), 3.39 (q, <sup>3</sup>*J* = 6.7 Hz, 8H, CH<sub>2</sub>CH<sub>3</sub>), 2.11 (s, 3H, CH<sub>3</sub>), 1.96 (s, 3H, CH<sub>3</sub>), 1.19 (t, <sup>3</sup>*J* = 6.7 Hz, 12H, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  196.91 + 192.92 (Re–CO), 152.24, 152.23, 151.64, 149.81, 146.45, 144.46, 141.36, 139.56, 137.72, 134.61, 132.44, 130.49, 128.07, 124.06, 123.45, 123.20, 122.52, 122.10, 121.42, 117.63, 111.78, 68.51 (py<sup>+</sup>–CH<sub>3</sub>), 44.87 (CH<sub>2</sub>CH<sub>3</sub>), 12.76 (CH<sub>2</sub>CH<sub>3</sub>); FAB<sup>+</sup> (*m*-NBA) 1251.5 [M – OTf]<sup>+</sup>, 1102.4 [M – 2OTf], 773.2 [M – 2OTf – (BPP-Me)], 12.68 (CH<sub>3</sub>C=), 12.53 (CH<sub>3</sub>C=); ES-MS (CH<sub>3</sub>CN) *m/z* 551.2 [M – 2OTf]<sup>2+</sup> calcd value 551.0; IR (KBr pellet, cm<sup>-1</sup>)  $\nu_{CO}$  2022, 1921, 1907. Anal. Calcd for C<sub>62</sub>H<sub>63</sub>N<sub>6</sub>O<sub>9</sub>F<sub>6</sub>S<sub>2</sub>Re (*M<sub>r</sub>* = 1400.545): C, 53.17; H, 4.53; N, 6.00. Found: C, 53.02; H, 4.26; N, 5.81.

**[(bpy)Re(BPP)(CO)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> Symbolized as [(bpy)Re(BPP)]<sup>2+</sup>.** AgCF<sub>3</sub>SO<sub>3</sub> (0.128 g, 0.498 mmol) was added as a solid to a solution of [(bpy)Re(CO)<sub>3</sub>Cl] (0.192 g, 0.417 mmol) in dry dichloromethane (40 mL). After the reaction mixture was refluxed under argon at 60 °C overnight, the suspension was filtered over Celite. The pale yellow solution was added dropwise to a solution of BPP (0.131 g, 0.417 mmol) in anhydrous ethanol (100 mL). At this point the color of the reaction mixture was deep-orange. The solution was stirred at 80 °C during 24 h, whereupon the color changed to deep-red. Evaporation of the solvent gave the crude product (0.326 g), which was chromatographed on alumina, activity II–III (110 g), with a gradient of 1–3% methanol in dichloromethane as eluant. The analytically pure [(bpy)Re(BPP)(CO)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> complex was obtained after recrystallization in dichloromethane/pentane (0.308 g, 83%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C)  $\delta$  9.08 (d, <sup>3</sup>*J* = 5.3 Hz, 2H), 8.78 (d, <sup>3</sup>*J* = 8.2 Hz, 2H), 8.51 (d, <sup>3</sup>*J* = 5.7 Hz, 2H), 8.31 (td, <sup>3</sup>*J* = 6.7, <sup>4</sup>*J* = 1.2 Hz, 2H), 7.95 (d, <sup>3</sup>*J* = 6.5 Hz, 2H), 7.75 (t, <sup>3</sup>*J* = 5.8 Hz, 2H), 7.25 (m, 4H), 7.04 (dd, <sup>3</sup>*J* = 5.8 Hz, <sup>3</sup>*J* = 5.6 Hz, 2H), 6.78–6.28 (m, 6H), 2.02 (s, 3H, CH<sub>3</sub>), 1.94 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 25 °C)  $\delta$  196.66 + 192.60 (Re–CO), 156.58, 154.64, 152.44, 150.81, 149.37, 145.67, 142.02, 141.95, 138.39, 138.19, 138.13, 136.88, 135.66, 133.57, 131.88, 129.60, 126.77, 125.56, 123.94, 123.65, 121.55, 12.77 (CH<sub>3</sub>C=), 12.58 (CH<sub>3</sub>C=); FAB<sup>+</sup> (*m*-NBA) 741.1 [M – OTf]<sup>+</sup>, 427.0 [M – OTf – BPP], 399.0 [M – OTf – BPP – CO], 371.0 [M – OTf – BPP – 2CO], 343.1 [M – OTf – BPP – 3CO]; ES-MS (CH<sub>3</sub>CN) *m/z* 740.8 [M – OTf]<sup>2+</sup> calcd value 740.9; IR (KBr pellet, cm<sup>-1</sup>)  $\nu_{CO}$  2030, 1927, 1909. Anal. Calcd for C<sub>36</sub>H<sub>30</sub>N<sub>4</sub>O<sub>6</sub>F<sub>3</sub>SRe (*M<sub>r</sub>* = 889.926): C, 48.59; H, 3.40; N, 6.30. Found: C, 48.37; H, 3.22; N, 6.14.

**[(DEAS-bpy)Re(CO)<sub>3</sub>]<sub>2</sub>( $\mu$ -BPP)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> Symbolized as [(DEAS-bpy)<sub>2</sub>Re<sub>2</sub>( $\mu$ -BPP)]<sup>2+</sup>.** AgCF<sub>3</sub>SO<sub>3</sub> (0.048 g, 0.186 mmol) was added as a solid to a solution of [(DEAS-bpy)Re(CO)<sub>3</sub>Cl] (0.150 g, 0.186 mmol) in dry acetone (50 mL). After the reaction mixture was refluxed under argon at 70 °C overnight, the suspension was filtered over Celite. The yellow solution was added dropwise to a solution of [(DEAS-bpy)Re(BPP)]<sup>+</sup> (0.230 g, 0.186 mmol) in anhydrous dichloromethane (50 mL). The color of the solution turned instantaneously deep red, showing very fast complexation of the free pyridine subunit to the rhenium precursor. The solution was stirred at room temperature for 10 h. Evaporation of the solvent gave the crude product (0.390 g),

which was chromatographed on alumina, activity II–III (110 g), with a gradient of 5–10% methanol in dichloromethane as eluant. The analytically pure [(DEAS-bpy)Re(CO)<sub>3</sub>]<sub>2</sub>( $\mu$ -BPP)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> complex was obtained after recrystallization in dichloromethane/hexane (0.272 g, 68%): <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  8.79 (d, <sup>3</sup>*J* = 6.0 Hz, 2H), 8.35 (s, 4H), 8.02 (d, <sup>3</sup>*J* = 6.0 Hz, 2H), 7.89 (m, 10H), 7.02 (m, 8H), 6.58 (d, <sup>3</sup>*J* = 6.0 Hz, 4H), 6.38 (m, 4H), 3.40 (q, <sup>3</sup>*J* = 6.9 Hz, 8H, CH<sub>2</sub>–CH<sub>3</sub>), 2.11 (s, 3H, CH<sub>3</sub>), 2.00 (s, 3H, CH<sub>3</sub>), 1.22 (t, <sup>3</sup>*J* = 6.9 Hz, 12H, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  197.21 + 192.93 (Re–CO), 156.54, 152.13, 150.27, 150.02, 141.79, 139.68, 138.28, 137.97, 135.86, 133.12, 131.03, 130.45, 126.28, 123.31, 121.58, 121.26, 117.25, 112.89, 111.56, 44.96 (CH<sub>2</sub>CH<sub>3</sub>), 12.86 (CH<sub>2</sub>CH<sub>3</sub>), 12.79 (CH<sub>3</sub>C=); ES-MS (CH<sub>3</sub>CN) *m/z* 929.9 [M – 2OTf]<sup>2+</sup> calcd value 930.2; IR (KBr pellet, cm<sup>-1</sup>)  $\nu_{CO}$  2023, 1922, 1903. Anal. Calcd for C<sub>98</sub>H<sub>98</sub>N<sub>10</sub>O<sub>12</sub>F<sub>6</sub>S<sub>2</sub>Re<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (*M<sub>r</sub>* = 2158.458 + 84.933): C, 53.00; H, 4.49; N, 6.24. Found: C, 52.79; H, 4.16; N, 6.13.

## Results and Discussion

**Synthesis.** Complexes depicted in Figure 1 were synthesized in a straightforward manner: (i) dehalogenation of the starting metal precursor [(bpy-RR)Re(CO)<sub>3</sub>Cl] (RR = DEAS or H) with silver salts afforded the [(bpy-RR)Re(CO)<sub>3</sub>]<sup>+</sup> cation; (ii) subsequent reaction with bis(pyridine)polyene (BPP) under stoichiometric conditions gave the corresponding [(bpy-RR)Re(CO)<sub>3</sub>(BPP)]<sup>+</sup> cation in 83–88% isolated yield; (iii) further reaction of [(DEAS-bpy)Re(CO)<sub>3</sub>(BPP)]<sup>+</sup> with 1 equiv of [(DEAS-bpy)Re(CO)<sub>3</sub>]<sup>+</sup> gave the dinuclear [(DEAS-bpy)Re(CO)<sub>3</sub>]<sub>2</sub>( $\mu$ -BPP)]<sup>2+</sup> complex in 68% yield; (iv) quaternization of the [(DEAS-bpy)Re(CO)<sub>3</sub>(BPP)]<sup>+</sup> compound with methyl triflate in anhydrous dichloromethane afforded the [(DEAS-bpy)Re(CO)<sub>3</sub>(BPP-Me)]<sup>2+</sup> dication in 93% yield. All complexes have been characterized by elemental analysis, and <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H NMR, IR, electronic absorption and emission spectroscopy, and mass spectroscopy (FAB<sup>+</sup> + ES-MS). It is noteworthy that electrospray mass spectroscopy (ES-MS) confirms the unique formation of these cationic complexes. The spectra obtained are clear and readily interpreted, due to the presence of several pseudomolecular peaks corresponding to successive loss of counteranion. Fragmentation of the complexes in solution was easily prevented by using a low acceleration potential. High resolution of the pseudo molecular peak confirms the global charge of the cations.

In general, all of the complexes and ligands under investigation are thermally inert in solution, as shown by the constancy of their absorption spectra for several days. Even during extensive laser flash experiments only minor decomposition was observed. In any case, all of the measurements were performed on freshly prepared samples.

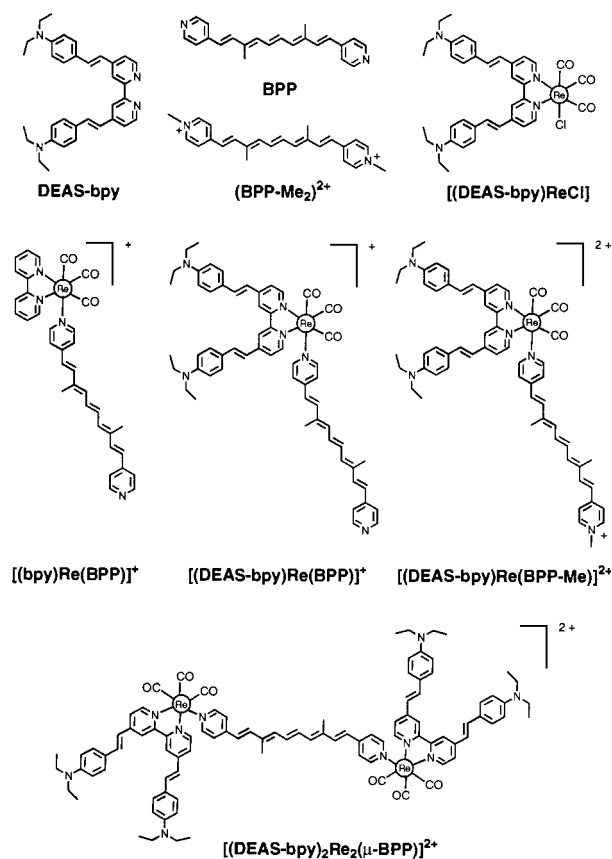
**General Properties.** The spectroscopic and electrochemical behavior of transition-metal complexes containing polypyridine ligands with N-N type coordination sites is usually discussed with the assumption that the ground state as well as the excited and redox states can be described by localized molecular orbital configurations.<sup>19,27–30</sup> Within such an approximation the oxidation and reduction processes are classified as metal or ligand centered, respectively, and the various spectroscopic transitions are classified as metal centered (MC), ligand centered (LC), or charge transfer (either metal to ligand, MLCT, or ligand to metal, LMCT).

- (27) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: London, 1970.  
 (28) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.  
 (29) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, 1992.  
 (30) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

**Table 1.** Electrochemical Results in Argon-Purged Acetonitrile Solution at Room Temperature<sup>a</sup>

compd	$E_{\text{red}} [n]^b$ (site)	$E_{\text{ox}} [n]^b$ (site)
DEAS-bpy	-2.00 [4]	+0.66 i [2], +1.00 i [1], +1.10 i
BPP	-0.86 [≈3], -1.46 i [≈5]	+1.00 i [≈1]
(BPP-Me <sub>2</sub> ) <sup>2+</sup>	-0.63 [≈3]	+1.23 [≈1.5]
[(DEAS-bpy)ReCl] <sup>c</sup>	-1.27 (DEAS-bpy)	+0.69 <sup>d</sup> (DEAS-bpy)
[(bpy)Re(BPP)] <sup>+</sup>	-0.81 [1] (BPP), -1.16 [1] (BPP), -1.32 [1] (bpy), -1.44 [1]	+1.00 i [1] (BPP), ≈+1.80 i (Re)
[(DEAS-bpy)Re(BPP)] <sup>+</sup>	-0.88 [1] (BPP), -1.13 [1] (BPP), -1.33 [1] (DEAS-bpy)	+0.75 i [2] (DEAS-bpy), +0.92 i [≈1] (DEAS-bpy), +1.06 [≈1] (DEAS-bpy or BPP)
[(DEAS-bpy)Re(BPP-Me)] <sup>2+</sup>	-0.83 [2] (BPP), -1.07 [ <1] (BPP), -1.31 [≈1] (DEAS-bpy)	+0.74 i [2] (DEAS-bpy), +0.90 <sup>e</sup> (DEAS-bpy), +1.00 <sup>e</sup> (DEAS-bpy or BPP), +1.26 i [1]
[(DEAS-bpy) <sub>2</sub> Re <sub>2</sub> (μ-BPP)] <sup>2+</sup>	-0.87 i [1.5] (BPP), -1.01 [1.5] (BPP), -1.30 [2] (DEAS-bpy), -1.48 <sup>e</sup>	+0.73 i [≈4] (DEAS-bpy), +0.90 <sup>e</sup> (DEAS-bpy), +1.10 <sup>e</sup> (DEAS-bpy or BPP), +1.40, <sup>e</sup> ≈+1.80 i (Re)

<sup>a</sup> Potentials in V vs SCE; unless otherwise noted, the waves are reversible or quasireversible; for irreversible waves (i) the reported value is taken from the differential pulse voltammetry peak. <sup>b</sup> Number of electrons exchanged. <sup>c</sup> Data from ref 22. <sup>d</sup> In DMF. <sup>e</sup> Ill-defined wave.

**Figure 1.** Formulas and abbreviations of the ligands and complexes used.

Previous investigations on Re(I)–tricarbonyl complexes containing polypyridine chelating ligands have shown that as a rule oxidation processes are metal centered (most often irreversible), while reduction processes are ligand centered (usually reversible).<sup>22,30–32</sup> As far as the photophysical properties are concerned, these complexes are usually MLCT emitters.<sup>29,33,34</sup> As the ligands DEAS-bpy and BPP are not typical polypyridine species, these rules will not be strictly followed in our complexes.

**Electrochemical Behavior.** Table 1 gathers all of the electrochemical results obtained in argon-purged acetonitrile

solution at room temperature. The study of the free ligands DEAS-bpy and BPP was difficult due to limited solubility of the two species in acetonitrile. The data concerning the model compound [(DEAS-bpy)ReCl] have been taken from the literature.<sup>22</sup>

**Reduction Processes.** The free ligand DEAS-bpy shows a single reduction wave at -2.00 V, which seems to involve four electrons. The potential of reduction is typical for a polypyridine unit.

The free ligand BPP shows a first reversible trielectronic wave at -0.86 V, followed by a second multielectronic wave at -1.46 V. By comparison, the molecule (BPP-Me<sub>2</sub>)<sup>2+</sup> (which has no solubility problems, so the data are much clearer) shows only a single trielectronic wave at -0.63 V. The easier reduction of this latter species with respect to BPP is consistent with the different molecular charge.

For the model compound [(DEAS-bpy)ReCl] only one reduction process at -1.27 V was reported,<sup>22</sup> which can be assigned to reduction of the DEAS-bpy ligand (the only electroactive ligand present). The shift in reduction potential featured by the DEAS-bpy ligand upon coordination appears normal for a polypyridine unit.

Model [(bpy)Re(BPP)]<sup>+</sup> shows a much more complex behavior due to the presence of two electroactive ligands (bpy and BPP). The first two reduction processes are assigned to BPP ligand reduction; most probably the first process is localized on the pyridine ring coordinated to the Re metal. The third reduction process should involve the bpy ligand, as the value of the potential (-1.32 V) is consistent with that of a coordinated polypyridine unit.

In compounds [(DEAS-bpy)Re(BPP)]<sup>+</sup>, [(DEAS-bpy)Re(BPP-Me)]<sup>2+</sup>, and [(DEAS-bpy)<sub>2</sub>Re<sub>2</sub>(μ-BPP)]<sup>2+</sup> the presence of the two electroactive ligands DEAS-bpy and BPP gives rise to a very rich electrochemical behavior. All three of these complexes feature reduction processes at very similar potential. By analogy with the behavior of model compounds [(DEAS-bpy)ReCl] and [(bpy)Re(BPP)]<sup>+</sup>, the first two processes are assigned to BPP reduction, whereas the third one (around -1.30 V) is assigned to DEAS-bpy reduction. Note in particular that this third wave is reversible, and bielectronic in the case of [(DEAS-bpy)<sub>2</sub>Re<sub>2</sub>(μ-BPP)]<sup>2+</sup>.

**Oxidation Processes.** Oxidation of the free ligand DEAS-bpy involves a number of irreversible processes. Noting the bielectronic nature of the first wave at +0.66 V, and taking into account that aliphatic amines are easily oxidized in irreversible processes, the oxidation processes observed on DEAS-bpy should be localized on the amine units. On the other

(31) Worl, L. A.; Duesing, R.; Chen, P.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849.

(32) Wallace, L.; Rillema, P. *Inorg. Chem.* **1993**, 32, 3836.

(33) Stufkens, D. J. *Comments Inorg. Chem.* **1992**, 13, 359.

(34) Schanze, K. S.; MacQueen, B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, 122, 63.

**Table 2.** Spectroscopic and Photophysical Data<sup>a</sup>

compd	absorption <sup>b</sup>		luminescence			
	298 K $\lambda_{\max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{\max}$ , nm	298 K		77 K	
			$\tau$ , ns	$\Phi$	$\lambda_{\max}$ , nm	$\tau$ , $\mu$ s
DEAS-bpy	394 (53 200)	516	<1	0.036	490 632 <sup>c</sup>	0.028 ≈2000
BPP	428 (52 500) <sup>d</sup>	557	<1	0.0058	490	<0.001
(BPP-Me <sub>2</sub> ) <sup>2+</sup>	483 (63 500)					
[(DEAS-bpy)ReCl] <sup>e</sup>	462 (57 100)	670	140	0.004	665	630
[(bpy)Re(BPP)] <sup>+</sup>	448 sh (55 700)	601	108	0.0019	562	0.023
[(DEAS-bpy)Re(BPP)] <sup>+</sup>	454 (98 100)				675	360
[(DEAS-bpy)Re(BPP-Me)] <sup>2+</sup>	457 (102 000)				676	355
[(DEAS-bpy) <sub>2</sub> Re <sub>2</sub> ( $\mu$ -BPP)] <sup>2+</sup>	472 (139 000)				678	385

<sup>a</sup> Data in acetonitrile solution at room temperature and in a 4:1 (v/v) methanol/ethanol rigid matrix at 77 K, unless otherwise noted. <sup>b</sup> Only the lowest energy maximum or shoulder is reported. <sup>c</sup> In C<sub>3</sub>H<sub>7</sub>I glass. <sup>d</sup>  $\epsilon$  value in ethanol, from ref 38. <sup>e</sup> Data from ref 22; DMF at 298 K and 9:1 (v/v) DMF/CH<sub>2</sub>Cl<sub>2</sub> matrix at 77 K.

hand it is known that the coordinated “bpy” unit is oxidized only at very high potential ( $E > 2$  V).<sup>35,36</sup>

Oxidation of the free ligand BPP features a single mono-electronic process at +1.00 V. By comparison, the molecule (BPP-Me<sub>2</sub>)<sup>2+</sup> is oxidized at +1.23 V; the shift toward more positive potential with respect to BPP is again consistent with the different molecular charge. The model [(DEAS-bpy)ReCl] complex features a wave at +0.69 V<sup>22</sup> which is unambiguously due to oxidation of the DEAS-bpy amines.

In the model [(bpy)Re(BPP)]<sup>+</sup> complex one can observe the mono-electronic wave due to BPP oxidation (+1.00 V) followed by a wave at about +1.8 V that is due to Re(I) oxidation. This latter value is close to that observed for Re(I) oxidation in similar complexes like [Re(CO)<sub>3</sub>(bpy)(Etpy)]<sup>+</sup> (Etpy = 4-ethylpyridine,  $E = +1.72$  V).<sup>37</sup>

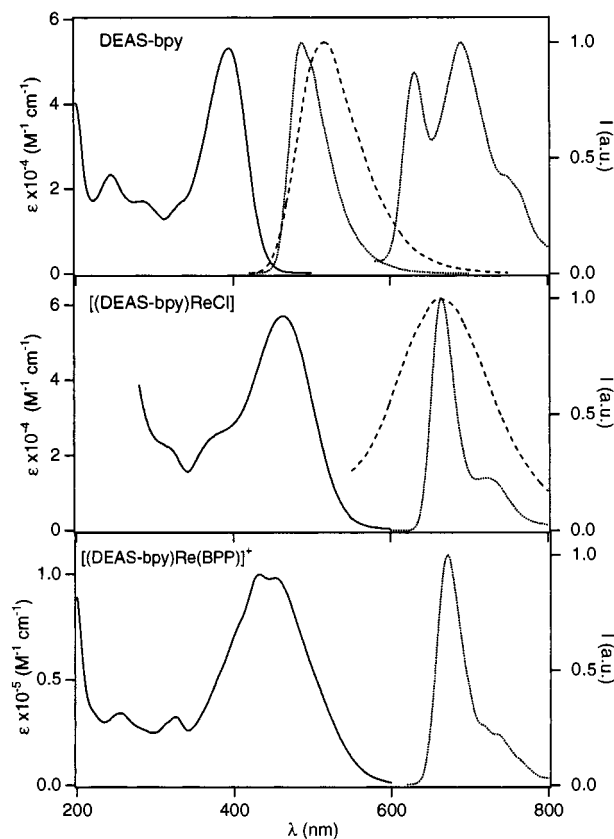
Complex [(DEAS-bpy)Re(BPP)]<sup>+</sup> shows three oxidation processes. The first two are irreversible and are due to DEAS-bpy amine oxidation (cf. the free ligand DEAS-bpy). The assignment of the third wave is difficult because oxidation processes of both DEAS-bpy and BPP ligands are possible around +1.0 V. The behavior of the corresponding methylated complex, [(DEAS-bpy)Re(BPP-Me)]<sup>2+</sup>, appears very similar.

As far as complex [(DEAS-bpy)<sub>2</sub>Re<sub>2</sub>( $\mu$ -BPP)]<sup>2+</sup> is concerned, the same assignments as for [(DEAS-bpy)Re(BPP)]<sup>+</sup> can be done for the first three oxidation processes. Note the increased number of exchanged electrons in the first wave at +0.73 V, due to the presence of two DEAS-bpy units. The process at +1.80 V is due to Re(I) oxidation (cf. model [(bpy)Re(BPP)]<sup>+</sup>).

In summary the introduction of ligands such as DEAS-bpy and BPP in Re(I)–tricarbonyl complexes gives rise to a very rich and complicated redox chemistry. As we will see later, this will profoundly influence the photophysical behavior of these complexes.

**Photophysical Properties.** Table 2 summarizes the absorption and luminescence data obtained for all of the examined compounds. Figures 2 and 3 show the absorption and luminescence spectra of the free ligands DEAS-bpy and BPP, of the model [(DEAS-bpy)ReCl] and [(bpy)Re(BPP)]<sup>+</sup> compounds, and of the [(DEAS-bpy)Re(BPP)]<sup>+</sup> complex.

**Absorption Spectra.** The free ligands DEAS-bpy and BPP feature a very intense band in the 400 nm region (Figures 2 and 3); this band is structured in the case of the BPP ligand.



**Figure 2.** Absorption spectrum (solid line) and uncorrected luminescence spectra at room temperature (dashed line) and at 77 K (dotted line) for DEAS-bpy, [(DEAS-bpy)ReCl], and [(DEAS-bpy)Re(BPP)]<sup>+</sup>. Solvents are acetonitrile at room temperature and 4:1 v/v methanol/ethanol at 77 K for DEAS-bpy and [(DEAS-bpy)Re(BPP)]<sup>+</sup>. For [(DEAS-bpy)ReCl], DMF and 9:1 v/v DMF/CH<sub>2</sub>Cl<sub>2</sub> were used at 293 and 77 K, respectively.

Model [(DEAS-bpy)ReCl] was previously investigated.<sup>22</sup> It was found that the absorption band is due to LC transitions of the DEAS-bpy ligand. Note the absence of structure both in the free ligand DEAS-bpy and in model [(DEAS-bpy)ReCl] (Figure 2).

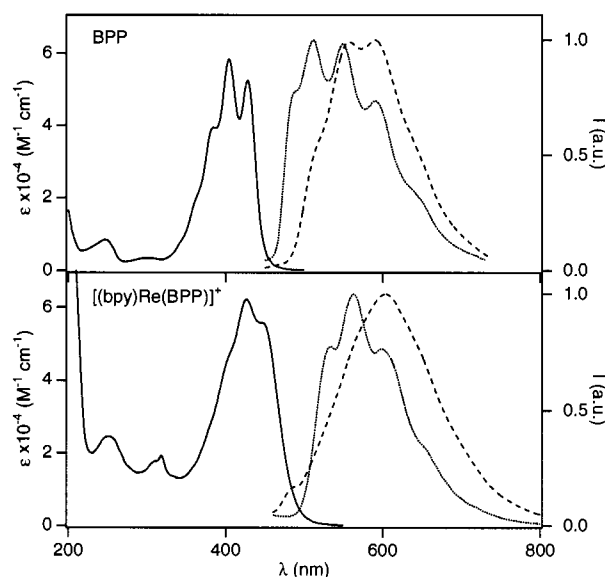
The model [(bpy)Re(BPP)]<sup>+</sup> contains the BPP but not the DEAS-bpy ligand. Comparison of the absorption spectra of [(bpy)Re(BPP)]<sup>+</sup> and BPP (Figure 3) clearly indicates that the band at about 450 nm of [(bpy)Re(BPP)]<sup>+</sup> is due to LC transition of the BPP ligand. Indeed, the structure observed in the absorption band of the free ligand is partially retained also in model [(bpy)Re(BPP)]<sup>+</sup>.

(35) Gaudiello, J. G.; Sharp, P. R.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6373.

(36) Chlistunoff, J. B.; Bard, A. J. *Inorg. Chem.* **1993**, *32*, 3521.

(37) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.

(38) Blanchard-Desce, M.; Arrhenius, T. S.; Lehn, J.-M. *Bull. Soc. Chim. Fr.* **1993**, *130*, 266.



**Figure 3.** Absorption spectrum (solid line, acetonitrile solution, room temperature) and uncorrected luminescence spectra (dashed line, acetonitrile at room temperature; dotted line, 4:1 v/v methanol/ethanol rigid matrix at 77 K) of BPP and  $[(bpy)Re(BPP)]^+$ .

It can be noticed that the three complexes  $[(DEAS-bpy)Re(BPP)]^+$ ,  $[(DEAS-bpy)Re(BPP-Me)]^{2+}$ , and  $[(DEAS-bpy)_2Re_2(\mu-BPP)]^{2+}$ , which contain both the DEAS-bpy and the BPP ligands, feature very similar absorption (and also luminescence, see below) bands around 450 nm (Table 2; only the absorption spectrum of  $[(DEAS-bpy)Re(BPP)]^+$  is shown in Figure 2). This absence of any remarkable effect of the total charge of the complex indicates that these bands are of substantial LC origin. One may argue that it is the BPP ligand which contributes primarily to the absorption band of the complexes, as the BPP absorption (428 nm) is closer in energy, and features a structure which appears clearly in the absorption band of the complexes. A contribution from the DEAS-bpy ligand is, however, also possible, as the absorption band of DEAS-bpy (394 nm) is not so far in energy.

**Luminescence.** The free ligand DEAS-bpy displays two emission bands at 77 K (Table 2 and Figure 2). The band at 490 nm is unstructured and has a lifetime and an energy position clearly indicative of a fluorescence band. Using  $C_3H_7I$  as solvent it is possible to evidence the second, structured band in the region 600–800 nm. Given the energy position and the very long lifetime (millisecond range), this second band is assigned to a phosphorescence emission of the free ligand.

The free ligand BPP shows a single, structured emission band at 77 K in the region 450–650 nm (Figure 3 and Table 2). As the lifetime is shorter than 1 ns, this emission can safely be assigned to a fluorescence. Even using  $C_3H_7I$  as solvent it is not possible to detect any phosphorescence band. This last finding is consistent with the behavior of the excited states of long linear polyenes, whose triplet state cannot be populated by direct excitation.<sup>39</sup>

Passing to the complexes, the model compound  $[(DEAS-bpy)ReCl]$  (containing DEAS-bpy but not BPP) was previously investigated. The emission observed at 77 K (Figure 2 and Table 2) was assigned to DEAS-bpy LC emission on the basis of the very long lifetime, and of the similarity with the phosphorescence band of the free DEAS-bpy ligand.<sup>22</sup>

Model  $[(bpy)Re(BPP)]^+$  features a 77 K emission that can be assigned to fluorescence emission from the BPP ligand. Indeed, the band is structured, its position is near the fluorescence emission at 77 K of the free BPP ligand (Figure 3 and Table 2), and the lifetime is in the nanosecond range. Emission from a CT state involving bpy can be ruled out, as in  $Re(I)$  complexes such states feature unstructured emission bands and lifetimes in the microsecond range.<sup>22,29,33</sup>

The three complexes  $[(DEAS-bpy)Re(BPP)]^+$ ,  $[(DEAS-bpy)Re(BPP-Me)]^{2+}$ , and  $[(DEAS-bpy)_2Re_2(\mu-BPP)]^{2+}$  show a luminescence emission at 77 K (see Table 2 and Figure 2) which is almost identical in position and shape, and very similar in lifetime to that featured by model  $[(DEAS-bpy)ReCl]$ . The 77 K emission of these three complexes can thus be assigned to DEAS-bpy LC phosphorescence. This LC assignment to the 77 K luminescence of all of the DEAS-bpy-containing compounds is further supported by their almost identical emission, irrespective of the total charge of the species. A similar behavior is also observed in the absorption spectrum (see above).

Passing to room temperature, both the free ligands DEAS-bpy and BPP show a luminescence emission, which is red shifted with respect to their own fluorescence band at 77 K. As the observed lifetime is shorter than 1 ns, this room temperature luminescence is assigned to a fluorescence emission.

In model  $[(DEAS-bpy)ReCl]$  the observed luminescence at room temperature was assigned to DEAS-bpy LC emission. Note, in particular, the very small red shift of the emission band on passing from 77 K to room temperature, as typically observed for LC emitters (Figure 2 and Table 2).

Concerning the 293 K emission of model  $[(bpy)Re(BPP)]^+$  (Figure 3), we can note that the lifetime is 108 ns, and the red shift with respect to 77 K emission is larger than in the case of  $[(DEAS-bpy)ReCl]$ . Both of these facts rule out a LC fluorescence from BPP. The lifetime value and the absence of structure indicate an emission of MLCT origin, which should involve the BPP unit (the ligand easier to reduce). Further support to this assignment comes from the value of the radiative rate constant ( $k_r = 1.8 \times 10^4 s^{-1}$ ), which can be calculated from the lifetime and quantum yield data at room temperature.

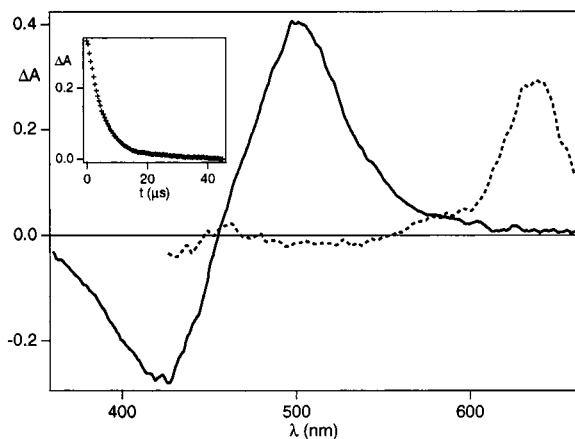
None of the complexes  $[(DEAS-bpy)Re(BPP)]^+$ ,  $[(DEAS-bpy)Re(BPP-Me)]^{2+}$ , and  $[(DEAS-bpy)_2Re_2(\mu-BPP)]^{2+}$  show emission at room temperature.

**Transient Measurements.** Transient absorption measurements were performed at room temperature on compounds  $[(DEAS-bpy)Re(BPP)]^+$ ,  $[(DEAS-bpy)Re(BPP-Me)]^{2+}$ , and BPP to clarify the nature of the lowest excited state in the nonemitting complexes.

In complex  $[(DEAS-bpy)Re(BPP)]^+$  a transient species is observed following laser flash excitation in deaerated acetonitrile (Figure 4). An absorption band around 520 nm is observed due to the new transient species formed, together with the bleaching of the ground state absorption around 430 nm. The maximum of the absorption band in  $[(DEAS-bpy)Re(BPP)]^+$  is at 454 nm; the bleaching maximum is shifted to the blue in the transient spectrum due to the presence of the 520 nm band. The kinetics of the back reaction to the ground state was followed both at 510 nm (decay of the transient species) and at 430 nm (ground state recovery). In both cases 95% of the decay could be fitted as a first-order process, with the same kinetic constant within the experimental errors ( $k = 0.23 \times 10^6 s^{-1}$ ). The remaining 5% of the decay, which is probably due to a decomposition side reaction, was not further investigated.

The same general behavior was observed also for the complex  $[(DEAS-bpy)Re(BPP-Me)]^{2+}$ . In the transient spectrum (not

(39) Bensasson, R.; Land, E. J.; Maudinas, B. *Photochem. Photobiol.* **1976**, *23*, 189.



**Figure 4.** Solid line: transient absorption spectrum at room temperature in deaerated acetonitrile for complex [(DEAS-bpy)Re(BPP)]<sup>+</sup>. The excitation wavelength is 355 nm. The spectrum was acquired with a delay of 0.1 μs after the pulse and a width of 0.5 μs. Inset: decay of the transient signal, monitored at 510 nm. Dashed line: transient absorption spectrum of <sup>3</sup>BPP (see text).

shown) a positive feature is observed at about 530 nm, and the bleaching of the ground state is observed around 440 nm. Both the recovery of the ground state and the decay of the transient species were exponential with the same kinetic constant within the experimental errors ( $k = 0.25 \times 10^6 \text{ s}^{-1}$ ).

Absorption of the triplet state of the free ligand BPP (<sup>3</sup>BPP) was measured populating it by energy transfer using anthracene as triplet donor. The spectrum (Figure 4) measured 2 μs after the excitation pulse features a single absorption band at 640 nm. This excludes that the transient spectra observed in complexes [(DEAS-bpy)Re(BPP)]<sup>+</sup> and [(DEAS-bpy)Re(BPP-Me)]<sup>2+</sup> may be due to a triplet energy transfer to the BPP unit. For this reason, in the following discussion we may ignore which is the actual energy position of the <sup>3</sup>BPP level.

**Energy-Level Scheme.** For a better understanding of the photophysical properties of DEAS-bpy- and BPP-containing complexes, it is useful to outline an energy-level diagram of the various states that can be reached after light excitation. As usual, one has to distinguish excited states from redox-separated states; their energy can be estimated by using spectroscopic and electrochemical data, respectively.<sup>40</sup> As far as the redox-separated states are concerned, throughout the discussion the work term corrections have been neglected. In similar cases such corrections have been shown to be small.<sup>40</sup> The diagrams obtained are displayed in Figure 5 and are valid at room temperature. In the following we discuss how the energies of the various levels are estimated, and what can be concluded on the basis of the energy-level diagram.

**Model [(DEAS-bpy)ReCl].** The energy of the LC triplet state of DEAS-bpy can be taken from the observed emission energy (674 nm, corresponding to 1.84 eV). This state is indicated as LC [<sup>3</sup>DEAS-bpy)ReCl].

A CT state Re → DEAS-bpy should also be present. The energy of this state can be estimated by taking the energy of the Re → bpy CT state in the analogous complex [Re(CO)<sub>3</sub>(bpy)Cl] ( $E = 2.02 \text{ eV}$ )<sup>41</sup> and considering the difference in the potential for bpy reduction in this complex ( $E_{\text{red}} = -1.32 \text{ V}$ ) with respect to DEAS-bpy reduction in [(DEAS-bpy)ReCl] ( $E_{\text{red}} = -1.27 \text{ V}$ ). These data show that DEAS-bpy in [(DEAS-bpy)ReCl] is a slightly better electron acceptor than bpy in [Re-

(CO)<sub>3</sub>(bpy)Cl]. The state CT Re → DEAS-bpy can thus be estimated at  $E = 2.02 - 0.05 = 1.97 \text{ eV}$ .

On the basis of the electrochemical results one can infer the presence of a redox-separated state centered on DEAS-bpy, which can be described as resulting from amine oxidation with simultaneous reduction of the “bpy” unit of DEAS-bpy. This state is indicated as [(<sup>+</sup>DEAS-bpy<sup>-</sup>)ReCl] and is expected at an energy of +1.96 eV.

The photophysical behavior of model [(DEAS-bpy)ReCl] is in agreement with this energy-level diagram. At room temperature (Figure 5) the lowest excited state is that centered on DEAS-bpy, LC [<sup>3</sup>DEAS-bpy)ReCl], and LC phosphorescence is observed. In the close vicinity of this emitting state, two different excited states (and in particular, the redox-separated state [(<sup>+</sup>DEAS-bpy<sup>-</sup>)ReCl]) are, however, present. This introduces a thermally accessible deactivation path; as a result the room temperature lifetime is shorter.

Passing to 77 K the level LC [<sup>3</sup>DEAS-bpy)ReCl] remains nearly at the same energy, whereas the other two states [(<sup>+</sup>DEAS-bpy<sup>-</sup>)ReCl] and CT Re → DEAS-bpy move to higher energy. Indeed these two latter states feature a charge-transfer character, so that in rigid media they are trapped in a nonequilibrium situation, as normally observed in such cases. As the energy difference between the lowest emitting LC [<sup>3</sup>DEAS-bpy)ReCl] state and both the [(<sup>+</sup>DEAS-bpy<sup>-</sup>)ReCl] and CT Re → DEAS-bpy states is increased, while the available thermal energy is reduced, there is no longer the possibility of deactivation via upper-lying excited states, and the lifetimes becomes very long (630 μs).

**Model [(bpy)Re(BPP)]<sup>+</sup>.** The energy of the Re → bpy CT level can be estimated starting from that known in the analogous complex [Re(CO)<sub>3</sub>(bpy)(Etpy)]<sup>+</sup> ( $E = 2.19 \text{ eV}$ ).<sup>37</sup> The bpy ligand is reduced 0.14 V more easily in this latter complex ( $E = -1.18 \text{ V}$ ) with respect to [(bpy)Re(BPP)]<sup>+</sup>. The Re → bpy CT level in [(bpy)Re(BPP)]<sup>+</sup> is thus expected at 2.33 eV.

The presence of the ligand BPP (both a chromophoric and an electroactive unit) introduces a number of additional levels. The LC [(bpy)Re(<sup>1</sup>BPP)]<sup>+</sup> fluorescence level at room temperature can be taken from the 77 K emission ( $E = 2.32 \text{ eV}$ , from the higher energy shoulder), as the energy of LC levels is usually temperature independent. The energy of the Re → BPP charge-transfer level (CT Re → BPP) can be taken from the observed emission energy at room temperature (601 nm, that is,  $E = 2.06 \text{ eV}$ ).

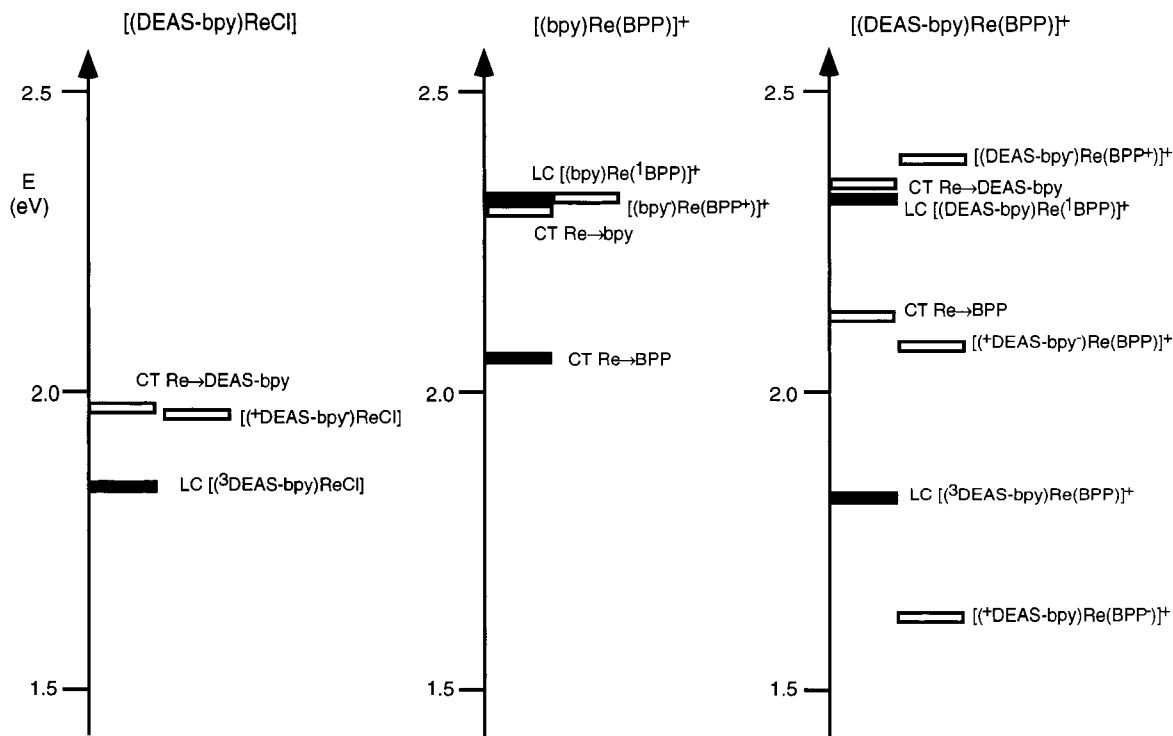
Then we have the redox-separated states. Reduction of bpy and oxidation of BPP, [(bpy<sup>-</sup>)Re(BPP<sup>+</sup>)]<sup>+</sup>, requires 2.32 eV. An additional level corresponding to BPP reduction and bpy oxidation should be very high in energy, as bpy oxidation is no doubt difficult;<sup>35,36</sup> this level can safely be ignored.

The photophysical behavior of complex [(bpy)Re(BPP)]<sup>+</sup> is in agreement with such an energy-level diagram. At room temperature the emission originates unambiguously from a MLCT state, and the energy-level diagram indicates that the lowest excited state is the CT Re → BPP one. Passing to 77 K, the two CT levels and the redox-separated state [(bpy<sup>-</sup>)Re(BPP<sup>+</sup>)]<sup>+</sup> are destabilized (vide supra) and move to higher energy, leaving the LC [(bpy)Re(<sup>1</sup>BPP)]<sup>+</sup> state as the lowest energy one. Fluorescence emission is thus observed from this latter LC state.

**Compounds [(DEAS-bpy)Re(BPP)]<sup>+</sup>, [(DEAS-bpy)Re(BPP-Me)]<sup>2+</sup>, and [(DEAS-bpy)<sub>2</sub>Re( $\mu$ -BPP)]<sup>2+</sup>.** In these complexes the simultaneous presence of DEAS-bpy and BPP, which are both chromophoric and electroactive units, gives rise to a very complicated energy-level diagram. Only [(DEAS-

(40) Jones, W. E., Jr.; Bignozzi, C. A.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 1167.

(41) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401.



**Figure 5.** Energy-level scheme for selected compounds. For each complex, the spectroscopic states (left column) are indicated separately from the redox-separated states (right column). Full levels are taken from direct spectroscopic measurements; the outlined ones are estimated indirectly (see text).

$\text{bpyRe(BPP)}^+$  will be discussed in detail; the energy-level scheme of the other two complexes is expected to be very similar, as their electrochemical and photophysical properties are much the same as those of  $[(\text{DEAS-bpy})\text{Re(BPP)}]^+$ .

The energy of the MLCT state  $\text{Re} \rightarrow \text{DEAS-bpy}$  (CT  $\text{Re} \rightarrow \text{DEAS-bpy}$ ) can be estimated starting from the already mentioned  $\text{Re} \rightarrow \text{bpy}$  CT energy in  $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Etpy})]^+$  ( $E = 2.19$  eV). In this latter complex  $\text{bpy}$  is reduced at  $E = -1.18$  V; as  $\text{DEAS-bpy}$  in  $[(\text{DEAS-bpy})\text{Re(BPP)}]^+$  is reduced at  $-1.33$  V, the state CT  $\text{Re} \rightarrow \text{DEAS-bpy}$  is expected at 2.34 eV.

The MLCT level  $\text{Re} \rightarrow \text{BPP}$  (CT  $\text{Re} \rightarrow \text{BPP}$ ) can be estimated starting from the energy of the analogous state in model  $[(\text{bpy})\text{Re(BPP)}]^+$  (2.06 eV), and considering that the BPP ligand is 0.07 V harder to reduce in  $[(\text{DEAS-bpy})\text{Re(BPP)}]^+$  with respect to  $[(\text{bpy})\text{Re(BPP)}]^+$  (Table 1). In this way the level CT  $\text{Re} \rightarrow \text{BPP}$  is expected at 2.13 eV in  $[(\text{DEAS-bpy})\text{Re(BPP)}]^+$ .

The room temperature energy of the LC  $[(^3\text{DEAS-bpy})\text{Re(BPP)}]^+$  state due to  $\text{DEAS-bpy}$  phosphorescence can be taken from the 77 K emission ( $E = 1.83$  eV), again considering that the energy of such a state is essentially temperature independent. The other LC state, due to BPP fluorescence,  $[(\text{DEAS-bpy})\text{Re}^1(\text{BPP})]^+$ , can be taken from model  $[(\text{bpy})\text{Re(BPP)}]^+$  ( $E = 2.32$  eV).

Then we have a lot of redox-separated states. A first one,  $[(^+\text{DEAS-bpy}^-)\text{Re(BPP)}]^+$ , is analogous to the  $[(^+\text{DEAS-bpy}^-)\text{ReCl}]$  state of model  $[(\text{DEAS-bpy})\text{ReCl}]$ ; from the electrochemical measurements we get  $E = 1.33 + 0.75 = 2.08$  eV.

A state due to BPP reduction and  $\text{DEAS-bpy}$  oxidation,  $[(^+\text{DEAS-bpy})\text{Re(BPP}^-)]^+$ , should be present at  $E = 0.88 + 0.75 = 1.63$  eV. The state due to BPP oxidation and  $\text{DEAS-bpy}$  reduction,  $[(\text{DEAS-bpy}^-)\text{Re(BPP}^+)]^+$ , is expected at  $E = 1.06 + 1.33 = 2.39$  eV.

Given the energy-level diagram sketched in Figure 5, the photophysical behavior of  $[(\text{DEAS-bpy})\text{Re(BPP)}]^+$  (and of

$[(\text{DEAS-bpy})\text{Re(BPP-Me)}]^{2+}$  and  $[(\text{DEAS-bpy})_2\text{Re}_2(\mu\text{-BPP})]^{2+}$ ) can be rationalized as follows. All of these  $\text{DEAS-bpy}$ - and  $\text{BPP}$ -containing complexes are not emissive at room temperature because of the presence of the redox-separated state  $[(^+\text{DEAS-bpy})\text{Re(BPP}^-)]^+$  as the lowest excited state, thus deactivating the LC  $[(^3\text{DEAS-bpy})\text{Re(BPP)}]^+$  state. The transient observed for  $[(\text{DEAS-bpy})\text{Re(BPP)}]^+$  (and  $[(\text{DEAS-bpy})\text{Re(BPP-Me)}]^{2+}$ ) in laser flash experiments (see above) is assigned to this species, which then decays, with  $k \approx 0.25 \times 10^6 \text{ s}^{-1}$ , to the ground state.

Passing to 77 K, the level  $[(^+\text{DEAS-bpy})\text{Re(BPP}^-)]^+$  (and the other CT or redox-separated states) moves to higher energy, so that emission is observed from the lowest lying LC  $[(^3\text{DEAS-bpy})\text{Re(BPP)}]^+$  state.

**Summary and Conclusions.** The new complexes  $[(\text{DEAS-bpy})\text{Re(BPP)}]^+$ ,  $[(\text{DEAS-bpy})\text{Re(BPP-Me)}]^{2+}$ ,  $[(\text{DEAS-bpy})_2\text{Re}_2(\mu\text{-BPP})]^{2+}$ , and  $[(\text{bpy})\text{Re(BPP)}]^+$  have been prepared, and their photophysical properties have been investigated. The simultaneous coordination of the  $\text{DEAS-bpy}$  and the  $\text{BPP}$  ligands to a  $\text{fac-Re}^1(\text{CO})_3$  center forms donor-acceptor complexes that give rise to a charge-separated state following light excitation. It is worth noting that this charge-separated state is noticeably long-lived ( $\approx 4 \mu\text{s}$ ) compared to that observed in other donor-acceptor complexes in homogeneous solution.<sup>11,13,15,16</sup> The slowness of the intramolecular back electron transfer reaction to the ground state can be justified by considering that its energy content (1.63 eV in the case of  $[(\text{DEAS-bpy})\text{Re(BPP)}]^+$ ) places it in the so-called "Marcus inverted region".<sup>42,43</sup> Alternatively, one can note that the electrochemical properties of the two subunits  $\text{DEAS-bpy}$  (on oxidation) and  $\text{BPP}$  (on reduction) are perturbed only to a small extent following coordination. This means that within the complex the electronic interaction between

(42) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078.

(43) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.



<sup>+</sup>DEAS-bpy and BPP<sup>−</sup> is so weak that charge recombination is expected to occur very slowly in the nonadiabatic regime.<sup>2</sup>

The modular approach advocated here represents a viable and highly versatile alternative to the common, and successful, practice of using other d<sup>6</sup> transition metal complexes for photoinduced charge-separated states. It also provides new opportunities for the construction of elaborated molecular architectures in which many redox centers are present that could serve to extend the charge-separation state so as to cover many redox partners. The presence of an uncoordinated pyridine group in [(DEAS-bpy)Re(BPP)]<sup>+</sup> could be very useful for the coating to macroscopic supports. Since one of the ultimate objectives of such research is to design systems comprising insulating lipidic bilayer membranes capable of allowing light-induced charge separation among the membrane, it is especially important to have molecules displaying long-lived charge-separated states. Whether or not it will become possible to design artificial systems capable of rapid and long-range charge-separated states remains an unanswered question. The solutions depend critically on the development of spacers spanning the

donor and acceptor subunits. Future studies will include increasing the length of the polyene bridge [from 5 to 15 double bonds] and changing the nature of the unsaturated systems. The engineering of molecular systems based on polyacetylenic bridges (molecular wires)<sup>44</sup> is now also currently under active investigation.

**Acknowledgment.** This work was supported by Consiglio Nazionale delle Ricerche (Progetto Strategico Tecnologie Chimiche Innovative) and Ministero dell'Università e della Ricerca Scientifica e Tecnologica and partially supported by the Centre National de la Recherche Scientifique. R.Z. is grateful to the ECPM for financial support and research facilities. We also warmly thank Dr. Mireille Blanchard-Desce for the gift of an analytical sample of the BPP ligand and Muriel Hissler for the measurement of the IR spectra.

IC9805700

---

(44) Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707.