Complexes Containing 2,9-Bis(*p*-biphenylyl)-1,10-phenanthroline Units Incorporated into a 56-Membered Ring. Synthesis, Electrochemistry, and Photophysical Properties

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We synthesized a new macrocycle (**1**) which is made of a 56-membered ring and contains two 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline ligands. Then we prepared the complexes $[Cu(\mathbf{1})(\mathbf{2})]^+$ (a catenate species), $[Cu(\mathbf{3})_2]^+$, $[Cu(\mathbf{2})(\mathbf{3})]^+$ (a threaded species), Re(**1**)$(CO)_3Cl$, and Re(**3**)$(CO)_3Cl$, where **2** is a 33-membered macrocycle containing a 2,9-di-*p*-phenyl-1,10-phenanthroline ligand and **3** is an acyclic ligand containing the same 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline unit which is present in **1**. The absorption spectra of the free ligands in CH_2Cl_2 solution show very intense bands in the near-UV region, characteristic of their aromatic moieties. In the Cu(I) complexes, besides the perturbed ligand-centered bands, weak metal-to-ligand charge-transfer (MLCT) bands can be observed in the 400−700 nm region. In the Re(I) complexes the MLCT bands lie at higher energy because the oxidation potential of Re(I) is much more positive than that of Cu(I). At room temperature, ligands **1** and **3**, which contain an extensively conjugated aromatic unit, show a very strong ($\Phi = 0.89$), short-lived (1.7 ns) fluorescence band with $\lambda_{max} = 419$ nm. The fluorescence of **2** is blue shifted ($\lambda_{max} = 387$ nm) and less intense ($\Phi = 0.29$) because of the less extended conjugation and rigidity of its chromophoric unit. Besides fluorescence, also a long-lived (second time scale) phosphorescence is displayed by the three ligands in a rigid matrix at 77 K. At room temperature the $[Cu(\mathbf{1})(\mathbf{2})]^+$, $[Cu(\mathbf{3})_2]^+$, and $[Cu(\mathbf{2})(\mathbf{3})]^+$ species exhibit a weak ($\Phi \sim 10^{-3}$), relatively long-lived (10^2 ns time scale) emission with λ_{max} around 750 nm, which can be assigned to a triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state. This emission is slightly red shifted and considerably longer lived ($\tau \sim 2\ \mu s$) at 77 K. The Re(**1**)$(CO)_3Cl$ and Re(**3**)$(CO)_3Cl$ complexes at room temperature show a moderately weak ($\Phi \sim 10^{-2}$), long-lived (10^2 ns time scale) ^{3}MLCT emission with λ_{max} around 610 nm. At 77 K this emission is blue shifted ($\lambda_{max} = 560$ nm) and considerably longer lived ($\tau \sim 10\ \mu s$). In the $[Cu(\mathbf{1})(\mathbf{2})]^+$ catenate and in the Re(**1**)$(CO)_3Cl$ complex one of the two chelating sites of the macrocycle **1** is coordinated to the metal and the other one is free. Besides a ^{3}MLCT emission, these species exhibit the fluorescence band of the 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline unit, strongly quenched by the nearby metal-based chromophoric unit ($k_q = 1.6 \times 10^{10}$ and $1.4 \times 10^{10}\ s^{-1}$ for the Cu(I) and the Re(I) complex, respectively). In aerated solution all of the complexes sensitize the $^1\Delta_g(O_2)$ luminescence at 1269 nm.

Introduction

There is currently a growing interest in the chemistry of macrocyclic ligands,[2] particularly in connection with the possibility of obtaining threaded and interlocked species like rotaxanes, catenanes, and related compounds.[3−6] Continuing our studies in this field, we have synthesized the new macrocycle **1** shown in Figure 1. Such a macrocycle, which bears two $(CH_2)_5CH_3$ substituents in the 4,7-positions of the two phenanthroline units for solubility reasons, is interesting for several reasons: (i) it is made of a very large (56-membered) ring; (ii) it contains two 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline chromophoric groups, which exhibit a very intense fluorescence; (iii) because of the long and very rigid diphenyl groups, folding up of the ring by coordination of the two phenanthrolines onto the same metal is prohibited; (iv) the 1,10-phenanthroline chelating units can be easily protonated[7] and can coordinate a variety of metal ions.[8] This last property opens the way to the construction of new catenates and catenands. We have also prepared the complexes $[Cu(\mathbf{1})(\mathbf{2})]^+$ (a catenate species), $[Cu(\mathbf{3})_2]^+$, $[Cu(\mathbf{2})(\mathbf{3})]^+$ (a threaded species), Re(**1**)$(CO)_3Cl$, and [Re(**3**)$(CO)_3Cl$], where **2** is a 33-membered macrocycle containing a 2,9-di-*p*-phenyl-1,10-phenanthroline ligand, and **3** is an acyclic ligand containing the same 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline unit which is present in **1**. The schematic formulas of the ligands and of the complexes are shown in Figure 1. We have investigated the absorption spectra and the luminescence properties of the free ligands and complexes and

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(1) (a) University of Strasbourg. (b) FRAE-CNR Institute. (c) University of Bologna.

(2) (a) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, U.K., 1989. (b) Vögtle, F. *Supramolecular Chemistry*; Wiley: New York, 1991. (c) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995.

(3) Chambron, J.-C.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. In *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Ed.; Pergamon Press: Oxford, 1996, Vol. 9, p 43.

(4) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725.

(5) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843.

(6) Vögtle, F.; Jäger, R.; Händel, M.; Ottens-Hildebrandt, S. *Pure Appl. Chem.* **1996**, *68,* 225.

(7) (a) Armaroli, N.; De Cola, L.; Balzani, V.; Sauvage, J.-P.; Dietrich-Buchecker, C. O.; Kern, J.-M. *J. Chem. Soc., Faraday Trans.* **1992**, *88,* 553. (b) Armaroli, N.; De Cola, L.; Balzani, V.; Sauvage, J.-P.; Dietrich-Buchecker, C. O.; Kern, J.-M.; Bailal, A. *J. Chem. Soc., Dalton Trans.* **1993**, 3241. (c) Armaroli, N.; Balzani, V.; De Cola, L.; Hemmert, C.; Sauvage, J.-P. *New J. Chem.* **1994**, *18*, 775. (d) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Armaroli, N.; Ceroni, P.; Balzani, V. *New J. Chem.* **1996**, *20*, 801.

(8) Constable, E. C. *Prog. Inorg. Chem.* **1994**, *42*, 67.

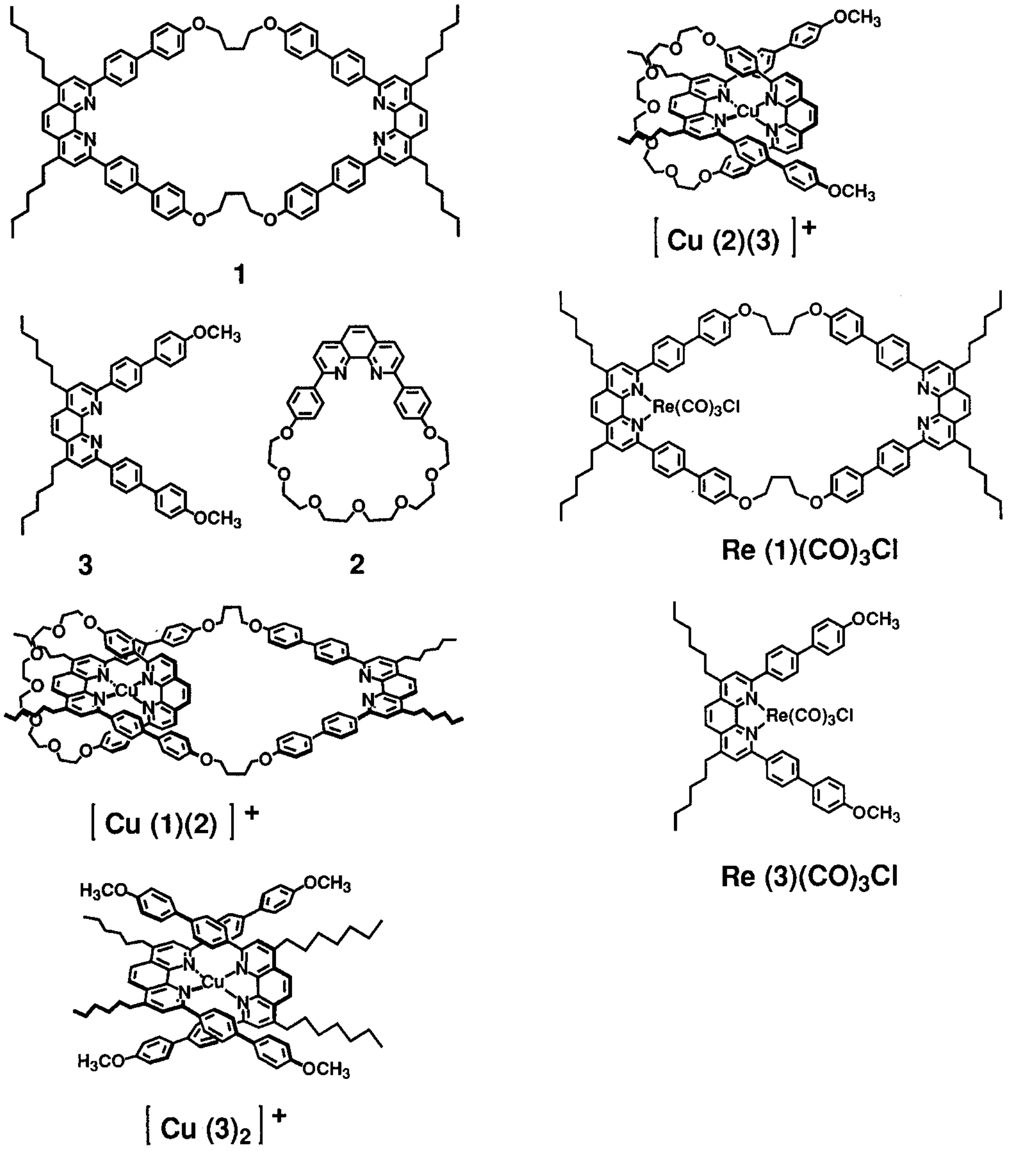

Figure 1. Schematic formulas of the ligands and of the Cu(I) and Re(I) complexes. The abbreviations used are also shown.

the electrochemical behavior of the complexes. Of particular photophysical interest are the supramolecular species [Cu(**1**)(**2**)]$^+$ and Re(**1**)(CO)$_3$Cl, since in these compounds one of the two chelating sites of the macrocycle **1** is coordinated to the metal and the other one is free. As a consequence, intramolecular quenching of the fluorescence of the free ligand moiety has been observed and the rate constant of this process has been measured with picosecond emission spectroscopy.

Results and Discussion

Synthesis of the Ligands and of the Complexes. In order to prepare supramolecular systems incorporating a transition metal complex unit and a second, coordination-free site in a macrocyclic compound we have followed two strategies. The first one (Figure 2, top) simply involves the coordination of a transition metal ion, Re(I), to one of the two chelating sites of a macrocycle. In this case a 1:1 stoichiometry of the ring and Re(I) is used and the reaction is expected to go on statistically; accordingly, mixtures of mono- and dinuclear complexes and unreacted ligand are obtained. The kinetic inertness of rhenium(I)–diimine complexes makes it possible to separate the various components in the crude mixture by chromatography, thus affording the pure mononuclear complex [Re(**1**)(CO)$_3$Cl]. The second strategy (Figure 2, bottom)[9] implies two steps. In the first one, a one-chelate ring reacts with a stoichiometric amount of an open-chain ligand and Cu(I), the latter being used as gathering and templating agent. The threaded intermediate so obtained consists of the two organic fragments arranged in a tetrahedral geometry around the coordinating metal center. In the second step, the threaded precursor is cyclized by an additional fragment containing a free coordination site, thus affording a [2]-catenate with a site available for further complexation.

The key substrate for the synthesis of the various ligands and complexes (Figure 3) is compound **6**, 4,7-di-*n*-hexyl-2,9-bis-[4-(4-hydroxyphenyl)phenyl]-1,10-phenanthroline.[10] It was obtained by addition of the lithio derivative of *O*-triisopropylsilyl-protected 4-(4-bromophenyl)phenol to 4,7-di-*n*-hexyl-1,10-phenanthroline followed by the rearomatization of the adduct with activated MnO$_2$. This reaction led to 42% of **5**, accompanied by 37% of the monosubstituted derivative. The latter was converted into **5** in 80% yield using the same procedure as

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(9) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1984**, *106*, 3043.

(10) (a) Kern, J.-M.; Sauvage, J.-P.; Weidmann, J.-L. *Tetrahedron* **1996**, *52*, 10921. (b) Weidmann, J.-L.; Kern, J.-M.; Sauvage, J.-P.; Geerst, Y.; Muscat, D.; Mullen, K. *J. Chem. Soc., Chem. Commun.* **1996**, 1243.

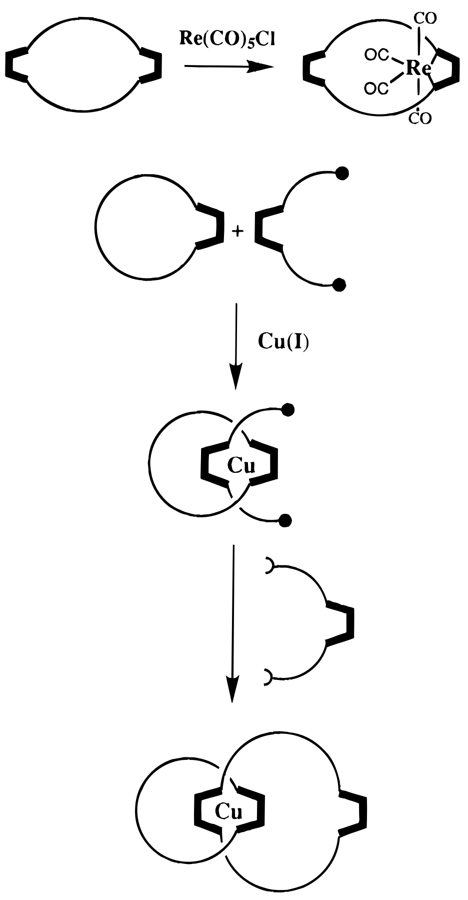

Figure 2. The two strategies developed to prepare supramolecular systems incorporating a transition metal complex and a free-coordination site. The U-shaped symbol refers to a 2,9-disubstituted 1,10-phenanthroline moiety.

above. The diphenolic phenanthroline **6** itself was easily recovered by treatment of **5** with a fluoride salt. Synthesis of macrocycle **1** and catenate [Cu(**1**)(**2**)]$^+$ was based on the reaction of the nucleophilic diphenolate derivative of **6** with the dielectrophiles **10** or **11**. Compounds **10** and **11** have the same coordination core as **6**, but the phenolic oxygens are linked to a polymethylene chain with halogenated terminals. A short polymethylene chain was chosen (four carbons) in order to avoid folding of the chelating subunits around a metallic species (Cu$^+$) in the bis-chelating macrocycle of type **1**. The dielectrophiles **10** and **11** were obtained following a sequence of successive reactions: **6** was treated in a basic medium (DMF, Cs_2CO_3) with 2-(4-bromobutoxy)tetrahydro-2*H*-pyran. The resulting bis(tetrahydropyranyl) derivative **7** was cleaved with pyridinium *p*-toluenesulfonate to yield **8**, and the bis(diol) was converted to the bis(mesylate) **9**. Substitution of the methylsulfonate groups with bromide or iodide (LiBr or LiI in acetone) led to the dielectrophiles **10** and **11**, respectively. Macrocycle **1** was obtained in 51% yield by reacting **6** with **10** in a Cs_2CO_3−DMF suspension, using high dilution conditions. Macrocycle **2** (a 33-membered ring) was prepared using conditions analogous to those used for the preparation of the homologous 30-membered-ring macrocycle.[11] The copper catenate [Cu(**1**)(**2**)]-BF_4 consists of the macrocycle **1** and the macrocycle **2**, which are interlocked around one coordinating site of **1** via a Cu(I) complex. The synthesis was performed in two steps. In the first one the "pre-catenate" structure [Cu(**2**)(**11**)]$^+$ was obtained quantitatively by threading the dielectrophile **11** through the monochelating macrocycle **2**, using the gathering and templating properties of copper(I), which forms tetrahedral complexes of high stability with 2,9-disubstituted phenanthrolines.[12] In the second step, the copper catenate [Cu(**1**)(**2**)]$^+$ itself was obtained (12% yield) by reacting [Cu(**2**)(**11**)]$^+$ with the diphenolic chelate **6** in basic medium (DMF, Cs_2CO_3) under high-dilution conditions. Mass spectrometry and NMR measurements (^{1}H, ^{13}C, NOSY, COESY) established the structure of [Cu(**1**)(**2**)]BF_4. Particularly, ^{1}H NMR clearly shows that in the bis-chelating macrocyclic subunit there are a noncoordinated site and a site bound to copper(I). Indeed, a strong shielding effect is observed for protons o_1 and m_1 (Figure 3), in a manner similar to that previously described for analogous copper(I) 2,9-disubstituted phenanthroline complexes.[13] Ligand **3** was prepared by methylation of **6** with methyl iodide in K_2CO_3 suspension in DMF. The corresponding homoleptic copper(I) complex was prepared by mixing the stoichiometric amounts of the ligand **3** and [Cu(CH_3CN)$_4$]BF_4 in an acetonitrile−dichloromethane solution; the yield was quantitative. Threading of **3** through macrocycle **2** was performed by adding 1 equiv of [Cu(CH_3CN)$_4$]BF_4 to 1 equiv of **2** in an acetonitrile−dichloromethane solution. Threading of **3** through **2** via Cu(I) complexation is instantaneous at room temperature. Complex Re(**1**)(CO)$_3$Cl, where only one coordinating subunit of the bis-chelating macrocycle **1** is coordinated to Re(I), was obtained as previously described for other Re(I)−polyimine complexes,[14] by refluxing stoichiometric amounts of Re(CO)$_5$Cl with **1** in toluene. The yield of purified monorhenium complex was 29%. Complex Re(**3**)(CO)$_3$Cl was prepared using the same procedure as above, the purification procedures being easier with the acyclic ligand **3** than using the macrocyclic bis-chelating ligand **1**.

Electrochemical Properties. The oxidation of the three Cu(I) complexes and Re(**3**)(CO)$_3$Cl was studied by cyclic voltammetry. All of the compounds examined undergo a reversible, one-electron oxidation process in the potential window examined (up to +1.6 V). The observed processes can be attributed to the oxidation of the metal center.[15] The potential values for the Cu(II)/Cu(I) couple are +0.575, +0.530, and +0.545 V for [Cu(**1**)(**2**)]$^+$, [Cu(**3**)$_2$]$^+$, and [Cu(**2**)(**3**)]$^+$, respectively. These values are in the range expected for Cu(I)−phenanthroline type complexes.[9,13,16] Previous investigations have shown that the potential of the Cu(II)/Cu(I) couple (i) depends on the nature of the substituents on the phen chelating sites and (ii) for complexes having the same chelating sites, becomes more positive when the metal ion is subjected to steric constraints that prevent rearrangement of the coordination geometry upon oxidation. In going from [Cu(**3**)$_2$]$^+$ to [Cu(**2**)(**3**)]$^+$ or [Cu(**1**)(**2**)]$^+$, a 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline ligand bearing alkyl chains in the 4,7-positions is replaced by a 2,9-di-*p*-phenyl-1,10-phenanthroline unit. The (small) increase in the Cu(II)/Cu(I) potential shows that the former ligand is a better σ-donor, presumably because of the effect of the alkyl substituents. In going from the [Cu(**2**)(**3**)]$^+$ complex to the [Cu(**1**)(**2**)]$^+$ catenate, both containing a 2,9-di-*p*-phenyl-1,10-phenanthroline unit and a 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline fragment, the increase of potential of the Cu(II)/Cu(I)

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[11] Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Tetrahedron* **1990**, *46*, 503.

[12] Arnaud-Neu, F.; Marquez, E.; Schwing-Weil, M. J.; Dietrich-Buchecker, C.O.; Sauvage, J.-P.; Weiss, J. *New J. Chem.* **1988**, *12*, 15.

[13] Dietrich-Buchecker, C.O.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1989**, *111,* 7791.

[14] Sacksteder, L. A.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; De Graff, B. A. *Inorg. Chem.* **1990**, *29*, 4335.

[15] Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic: London, U.K., 1992; p 321.

[16] (a) Dietrich-Buchecker, C. O.; Nierengarten, J.-F.; Sauvage, J.-P.; Armaroli, N.; Balzani, V.; De Cola, L. *J. Am. Chem. Soc.* **1993**, *115*, 11237. (b) Federlin, P.; Kern, J.-M.; Rastegar, A.; Dietrich-Buchecker, C.; Marnot, P. A.; Sauvage, J.-P. *New J. Chem.* **1990**, *14*, 9.

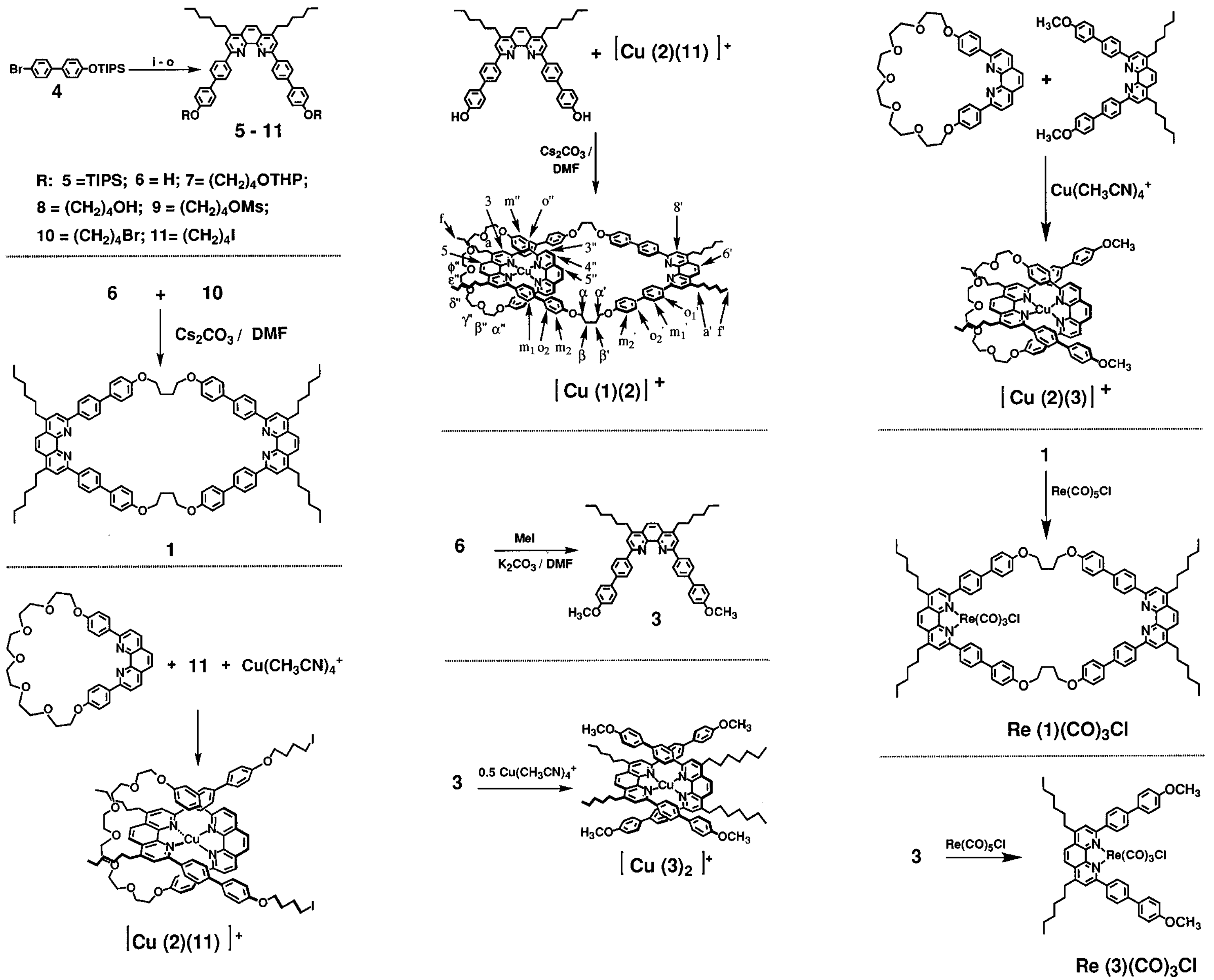

Figure 3. Synthetic route for the preparation of the ligands and complexes. (i) 4,7-di-*n*-hexyl-1,10-phenanthroline + 2 equiv of BuLi; H_2O; MnO_2. (j) $(^nBu)_4NF$, THF, H_2O. (k) $Br(CH_2)_4OTHP$, K_2CO_3, DMF. (l) PyH^+ TSO^-, EtOH. (m) MsCl, Et_3N, CH_2Cl_2. (n) **9** + LiBr, acetone. (o) **9** + NaI, acetone.

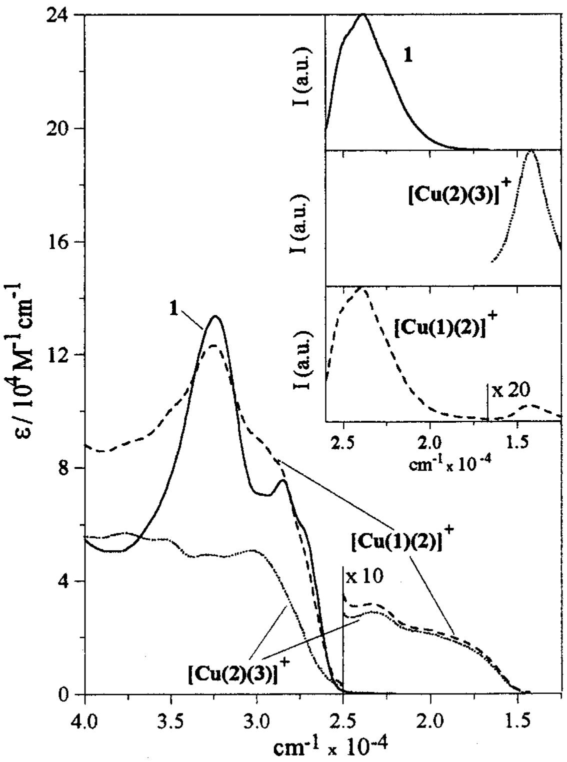

Figure 4. Absorption and (inset) luminescence spectra in CH_2Cl_2 solution of the free ligand **1** and of the $[Cu(\mathbf{1})(\mathbf{2})]^+$ and $[Cu(\mathbf{2})(\mathbf{3})_2]^+$ complexes.

couple is much smaller than that previously observed in going from acyclic ligands to small catenates and knots.[16] This is an expected result because the 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline unit is rigid and the macrocycle **1** is very large, so that replacing the "open" ligand **3** with the same ligand incorporated in the macrocycle **1** does not introduce any significant constraint into the coordination arrangement around the metal ion.

The potential for the Re(II)/Re(I) couple for $Re(\mathbf{3})(CO)_3Cl$ is +1.265 V, close to that reported for $Re(phen)(CO)_3Cl$.[17]

Absorption Spectra. The absorption spectra in CH_2Cl_2 solution of $[Cu(\mathbf{1})(\mathbf{2})]^+$ and $[Cu(\mathbf{2})(\mathbf{3})]^+$ are shown in Figure 4, and those of $Re(\mathbf{1})(CO)_3Cl$ and $Re(\mathbf{3})(CO)_3Cl$ are displayed in Figure 5. In both figures the absorption spectrum of the free ligand **1** is also shown.

The absorption spectrum of **1** is characterized by $\pi\pi^*$ bands with a partial charge-transfer character, as already shown for other 1,10-phenanthroline derivatives.[7a] The absorption spectrum of the free ligand **3** (not shown in the figures) is, as expected, identical in shape to that of **1** with a molar absorption coefficient half that of **1** throughout the UV spectral region of interest. The absorption spectrum of the free ligand **2** is identical to that of its 2,9-dianisyl-1,10-phenanthroline chromophoric moiety.[7a]

The Cu(I) and Re(I) complexes show very intense ligand-centered (LC) bands in the UV region and much weaker metal-to-ligand charge-transfer (MLCT) bands in the visible region. The LC transitions are perturbed by metal coordination, as one can see by comparing the absorption spectra of **1** with that of $[Cu(\mathbf{1})(\mathbf{2})]^+$ (Figure 4) and $Re(\mathbf{1})(CO)_3Cl$ (Figure 5). In both cases there is a strong decrease in intensity of the band with a maximum at 310 nm (3.2×10^4 cm^{-1}). The MLCT bands exhibit much lower intensities than the LC bands and occur in different spectral regions for the Cu(I) and Re(I) complexes.

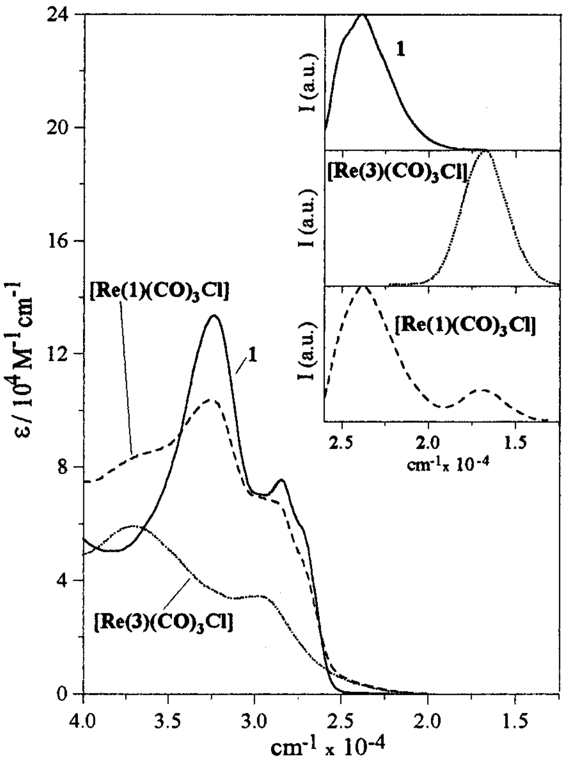

Figure 5. Absorption and (inset) luminescence spectra in CH_2Cl_2 solution of the free ligand **1** and of the $Re(\mathbf{1})(CO)_3Cl$ and $Re(\mathbf{3})(CO)_3Cl$ complexes.

The energy of the MLCT transitions is related to the oxidation potential of the metal ion.[18] As we have seen above, Cu(I) is easy to oxidize. Therefore in the Cu(I) complexes the MLCT bands are found at low energy, as shown in Figure 4 ($2.5-1.4 \times 10^4$ cm^{-1}, i.e., 400−700 nm). Re(I) is much more difficult to oxidize (*vide supra*), and therefore in the Re(I) complexes the MLCT bands lie at higher energy and may be partly hidden by the more intense LC bands.[15] In fact in our Re(I) complexes the MLCT bands only show up as an absorption tail above 2.5×10^4 cm^{-1} (Figure 5).

The absorption bands of the Cu(I)−phenanthroline complexes in the visible spectral region are known to be very broad because the MLCT excited states formally correspond to Cu(II) complexes and therefore exhibit an equilibrium geometry very different from that of the ground state.[19] It should also be noted that the MLCT bands of $[Cu(\mathbf{1})(\mathbf{2})]^+$ and $[Cu(\mathbf{2})(\mathbf{3})]^+$ are broader than those of $[Cu(\mathbf{3})_2]^+$ because the first two complexes are heteroleptic in nature and the MLCT transitions corresponding to the two different ligands are very close in energy.

Luminescence Properties. The most important luminescence data at room temperature and at 77 K are collected in Tables 1 and 2, respectively. The radiative (k_r) and nonradiative (k_{nr}) rate constants have been obtained from the equations $k_r = \Phi/\tau$ and $k_{nr} = (1/\tau - k_r)$, respectively. The emission spectra at 298 K in CH_2Cl_2 solution of **1**, $[Cu(\mathbf{2})(\mathbf{3})]^+$, and $[Cu(\mathbf{1})(\mathbf{2})]^+$ are displayed in the insets of Figure 4, and those of **1**, $[Re(\mathbf{3})(CO)_3Cl]$, and $[Re(\mathbf{1})(CO)_3Cl]$ are shown in the insets of Figure 5.

In CH_2Cl_2 solution at room temperature the three ligands **1**, **3**, and **2** show intense fluorescence bands with maxima in the $2.6-2.4 \times 10^4$ cm^{-1} spectral region (380−400 nm), as it usually

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(17) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7892.

(18) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds;* Academic Press: London, U.K., 1970.

(19) (a) Gushurst, A. K. I.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Inorg. Chem.* **1989**, *28*, 4070. (b) Everly, R. M.; McMillin, D. R. *J. Phys. Chem.* **1991**, *95*, 9071 and references therein.

Table 1. Luminescence Properties at 298 K[a]

	ligand-based emission ^{1}LC					metal-based emission ^{3}MLCT[b]				
	λ_{max} (nm)	τ (ns)	Φ[c]	k_r ($\times10^{-8}$, s^{-1})	k_{nr} ($\times10^{-8}$, s^{-1})	λ_{max} (nm)	τ (ns)	$10^3\Phi$[d]	k_q[O$_2$] ($\times10^{-6}$, s^{-1})	$I_{rel}(^1\Delta_g)$[e]
1	419	1.7[f]	0.89	5.2	0.68					
3	419	1.6	0.89	5.6	0.65					
2	387	2.1	0.29	1.4	3.4					
[Cu(**1**)(**2**)]$^+$	419	0.060[g]	(0.085)[h]			743	100	0.5	4.1	40
							170[i]	0.7[i]		
[Cu(**3**)$_2$]$^+$						726	130	1.8	4.8	50
							350[i]	3.1[i]		
[Cu(**2**)(**3**)]$^+$						750	100	0.5	4.4	35
							180[i]	0.6[i]		
[Re(**1**)(CO)$_3$Cl]	422	0.070[g]	(0.051)[h]			610	165	16	3.1	90
							340[i]	30[i]		
[Re(**3**)(CO)$_3$Cl]						612	170	14	2.8	100
							320[i]	31[i]		

[a] In air-equilibrated CH_2Cl_2 solutions, unless otherwise noted. [b] In Cu(I) complexes part of the emission is likely due to a singlet state (see text). [c] $\lambda_{exc} = 320$ nm. [d] $\lambda_{exc} = 540$ nm. [e] Relative emission intensities of the sensitized $^1\Delta_g$ emission. [f] 2.4 ns in butyronitrile. [g] In butyronitrile; CH_2Cl_2 solutions undergo photodegradation under laser excitation. [h] Partly due to some free ligand impurity; see text. [i] Deaerated solutions.

Table 2. Luminescence Properties at 77 K[a]

	ligand-based emission				metal-based emission	
	^{1}LC		^{3}LC		^{3}MLCT	
	λ_{max} (nm)	τ (ns)	λ_{max} (nm)	τ (s)	λ_{max} (nm)	τ (μs)
1	400	1.6[b]	538	0.8		
3	399	1.6	532	0.8		
2	383	3.7	513	0.9		
[Cu(**1**)(**2**)]$^+$	413	0.095[c]			750	1.8
[Cu(**3**)$_2$]$^+$					745	1.7
[Cu(**2**)(**3**)]$^+$					760	1.8
[Re(**1**)(CO)$_3$Cl]	420	0.100[c]	540	0.5	566	10.8
[Re(**3**)(CO)$_3$Cl]					545	10.4

[a] In air-equilibrated CH_2Cl_2 solutions, unless otherwise noted. [b] 2.0 ns in butyronitrile. [c] In butyronitrile; CH_2Cl_2 solutions undergo photodegradation under laser excitation.

happens for phenanthroline derivatives. These bands are due to emission of $\pi\pi^*$ excited states with partial charge-transfer character, as previously shown for 2,9-*p*-dianisyl-1,10-phenanthroline.[7a] In a rigid matrix at 77 K, the fluorescence band is slightly shifted to higher energy (because of its partial charge-transfer character), and a phosphorescence band is also present above 500 nm. The luminescence properties (maximum of the emission bands, fluorescence quantum yields, fluorescence and phosphorescence lifetimes) are substantially identical for **1** and **3**, as expected because the chromophoric unit is the same for the two ligands. The very high fluorescence quantum yield is typical of rigid and delocalized organic molecules which exhibit large radiative and small nonradiative deactivation rate constants.[20] For example, terphenyl and its derivatives have quantum yields around 0.9.[21] Macrocycle **2** emits at higher energy and with a lower fluorescence quantum yield, as expected for a less extended π system. Note in particular that the nonradiative rate constant for **1** and **3** is about 5 times smaller than for **2** (Table 1). Such a low rate constant for nonradiative decays indicates that the excited state and the ground state have a similar geometry.[22]

At room temperature the [Cu(**1**)(**2**)]$^+$, [Cu(**2**)(**3**)]$^+$, and [Cu(**3**)$_2$]$^+$ complexes exhibit a weak ($\Phi \sim 10^{-3}$) and long lived (10^2 ns time scale) emission, with λ_{max} around 750 nm (Table 1, Figure 4). By analogy with the behavior of several other Cu(I)-polypyridine complexes,[16a,19,23] this band can be assigned to the lowest ^{3}MLCT level (or a set of thermally equilibrated ^{3}MLCT levels, *vide infra*). In the case of [Cu(**3**)$_2$]$^+$ and [Cu(**2**)(**3**)]$^+$, only emission from such level(s) is observed, as expected for simple Cu(I) complexes. For [Cu(**1**)(**2**)]$^+$, however, in which two distinct chromophoric groups are present (namely, a metal complex and a free ligand unit), the low-energy ^{3}MLCT emission is accompanied by a relatively weak ligand-centered fluorescence. This point will be discussed in detail in the next section.

In going from a room temperature fluid solution to a rigid matrix at 77 K, ^{3}MLCT emission becomes considerably longer lived ($\tau \sim 2$ μs), as usually happens for this kind of transitions.[15,24] It is surprising, however, to see that the emission maximum moves to *lower* energies, since the reverse would be expected (and is indeed generally observed)[15,24] for CT bands because, in a rigid matrix, solvent repolarization is prevented. Such a red shift, however, is common for Cu(I) complexes.[16a,19b,25] It can be accounted for by the presence of a (higher energy) singlet and a (lower energy) triplet MLCT level in thermal equilibrium. At high temperature most of the emission comes from the singlet, whereas at 77 K the singlet is less populated and most of the emission comes from the lower energy triplet.

It can be noted (Tables 1 and 2) that the emission band of the homoleptic [Cu(**3**)$_2$]$^+$ complex, which is that displaying the less positive oxidation potential, lies at higher energy than the bands of the two heteroleptic compounds [Cu(**1**)(**2**)]$^+$ and [Cu(**2**)(**3**)]$^+$. This indicates that the 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline unit is more difficult to reduce than the 2,9-di-*p*-phenyl-1,10-phenanthroline unit probably because of the presence of alkyl σ-donor chains on the former. This also implies that in [Cu(**1**)(**2**)]$^+$ and [Cu(**2**)(**3**)]$^+$ the lowest excited state involves the ligand **2**.

In the Re(I) complexes of the Re(phen)(CO)$_3$Cl family, luminescence originates from a triplet Re → phen CT level.[15] Because of their interesting photophysical properties, several complexes of this family have been extensively investigated. The Re(**1**)(CO)$_3$Cl and Re(**3**)(CO)$_3$Cl complexes exhibit a quite similar ^{3}MLCT emission (Tables 1 and 2), as a consequence of

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(20) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1964.

(21) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic: London, U.K., 1965; p 220.

(22) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, W. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473.

(23) Armaroli, N.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Sauvage, J.-P.; Hemmert, C. *J. Am. Chem. Soc.* **1994**, *116*, 5211.

(24) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(25) Kirchhoff, J. R.; Gamache, R. E.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K. D.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380.

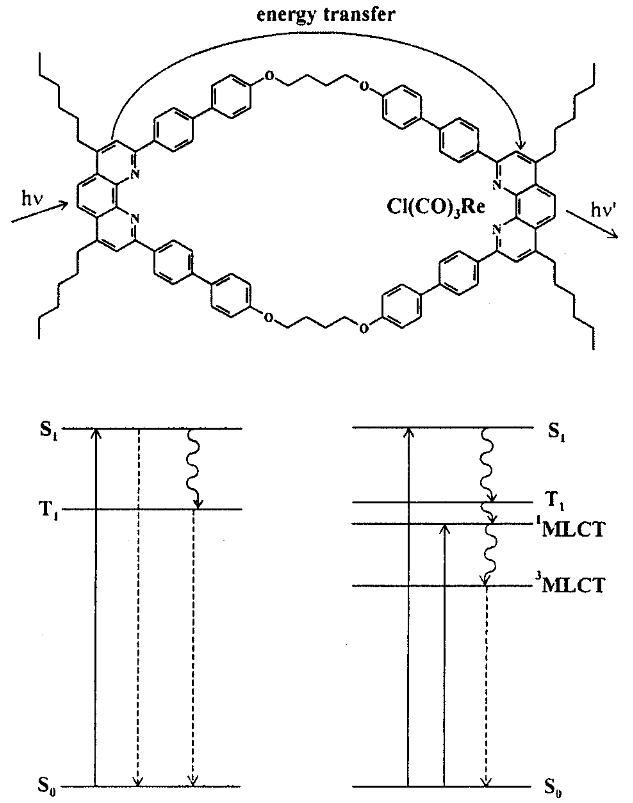
the same chemical nature of the metal coordinating units. The moderately weak ($\Phi \sim 10^{-2}$), long-lived (10^2 ns time scale) emission band with λ_{max} around 610 nm at room temperature is very similar to that exhibited by Re(phen)$(CO)_3Cl$ and its derivatives.[15,26]

In the complexes of the Re(phen)$(CO)_3Cl$ family the Re → phen CT transition causes a strong change in the dipole moment. Therefore, the ^{3}MLCT band undergoes a strong blue shift in going from fluid solution to rigid matrix, because in the latter environment the solvent molecules cannot undergo reorientation around the excited state. As one can see from Tables 1 and 2, this is also the case for Re(**1**)$(CO)_3Cl$ and Re(**3**)$(CO)_3Cl$. The blue shift is accompanied by an increase in lifetime, since in Re(I) complexes the nonradiative deactivation rate constant decreases with increasing excited state energy (energy gap law).[27] This is particularly evident when the Cl ligand is replaced by a neutral, weak electron-donor ligand. For example, $[Re(bpy)(CO)_3(CH_3CN)]^+$ in CH_2Cl_2 solution at room temperature emits at 536 nm with $\Phi = 0.41$ and $\tau \sim 1.2$ μs.[28]

It should be noted that, in the case of Re(**1**)$(CO)_3Cl$, the ^{3}MLCT emission is accompanied by a relatively weak ligand-centered fluorescence (Tables 1 and 2). This point will be discussed in detail in the next section.

Intercomponent Photoinduced Processes in [Cu(1)(2)]$^+$ and Re(1)(CO)$_3$Cl. As schematically represented in Figures 1 and 2, in the [Cu(**1**)(**2**)]$^+$ catenate and in the Re(**1**)$(CO)_3Cl$ complex one of the two chelating sites of the macrocycle **1** is coordinated to the metal and the other one is free. These compounds can thus be considered as a supramolecular species[29] made of two distinct chromophoric units: the noncoordinated (free) ligand and the metal-based unit. In the ground state the two subunits do not interact appreciably, as shown by the fact that the absorption spectrum of [Cu(**1**)(**2**)]$^+$ is identical to that obtained summing the absorption spectra of the model compounds [Cu(**2**)(**3**)]$^+$ and **3** (all expressed in ϵ units). Analogous considerations apply to Re(**1**)$(CO)_3Cl$. In the excited state, however, the two subunits interact, as shown by the different luminescence behavior of **3** (or free **1**) and the noncoordinated moiety of **1** in [Cu(**1**)(**2**)]$^+$. From the insets of Figures 4 and 5 and from the data reported in Table 1 one can see that at room temperature both [Cu(**1**)(**2**)]$^+$ and Re(**1**)$(CO)_3Cl$ do exhibit the characteristic fluorescence of the 2,9-bis(*p*-biphenylyl)-1,10-phenanthroline unit ($\lambda_{max} \sim 420$ nm). However, such an emission is strongly quenched, as shown by its very short lifetime and very low quantum yield. A careful examination of this emission evidences a biexponential decay, with a short-lived component with $\tau = 60$ ps for [Cu(**1**)(**2**)]$^+$ and 70 ps for Re(**1**)$(CO)_3Cl$, and a long-lived component with $\tau \sim 2$ ns. Evaluation of these data suggests that part of the observed emission intensity originates from small amounts (~5% for [Cu(**1**)(**2**)]$^+$, ~3% for Re(**1**)$(CO)_3Cl$) of **1** or **3** impurities. We can conclude that in both compounds the fluorescence of the free ligand moiety is strongly quenched (>95%) by the metal-based moiety.

The rate constant of the quenching process can be calculated from eq 1, where τ and $\tau°$ are the fluorescence lifetimes of the free ligand moiety in the complexes and in **3** and **1**, respectively. The values obtained are 1.6×10^{10} s^{-1} for [Cu(**1**)(**2**)]$^+$ and 1.4×10^{10} s^{-1} for Re(**1**)$(CO)_3Cl$ (Table 1). Similar values are obtained at 77 K (Table 2).



3 [Re(**3**)(CO)$_3$Cl]

Figure 6. Top: Schematic representation of the quenching of the fluorescent excited state of the noncoordinated moiety of the macrocycle **1** by energy transfer to the metal-based unit in Re(**1**)$(CO)_3Cl$; bottom: schematic energy level diagram for the **3** and Re(**3**)$(CO)_3Cl$ reference compounds (solid arrows, absorption; dashed arrows, emission; wavy arrows, intersystem crossing).

$$k_q = 1/\tau - 1/\tau° \qquad (1)$$

In principle, such a fast quenching process can occur by energy or electron transfer. As shown by the position of the emission bands, energy transfer is clearly exoergonic. Whether or not quenching by electron transfer is thermodynamically allowed can be estimated by eq 2,[24] where ΔE is the excited state energy and $E[A/A^-]$ and $E[D^+/D]$ are the one-electron energies corresponding to reduction of the (free ligand) electron acceptor and oxidation of the (metal-centered) electron donor.

$$\Delta G° \sim -\Delta E - E[A/A^-] + E[D^+/D] \qquad (2)$$

The energy of the fluorescent excited state of the free ligand moiety is ~3.1 eV (Table 2), and the redox energies are ~−2.1 eV for the A/A$^-$ couple[30] and ~+0.55 and ~+1.27 eV for the Cu(I) and Re(I) metal-based units (see electrochemical section). Therefore electron-transfer quenching can be ruled out for Re(**1**)$(CO)_3Cl$ ($\Delta G° \sim +0.3$ eV), but it is allowed in the case of [Cu(**1**)(**2**)]$^+$ ($\Delta G° \sim -0.5$ eV). In the case of Re(**1**)$(CO)_3Cl$, there is a substantial agreement between the excitation spectrum ($\lambda_{em} = 610$ nm) and the absorption spectrum throughout the entire spectral region. This shows that excitation of the noncoordinated ligand moiety leads to the emission of the metal-based unit, as expected for an energy transfer quenching mechanism (Figure 6). For [Cu(**1**)(**2**)]$^+$, it is not possible to

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(26) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

(27) (a) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

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

(29) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood; Chichester, U.K., 1991.

(30) Kern, J.-M.; et al. Unpublished results.

say whether the quenching of the fluorescence of the noncoordinated ligand is accompanied by the sensitization of the emission of the metal-based chromophoric unit, because the tail of the residual free ligand fluorescence is strong enough to affect a quantitative measurement of the very weak MLCT emission. As shown in Table 2, the phosphorescence of the free ligand (at 77 K) is completely quenched for $[Cu(\mathbf{1})(\mathbf{2})]^+$, whereas for $Re(\mathbf{1})(CO)_3Cl$ the quenching is only partial. This different behavior can be accounted for by the fact that, as one can understand from the maxima of the relevant bands reported in Table 2, the ^{3}MLCT level of $[Cu(\mathbf{1})(\mathbf{2})]^+$ lies well below the T_1 level of the ligand, whereas in the case of $Re(\mathbf{1})(CO)_3Cl$ the two levels are very close in energy. It should also be noted that in the Re(I) complex, because of the much longer intrinsic lifetime of the ligand-centered T_1 level, quenching of the ligand phosphorescence can also occur by thermal activation through the ^{3}MLCT which lies (slightly) above T_1.

Energy Transfer to Dioxygen. It is known that in fluid solution at room temperature the luminescent ^{3}MLCT excited state of Cu(I) and Re(I) complexes can be quenched by dioxygen.[15,23] In our systems the quenching process is accompanied in all cases by the sensitization of the $^1\Delta_g(O_2)$ emission at 1269 nm. The rate constants of the quenching processes and the relative efficiencies of $^1\Delta_g(O_2)$ emission are reported in Table 1. As one can see, the quenching process is faster for the Cu(I) complexes, but the efficiency of $^1\Delta_g(O_2)$ emission is larger for the Re(I) compounds. Therefore, for the Cu(I) complexes also a quenching mechanism different from energy transfer must be operative. An obvious possibility is quenching via electron transfer. Whether or not quenching by electron transfer is thermodynamically allowed can again be estimated by eq 2, where ΔE is now the excited state energy of the metal-based unit, and $E[A/A^-]$ and $E[D^+/D]$ are the one-electron energies corresponding to reduction of dioxygen and oxidation of the metal center. The MLCT excited state energy is about 1.7 eV for the Cu(I) complexes and 2.3 eV for the Re(I) compounds (Table 2), and as we have seen above, the reduction potential of the D^+/D couple is $\sim+0.55$ and $\sim+1.27$ eV for the Cu(I) and Re(I) metal-based units, respectively. Accordingly, quenching by electron transfer is expected to be endoergonic in both cases;[31] furthermore, it seems to be thermodynamically slightly *less* favored in the case of the Cu(I) compounds. It has been shown that the intimate nature of excited state quenching by dioxygen is often quite difficult to elucidate.[33-35] Specific donor−acceptor interactions (e.g., exciplex formation), often related to the oxidation potential of the quencher, can play an important role.[34,35] The different behavior of Cu(I) and Re(I) complexes is likely linked to such specific interactions.

It can also be noticed that the quenching constants for the Cu(I) compounds are higher by a factor of about 2 than those found for previously studied Cu(I) [2]- and [3]-catenates.[23] This is probably due to the lower steric hindrance toward orbital overlap between the Cu(I)−phenanthroline chromophoric unit and dioxygen for the present compounds.

Experimental Section

Syntheses of the Ligands and of the Complexes. $Cu(CH_3CN)_4BF_4$ was prepared by reduction of $Cu(BF_4)_2$ by an excess of copper powder in CH_3CN under argon at room temperature, the mixture being stirred until complete bleaching of the solution was effected. All other chemicals were of the best commercially available grade and were used without further purification.

Compound 4. Triisopropylchlorosilane (6 mL; 5.42 g; 28 mmol) was added to a degassed solution of 4-(4-bromophenyl)phenol (5.0 g; 20 mmol) in dry DMF (80 mL). After heating for 18 h at 50 °C under argon, the solvent was removed under high vacuum and the residue taken up in ether (100 mL). The resulting solution was washed three times with water, dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel (eluent: hexane) giving pure **4** (7.92 g; 19.5 mmol; 97% yield).

4: white solid (mp 40 °C). ^{1}H-NMR ($CDCl_3$): 7.53, d ($J = 8.7$ Hz), 2H; 7.42, d ($J = 8.7$ Hz), 4H; 6.94, d ($J = 8.7$ Hz), 2H; 1.20−1.05, m, 21H. Anal. Calcd for $C_{21}H_{29}OSiBr$: C, 62.21; H, 7.21. Found: C, 62.45; H, 7.44.

Compound 5. Compound **4** (11.6 g; 28.7 mmol) was dissolved under argon in dry THF (100 mL). The solution was cooled to −78 °C, and then ^{t}BuLi (41 mL of a 1.4 mol·L^{-1} solution in pentane; 57 mmol) was added over 2 h. After stirring at −78 °C (30 min), the resulting 4-lithio-4′-[(triisopropylsilyl)oxy]biphenyl solution was warmed gradually (30 min) to 5 °C and added via cannula to a solution of 4,7-di-*n*-hexyl-1,10-phenanthroline[10] (4.0 g; 11,5 mmol) in dry toluene (80 mL) at room temperature. Subsequently, stirring of the resulting dark red solution was continued for 48 h under argon at room temperature. The solution was hydrolyzed at 0 °C with water and concentrated by partial evaporation of the THF. The aqueous layer was extracted several times with CH_2Cl_2, and the combined organic layers were thereafter rearomatized by successive additions of MnO_2 (Merck No. 895958; 60 g, overall amount) over 3 h. A large amount of $MgSO_4$ was added, the black slurry was filtered off on Celite, and the filtrate was evaporated to dryness. The crude product was purified by two successive flash column chromatographies on silica gel (eluent: hexane/CH_2Cl_2, 1/1, v/v), giving pure **5** (4.8 g; 4.8 mmol; 42% yield) and pure monosubstituted derivative (2.9 g; 4.3 mmol; 37% yield). This derivative was converted into **5** using the same procedure as above (yield 80%).

5: yellow needles (mp 104−106 °C). ^{1}H-NMR ($CDCl_3$): 8.55, d ($J = 8.4$ Hz), 4H; 8.03, s, 2H; 8.00, s, 2H; 7.80, d ($J = 8.4$ Hz), 4H; 7.61, d ($J = 8.6$ Hz), 4H; 6.99, d ($J = 8.6$ Hz), 4H; 3.21, t ($J = 7.6$ Hz), 4H; 1.87, m, 4H; 1.60−1.20, m, 12H; 1.20−1.05, m, 42H; 0.91, t ($J = 6.8$ Hz), 6H. Anal. Calcd for $C_{66}H_{88}N_2O_2Si_2$: C, 79.46; H, 8.89; N, 2.81. Found: C, 79.66; H, 9.11; N, 2.62.

Compound 6. A solution of THF (180 mL) and H_2O (20 mL), containing **5** (3.35 g; 3.36 mmol) and $(^nBu)_4NF\cdot 3H_2O$ (5.29 g; 16.8 mmol), was stirred for 7 h under argon at room temperature. An aqueous pH 7.0 buffer solution was added until a solid began to precipitate. The THF was removed, the water was carefully eliminated, and the solid was washed with water. The crude product was taken up another time in THF/H_2O, and after elimination of the solvents in the same way, the residue was dried by azeotropic removal of water after dissolution in a mixture of THF and toluene. The residue was recrystallized from acetone to afford pure **6** (2.15 g; 3.14 mmol; 94% yield).

6: pale yellow solid (mp 259−261 °C). ^{1}H-NMR (CD_3COCD_3): 8.71, d ($J = 8.5$ Hz), 4H; 8.26, s, 2H; 8.19, s, 2H; 7.85, d ($J = 8.5$ Hz), 4H; 7.68, d ($J = 8.7$ Hz), 4H; 7.00, d ($J = 8.7$ Hz), 4H; 3.30, t ($J = 7.8$ Hz), 4H; 1.95−1.80, m, 4H; 1.65-1.45, m, 4H; 1.45−1.25, m, 8H; 0.91, t ($J = 7.0$ Hz), 6H. CI-MS: *m/z* found 685.5 $[\mathbf{6} + H^+]^+$ (calcd 685.9).

Compound 7. 2-(4-Bromobutoxy)tetrahydro-2*H*-pyran (156 mg; 0.66 mmol) dissolved in DMF (10 mL) was added dropwise over 10 min to an argon-flushed suspension of K_2CO_3 (151 mg; 1.1 mmol) in dry DMF (40 mL) kept at 60 °C containing **6** (150 mg; 0.22 mmol). After addition, stirring and heating were continued for 18 h, and then DMF was removed under high vacuum and the residue taken up in $CH_2Cl_2-H_2O$. The organic layer was washed twice with H_2O, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2), giving pure **7** (183 mg; 0.184 mmol; 84 % yield).

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(31) The O_2 reduction potential is about −0.85 V in several organic solvents (DMF, pyridine, MeCN), and it is expected to be more negative with decreasing dielectric constants.[32] An experiment carried out in our laboratory has shown an irreversible reduction wave in CH_2Cl_2 at about −1.5 V vs SCE.

(32) Sawyer, D. T.; Chiericato, G., Jr.; Angelis, C. T.; Nanni, E. J., Jr.; Tsuchiya, T. *Anal. Chem.* **1982**, *54*, 1720.

(33) Zhang, X.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 12797.

(34) Wilkinson, F.; McGarvey, D. J. ; Oles, A. F. *J. Phys. Chem.* **1994**, *98*, 3762.

(35) Kikuchi, K.; Sato, C.; Watable, M.; Ikeda, H.; Takahashi, Y.; Miyashi, T. *J. Am. Chem. Soc.* **1993**, *115*, 5180.

7: pale yellow solid. ^{1}H-NMR ($CDCl_3$); 8.55, d ($J = 8.5$ Hz), 4H; 8.04, s, 2H; 8.00, s, 2H; 7.79, d ($J = 8.5$ Hz), 4H; 7.66, d ($J = 8.8$ Hz), 4H; 7.01, d ($J = 8.8$ Hz), 4H; 4.63, two unresolved t, 2H; 4.08, t ($J = 6.2$ Hz), 4H; 3.95−3.75, two unresolved t, 4H; 3.60−3.40, two unresolved t, 4H; 3.21, t ($J = 7.7$), 4H ; 2.00−1.65, m, 12H; 1.65−1.20, m, 24H; 0.91, t ($J = 6.9$ Hz), 6H. Anal. Calcd for $C_{66}H_{80}N_2O_6$: C, 79.48; H, 8.08; N, 2.81. Found: C, 79.56; H, 8.07; N, 2.70.

Compound 8. Pyridinium *p*-toluenesulfonate (504 mg; 2.0 mmol) dissolved in ethanol (15 mL) was added dropwise over 40 min to a refluxing solution of **7** (500 mg; 0.5 mmol) in ethanol (250 mL). After addition, refluxing was continued for 3 h. Then the solution was neutralized by the addition of a pH 7.0 buffer solution. The solvent was removed and the residue taken up in CH_2Cl_2. The organic layer was washed with H_2O, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2 containing 1.0−2.0% MeOH), giving pure **8** (340 mg; 0.41 mmol; 82% yield).

8: pale yellow solid. ^{1}H-NMR ($CDCl_3$): 8.55, d ($J = 8.4$), 4H; 8.04, s, 2H; 8.00, s, 2H; 7.79, d ($J = 8.4$ Hz), 4H; 7.67, d ($J = 8.7$ Hz), 4H; 7.01, d ($J = 8.7$ Hz), 4H; 4.08, t ($J = 5.9$ Hz), 4H; 3.76, t ($J = 5.8$ Hz), 4H; 3.21, t ($J = 7.6$ Hz), 4H; 2.05−1.70, m, 12H; 1.65−1.20, m, 12H; 0.91, t ($J = 6.9$ Hz), 6H. Anal. Calcd for $C_{56}H_{64}N_2O_4$: C, 81.12; H, 7.78; N, 3.38. Found: C, 81.03; H, 7.84; N, 3.26.

Compound 9. Mesyl chloride (0.14 mL; 207 mg; 1.81 mmol) in anhydrous CH_2Cl_2 (25 mL) was added over 1 h to a solution of **8** (250 mg; 0.30 mmol) in anhydrous CH_2Cl_2 (75 mL) at 0 °C containing triethylamine (0.5 mL; 366 mg; 3.60 mmol). After stirring for 2.5 h at 0 °C, the solution was washed twice with water, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel (eluent CH_2Cl_2 containing 0.0−1.0% MeOH) giving pure **9** (293 mg; 0.30 mmol; 99% yield).

9: pale yellow solid. ^{1}H-NMR ($CDCl_3$): 8.55, d ($J = 8.4$ Hz), 4H; 8.03, s, 2H; 8.00, s, 2H; 7.79, d ($J = 8.4$ Hz), 4H; 7.67, d ($J = 8.7$ Hz), 4H; 7.00, d ($J = 8.7$ Hz), 4H; 4.34, t ($J = 5.9$ Hz), 4H; 4.08, t ($J = 5.4$ Hz), 4H; 3.20, t ($J = 7.6$ Hz), 4H; 3.03, s, 6H; 2.10−1.75, m, 12H; 1.60−1.20, m, 12H; 0.91, t ($J = 6.9$ Hz), 6H.

Compound 10. A solution of acetone (100 mL) containing **9** (293 mg; 0.30 mmol) and LiBr (516 mg; 5.9 mmol) was refluxed for 3 h. The solvent was removed and the residue taken up in CH_2Cl_2/H_2O. The organic layer was washed twice with water, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2 containing 0.0−0.5% MeOH), giving pure **10** (252 mg; 0.26 mmol; 89% yield).

10: pale yellow solid (mp 129−131 °C). ^{1}H-NMR ($CDCl_3$): 8.55, d ($J = 8.4$ Hz), 4H; 8.04, s, 2H; 8.00, s, 2H; 7.79, d ($J = 8.4$ Hz), 4H; 7.67, d ($J = 8.7$ Hz), 4H; 7.01, d ($J = 8.7$ Hz), 4H; 4.07, t ($J = 5.8$ Hz), 4H, 3.52, t ($J = 6.4$ Hz), 4H; 3.21, t ($J = 7.6$ Hz), 4H; 2.20−1.90, m, 8H; 1.87, m, 4H; 1.60−1.20, m, 12H; 0.91, t ($J = 6.9$ Hz), 6H. Anal. Calcd for $C_{56}H_{62}N_2O_2Br_2$: C, 70.44; H, 6.54; N, 2.93. Found: C, 70.58; H, 6.69; N, 2.74.

Compound 11. The same procedure as for the preparation of **10** but using NaI instead of LiBr led to **11** in 93% yield.

11: pale yellow solid (mp 131−133 °C). ^{1}H-NMR ($CDCl_3$): 8.55, d ($J = 8.4$ Hz), 4H ; 8.04, s, 2H; 8.00, s, 2H; 7.79, d ($J = 8.4$ Hz), 4H; 7.67, d ($J = 8.7$ Hz), 4H; 7.00, d ($J = 8.7$ Hz), 4H; 4.06, t ($J = 5.8$ Hz), 4H; 3.30, t ($J = 6.7$ Hz), 4H; 3.21, t ($J = 7.8$ Hz), 4H; 2.20-1.70, m, 12H; 1.60-1.20, m, 12H; 0.91, t ($J = 6.8$ Hz), 6H. Anal. Calcd for $C_{56}H_{62}N_2O_2I_2$: C, 64.12; H, 5.96; N, 2.67. Found: C, 64.21; H, 6.21; N, 2.51.

Macrocycle 1. A mixture of **6** (94.5 mg; 0.138 mmol) and **10** (140 mg; 0.147 mmol) in DMF (100 mL) was added dropwise over 36 h with efficient stirring to an argon-flushed suspension of Cs_2CO_3 (134 mg; 0.41 mmol) in DMF (70 mL) kept at 55 °C. DMF was removed under high vacuum and the residue taken up in CH_2Cl_2/H_2O. The organic layer was washed twice with water, dried over Na_2SO_4, and evaporated to dryness to give a crude yellow product (234 mg). The crude product was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2 containing 0.5−1.5% MeOH), giving pure macrocycle **1** (105 mg; 0.071 mmol; 51% yield).

1: pale yellow solid (mp >280 °C, dec). ^{1}H-NMR ($CDCl_3$): 8.55, d ($J = 8.4$ Hz), 8H; 8.04, s, 4H; 8.00, s, 4H; 7.80, d ($J = 8.4$ Hz), 8H; 7.68, d ($J = 8.7$ Hz), 8H; 7.05, d ($J = 8.7$ Hz), 8H; 4.15, unresolved t, 8H; 3.21, t ($J = 7.6$ Hz), 8H ; 2.15−1.95, m, 8H; 1.95−1.70, m, 8H; 1.60−1.20, m, 24H; 0.90, t ($J = 6.9$ Hz), 12H. FAB-MS: *m/z* found: 1478.7 $[\mathbf{1} + H^+]^+$, 739.3 $[\mathbf{1} + 2H^+]^{2+}$ (calcd 1479.0, 740.0).

Macrocycle 2. A solution of 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline[11] (2.09 g; 5.74 mmol) and 1,17-diodo-3,6,9,12,15-pentaoxaheptadecane (3.17 g; 6.31 mmol) in DMF (150 mL) was added dropwise over 24 h with efficient stirring to an argon-flushed suspension of Cs_2CO_3 (6 g; 18.4 mmol) in DMF (800 mL) kept at 55−60 °C. After addition, stirring and heating were continued for 24 h, and then DMF was removed under high vacuum and the residue taken up in CH_2Cl_2/H_2O. The organic layer was washed twice with water, dried over Na_2SO_4, and evaporated to dryness to give a crude yellow product (5.63 g). The crude product was purified by two successive flash column chromatographies on silica gel (eluent CH_2Cl_2 containing 0.5−1.0% MeOH), giving pure macrocycle **2** (2.00 g; 3.27 mmol; 57% yield).

2: pale yellow solid (mp 128−130 °C). ^{1}H-NMR ($CDCl_3$): 8.44, d ($J = 8.8$ Hz), 4H; 8.26, d ($J = 8.4$ Hz), 2H; 8.07, d ($J = 8.4$ Hz), 2H; 7.74, s, 2H; 7.16, d ($J = 8.8$ Hz), 4H; 4.31, t ($J = 5.3$ Hz), 4H; 3.90, t ($J = 5.3$ Hz), 4H; 3.85-3.55, m, 16H. ES-MS: *m/z* found 611.2 $[\mathbf{2} + H^+]^+$ (calcd 611.7). Anal. Calcd for $C_{36}H_{38}N_2O_7$: C, 70.80; H, 6.27; N, 4.59. Found: C, 70.70; H, 6.18; N, 4.49.

Compound 3. A mixture of **6** (150 mg; 0.22 mmol), methyl iodide (0.14 mL; 311 mg; 2.2 mmol), and K_2CO_3 (303 mg; 2.2 mmol; suspension) in DMF (40 mL) was stirred for 4 h at 40 °C under argon. The solvent was removed under high vacuum and the residue taken up in CH_2Cl_2/H_2O. The organic layer was washed twice with water, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel (eluent CH_2Cl_2), giving pure **3** (140 mg; 0.20 mmol; 90% yield).

3: pale yellow solid (mp 174−176 °C). ^{1}H-NMR ($CDCl_3$): 8.56, d ($J = 8.4$ Hz), 4H; 8.03, s, 2H; 8.00, s, 2H; 7.80, d ($J = 8.4$ Hz), 4H; 7.68, d ($J = 8.8$ Hz), 4H; 7.03, d ($J = 8.8$ Hz), 4H; 3.88, s, 6H; 3.21, t ($J = 7.7$ Hz), 4H. 1.87, m, 4H ; 1.60−1.45, m, 4H; 1.45−1.30, m, 8H; 0.91, t ($J = 7.0$ Hz), 6H. Anal. Calcd for $C_{50}H_{52}N_2O_2$: C, 84.23; H, 7.35; N, 3.93. Found: C, 83.95; H, 7.50; N, 3.99.

[Cu(2)(11)]BF$_4$. A solution of $Cu(CH_3CN)_4BF_4$ (64 mg; 0.20 mmol) in degassed acetonitrile (10 mL) was added via cannula to a stirred degassed solution of **2** (125 mg; 0.20 mmol) in degassed CH_2Cl_2 (20 mL) at room temperature under argon. Instantaneously, a deep orange coloration of the solution appeared. After stirring for 15 min at room temperature, a solution of **11** (210 mg; 0.20 mmol) in degassed CH_2Cl_2 (20 mL) was added, and the solution turned dark red immediately. Subsequently, the solution was stirred for 1 h under argon at room temperature and the solvents were removed. A dark red solid of crude [Cu(**2**)(**11**)]BF$_4$ was obtained in nearly quantitative yield, and this compound was used without further purification.

[Cu(**2**)(**11**)]BF$_4$: dark red solid (mp 89−91 °C). ^{1}H-NMR ($CDCl_3$): 8.41, s, 2H; 8.39, d ($J = 8.2$ Hz), 2H; 7.80, s, 2H; 7.80, d ($J = 8.3$ Hz), 2H; 7.73, broad s, 2H; 7.60−7.45, broad unresolved d, 4H; 7.40, d ($J = 8.5$ Hz), 4H; 7.07, d ($J = 8.7$ Hz), 4H; 6.93, d ($J = 8.7$ Hz), 4H; 6.71, d ($J = 8.0$ Hz), 4H; 6.03, d ($J = 8.6$ Hz), 4H; 4.06, t ($J = 5.8$ Hz), 4H; 3.74, s, 8H; 3.68, s, 16H; 3.33, t ($J = 7.4$ Hz), 4H; 3.30, t ($J = 6.7$ Hz), 4H; 2.20−1.80, m, 12H; 1.70−1.50, m, 4H; 1.50−1.30, m, 8H; 0.95, t ($J = 7.0$ Hz), 6H.

[2]-Catenate [Cu(1)(2)]BF$_4$: Two high-dilution dropping funnels were charged with respectively [Cu(**2**)(**11**)]BF$_4$ (362 mg; 0.20 mmol) in degassed DMF (75 mL) and **6** (137 mg; 0.20 mmol) in degassed DMF (75 mL). These two solutions were added over 18 h, at the same rate, to an argon-flushed suspension of Cs_2CO_3 (391 mg; 1.2 mmol) in DMF (75 mL) kept at 60 °C. After addition, stirring and heating were continued for 2 h, and then DMF was removed under high vacuum and the residue taken up in CH_2Cl_2/H_2O. The organic layer was washed twice with water and thereafter treated for 2 h with a HBF_4 solution (50 mL; 34% by weight in water) in order to eliminate open-chain complexes. The organic layer was washed again twice with water, concentrated to 25 mL, and treated for 2 h under efficient stirring, with a saturated $NaBF_4$ aqueous solution (25 mL). By means of this anion exchange reaction, it was possible to isolate $[Cu(\mathbf{1})(\mathbf{2})]^+$, originally formed as carbonate, iodide, and tetrafluoroborate, exclusively as its BF_4^- salt. The resulting organic layer was washed twice with water, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by two successive flash column chromatographies on silica gel (eluent: CH_2Cl_2 containing 0.5−1.0% MeOH) followed by a third flash column chromatography on aluminum oxide 90 (activity grade II−III) (eluent: CH_2Cl_2 containing 0.0−0.5% MeOH), giving pure [Cu(**1**)(**2**)]BF_4 (55 mg; 24.6 μmol; 12% yield). Pure macrocycle **1** (64 mg; 43.3 μmol) and pure macrocycle **2** (83 mg; 136 μmol) were also isolated.

[Cu(**1**)(**2**)]BF_4: dark red solid (mp 152−154 °C). ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.57, d ($J = 8.4$ Hz), 4H, ($H_{o_1'}$); 8.40, s, 2H ($H_{5,6}$); 8.39, d ($J = 8.3$ Hz), 2H ($H_{4'',7''}$); 8.03, s, 2H ($H_{5',6'}$); 8.01, s, 2H ($H_{3',8'}$); 7.82, d ($J = 8.5$ Hz), 4H ($H_{m_1'}$); 7.81, s, 2H ($H_{5'',6''}$); 7.79, d ($J = 8.5$ Hz), 2H ($H_{3'',8''}$); 7.73, s, 2H ($H_{3,8}$); 7.71, d ($J = 8.6$ Hz), 4H ($H_{o_2'}$); 7.49, broad unresolved d, 4H (H_{o_1}); 7.41, d ($J = 8.6$ Hz), 4H ($H_{o''}$); 7.07, d ($J = 8.8$ Hz), 4H, ($H_{m_2'}$); 7.05, unresolved d, 4H (H_{o_2}); 6.97, d ($J = 8.8$ Hz), 4H (H_{m_2}); 6.69, d ($J = 8.0$ Hz), 4H (H_{m_1}); 6.02, d ($J = 8.6$ Hz), 4H ($H_{m''}$); 4.17 and 4.15, 2 unresolved t, 8H (H_α, $H_{\alpha'}$); 3.74 and 3.66, 2 broad s, 24H ($H_{\alpha''}$, $H_{\beta''}$, $H_{\gamma''}$, $H_{\delta''}$, $H_{\epsilon''}$, $H_{\phi''}$); 3.33, t ($J = 7.5$ Hz), 4H (H_a); 3.21, t ($J = 7.5$ Hz), 4H ($H_{a'}$) ; 2.09, m, 8H ($H_{\beta,\beta'}$), 1.94, m, 4H (H_b); 1.87, m, 4H ($H_{b'}$); 1.65−1.30, m, 24H, ($H_{c,c',d,d',e,e'}$); 1.00−0.85, 2 unresolved t, 12H, ($H_{f,f'}$). FAB-MS: *m/z* found 2152.0 [Cu(**1**)(**2**)]$^+$, 1541.6 [**1** + Cu^+]$^+$, 1075.9 [Cu(**1**)(**2**)H]$^{2+}$, and 673.2 [**2** + Cu^+]$^+$ (calcd 2152.3, 1541.6, 1076.6, and 674.3).

[Cu(3)$_2$]BF$_4$. A solution of $Cu(CH_3CN)_4BF_4$ (19.4 mg; 62 μmol) in degassed acetonitrile (5 mL) was added via cannula to a stirred degassed solution of **3** (40 mg; 56 μmol) in degassed CH_2Cl_2 (20 mL) at room temperature under argon. The solution turned dark red instantaneously. After stirring for 90 min at room temperature, the solvents were removed. The crude product was purified by flash column chromatography on aluminum oxide 90 (activity grade II−III) (eluent CH_2Cl_2), giving pure [Cu(**3**)$_2$]BF_4 (34 mg; 25.4 μmol; 77% yield).

[Cu(**3**)$_2$]BF_4: dark red solid (mp 199−201 °C). ^{1}H-NMR ($CDCl_3$): 8.10, s, 4H; 7.67, s, 4H; 7.57, d ($J = 8.3$ Hz), 8H; 7.07, d ($J = 8.9$ Hz), 8H; 6.93, d ($J = 8.9$ Hz), 8H; 6.74, d ($J = 8.3$ Hz), 8H; 3.88, s, 12H; 3.09, t ($J = 7{,}7$ Hz), 8H; 1.75−1.55, m, 8H; 1.55−1.20 m, 24H; 0.93, t ($J = 6.5$ Hz), 12H. FAB-MS: *m/z* found 1488.2 [Cu(**3**)$_2$]$^+$ and 775.1 [Cu(**3**)]$^+$ (calcd 1489.5 and 776.5).

[Cu(2)(3)]BF$_4$. This complex was obtained in 80% yield after purification by flash column chromatography on aluminum oxide 90 (activity grade II−III) (eluent: CH_2Cl_2) using the same procedure as for [Cu(**2**)(**11**)]$^+$.

[Cu(**2**)(**3**)]BF_4: dark red solid (mp 93−95 °C). ^{1}H-NMR ($CDCl_3$): 8.41, d ($J = 8.4$ Hz), 2H; 8.41, s, 2H; 7.82, d ($J = 8.3$ Hz), 2H; 7.80, s, 2H; 7.74, broad s, 2H; 7.60−7.45, m, 4H; 7.41, d ($J = 8.7$ Hz), 4H; 7.09, d ($J = 8.7$ Hz), 4H; 6.95, d ($J = 8.8$ Hz), 4H; 6.72, d ($J = 8.0$ Hz), 4H; 6.03, d ($J = 8.6$ Hz), 4H; 3.88, s, 6H; 3.74, s, 8H; 3.69, s, 16H; 3.34, t ($J = 7.7$ Hz), 4H; 2.05−1.85, m, 4H; 1.70−1.30, m, 12H; 0.95, t ($J = 7.0$ Hz), 6H. FAB-MS: *m/z* found 1385.1 [Cu(**2**)(**3**)]$^+$, 775.1 [Cu(**3**)]$^+$, and 673.0 [Cu(**2**)]$^+$ (calcd 1387.2, 776.5, and 674.3).

Re(1)(CO)$_3$Cl. A suspension of **1** (150 mg; 0.10 mmol) in anhydrous toluene (100 mL) was heated until the mixture became homogeneous. $Re(CO)_5Cl$ (36.7 mg; 0.10 mmol) was then added, and a yellow coloration appeared immediately. After the solution was refluxed for 1 h, it was evaporated to dryness, to give a crude yellow product. This crude product was purified by two successive flash column chromatographies on silica gel (eluent CH_2Cl_2), giving pure Re(**1**)(CO)$_3$Cl (52 mg; 29 mmol; 29% yield).

Re(**1**)(CO)$_3$Cl: yellow solid (mp >275 °C, dec). ^{1}H-NMR ($CDCl_3$): 8.54, d ($J = 8.4$ Hz), 4H; 8.23, s, 2H ; 8.04, s, 2H ; 8.00, s, 2H; 7.90−7.70, m, 14H; 7.68, d ($J = 8.7$ Hz), 4H; 7.62, d ($J = 8.7$ Hz), 4H; 7.03, 2 superimposed d ($J = 8.7$ Hz), 8H; 4.20−4.05, 2 unresolved t, 8H; 3.35−3.10, 2 unresolved t, 8H ; 2.10−1.95, m, 8H; 1.95−1.75, m, 8H; 1.60−1.20, m, 24H; 0.92, 2 unresolved t, 12H. FAB-MS: *m/z* found 1783.6 [M − e^-]$^+$, 1748.6 [M − Cl^-]$^+$, 1661.6 [M − Cl^- − 3CO]$^+$, and 1477.7 [**1** + H^+]$^+$ (calcd 1783.7, 1748.1, 1664.2, and 1479.0).

Re(3)(CO)$_3$Cl. The same procedure as that described for Re(**1**)(CO)$_3$Cl was used.

Re(**3**)(CO)$_3$Cl: yellow solid (mp 203−205 °C). ^{1}H-NMR ($CDCl_3$): 8.24, s, 2H; 7.90−7.70, m, 10H; 7.63, d ($J = 8.7$ Hz), 4H; 7.01, d ($J = 8.7$ Hz), 4H; 3.87, s, 6H ; 3.26, m, 4H; 1.95−1.75, m, 4H; 1.60−1.25, m, 12H; 0.92, t ($J = 6.9$ Hz), 6H. FAB-MS: *m/z* found 2001.7 [2M − Cl^-]$^+$, 1018.4 [M − e^-]$^+$, 983.4 [M − Cl^-]$^+$, 954.4 [M − Cl^- − CO]$^+$, 925.4 [M - Cl^- − 2CO]$^+$, and 898.4 [M − Cl^--3CO]$^+$ (calcd 2001.9, 1018.7, 983.2, 955.2, 927.2, and and 899.2).

Equipment. ^{1}H-NMR spectra were recorded with a Bruker WP 200 SY or with an AM 400 spectrometer. Mass spectra were obtained either by chemical ionization (CI-MS), by positive fast atom bombardment (FAB-MS), or by electrospray (ES-MS) mass spectrometry. Melting points were determined on a Bioblock IA 8103 apparatus and are uncorrected.

Electrochemical experiments were carried out in CH_3CN or in CH_3CN/CH_2Cl_2, 80:20 v/v, with 0.1 M Et_4NPF_6 as supporting electrolyte. The equipment used was previously described.[16b] The reference electrode was a saturated calomel electrode (SCE). The potential values were determined by cyclic voltammetry at a scan rate of 100 mV/s for Re(**3**)(CO)$_3$Cl and 50 mV/s for the Cu(I) complexes.

The solvents used for the photophysical studies were CH_2Cl_2 (Merck, pro analysi) and butyronitrile (Fluka). Absorption spectra were recorded with a Perkin-Elmer λ6 spectrophotometer. Corrected emission spectra, excitation spectra, and phosphorescence lifetimes (second time scale) were obtained with a Perkin-Elmer LS-50 spectrofluorimeter. Luminescence quantum yields were measured following the method described by Demas and Crosby[36] (standards used: anthracene in cyclohexane, $\Phi = 0.34$;[37] [Ru(bpy)$_3$]Cl_2 in water, $\Phi = 0.028$[38]). An Edinburgh Instruments single-photon counting apparatus (N_2 lamp) was used to obtain luminescence lifetimes (nano- and microsecond time scale). Picosecond fluorescence lifetimes were measured by a system based on a Nd:YAG laser ($\lambda_{exc} = 532$ nm) and a Hamamatsu C1587 streak camera described previously.[23] Estimated experimental uncertainties are λ_{abs}, 2 nm; λ_{em}, 5 nm; τ, 10%; and Φ_{em}, 20%.

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

(37) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic: London, U.K., 1965; p 356.

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