From Homoleptic to Heteroleptic Double Stranded Copper(I) Helicates: The Role of Self-Recognition in Self-Assembly Processes

Moshe Greenwald,[†] Dana Wessely,[†] Eugenii Katz,[‡] Itamar Willner,[‡] and Yoram Cohen*,[†]

School of Chemistry, The Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel, and Institute of Chemistry, Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received September 16, 1999

The ligands 2,9-bis[(6-methyl-2,2′-bipyridin-6′-yl)methyleneoxymethylenyl]-1,10-phenanthroline (**6**), 6″,6‴-bis[(6-methyl-2,2′-bipyridin-6′-yl)methyleneoxymethylenyl)]-2″,2‴-bipyridine (**2**), 5,5′-bis[(6-methyl-2,2′-bipyridin-6′yl)methyleneoxymethylenyl]-2,2′-bithiophene (**7**), and 6,6′-bis[(6-methyl-2,2′-bipyridin-6′-yl)methyleneoxymethylenyl]-2,2′-biphenyl (**8**) and their respective homo- and heteroleptic double-stranded copper(I) complexes were prepared and characterized in order to estimate the importance of self-recognition in the self-assembly processes of double-stranded copper complexes. The homoleptic double-stranded copper complexes of **2**, **6**, **7,** and **8** were characterized by NMR, FAB-MS, and electrochemistry. It was found that **6** and **2** each form a single double-stranded helicate having the structure of $[(\mathbf{L})_2Cu_3]^{3+}$ (**L** = **2** or **6**), **7** forms two double-stranded $[(\mathbf{7})_2Cu_3]^{3+}$ complexes, and **8** results in a mixture of at least two $[(\mathbf{8})_2Cu_2]^{2+}$ complexes. The potential shift, $\Delta E°$, of the Cu^+/Cu^{2+} redox process of these complexes reflects the binding affinity of the different binding sites to the copper cation. The electrochemical data show that the central units have a higher affinity to Cu^+ as compared to the off-center binding sites. NMR was used to determine the actual complex composition obtained from different mixtures of **2**, **6**, or **7** with Cu^+. Interestingly, we have found that, although **6**, **2**, and **7** each form homoleptic double-stranded complexes, no heteroleptic double-stranded copper complexes were formed from the mixtures of **7** with either **6** or **2**. However, when mixtures of **6** and **2** are used, helicate distributions seem to follow simple statistics. These results are discussed in terms of the relative importance of self-recognition in the self-assembly of double-stranded helicates.

Introduction

The self-assembly of molecular components to large supramolecular systems capable of performing specific functions is one of the basic principles in biology.[1] Recent research activities are devoted to the development of chemical concepts for self-assembly of molecular systems in supramolecular arrays.[2,3] Supramolecular assemblies formed by noncovalent bonds and using hydrogen bonds, $\pi-\pi$ stacking, donor−acceptor interactions, or metal coordination were reported.[4,5] Metallosupramolecular architectures differing in size, shape, and dimensionality were reported using predesigned organic ligands and specific metal ions.[6]

Extensive research activities are directed toward the preparation and self-organization of supramolecular metallohelicates.[7−11] Bidentate ligands were shown to form double- and triple-stranded helicates with tetrahedral and octahedral cations, respectively. Tridentate ligands were used to prepare double- and triple-stranded helicates with octahedral cations and with nine coordinated lanthanide ions.[7−9] In addition, both homo- and heteronuclear helicates have been prepared, [7−10] some of which were shown to function as molecular sensors and molecular switches.[11] Most helicates prepared to date are homoleptic helicates, consisting of identical strands.[7−11] Recently, some heteroleptic double-stranded helicates composed of different strands were reported.[12] In these helicates, the ligands were designed so that the super-

---

* To whom correspondence should be addressed. Fax: 972-3-6409293. Tel: 972-3-6407232. E-mail: ycohen@ccsg.tau.ac.il.

[†] Tel Aviv University.

[‡] Hebrew University of Jerusalem.

(1) Vaener, J. E., Ed. *Self-Assembly Architecture*; Alan R. Liss: New York, 1988.

(2) Vögtle, F. *Supramolecular Chemistry*; John Wiley & Sons: Chichester, 1991.

(3) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, 1995.

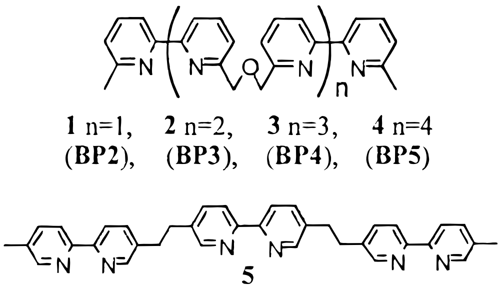
(4) (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (b) Lindsey, J. S. *New. J. Chem.* **1991**, *15*, 153. (c) Lehn, J.-M. *Science* **1993**, *260*, 1762. (d) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mamman, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. (e) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725.

(5) (a) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312. (b) Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229. (c) Philp, D.; Stoddart, J. F., *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (d) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647.

(6) For some selected examples, see: (a) Baxter P.; Lehn, J.-M.; DeCian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 69. (b) Drain, C. M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2313. (c) Baxter, P. N. W.; Lehn, J.-M.; Fischer, J.; Youinou, M.-T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2284. (d) Baxter, P.; Sleiman, H.; Lehn, J.-M.; Rissanen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1294. (e) Fujita, M.; Nagao, S.; Iida, M.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574. (f) Fujita, M.; Ibukuro, F.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 4145. (g) Constable, E. C.; Schofield, E. *Chem. Commun.* **1998**, 403. (h) Stang, P. J. *Acc. Chem. Res.* **1997**, *30*, 502 and references therein. (i) Baxter, P. N. W. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vogtle, F., Eds.; Pergamon Press: Oxford, U.K., 1996; Vol. 9, p 165 and references therein. (j) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1838. (k) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795. (l) Garcia, A. M.; Bassani, D. M.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, 5, 1234. (m) Garcia, A. M.; Romero-Salguero, F. J.; Bassani, D. M.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, 5, 1803.

10.1021/jo991469j CCC: $19.00

Scheme 1

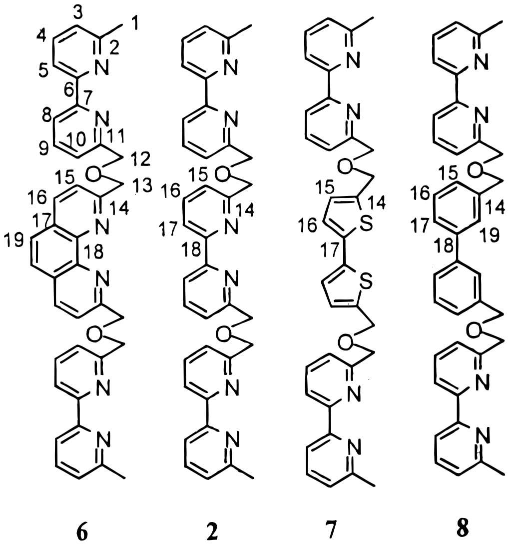


position of the binding sites from the two strands are complementary with the coordination requirements of the metal cation used.[12b] These heteroleptic helicates have been, however, less studied as compared to the homoleptic helicates.[13]

The importance of self-recognition in the self-assembly of helicates was demonstrated by Lehn and co-workers.[14a] It was found that strands of oligo(2,2′-bipyridine) of different lengths (**1**−**4**, Scheme 1) do not form heteroleptic double-stranded helicates upon addition of the Cu$^+$ cation to mixtures of these ligands.[14a] In addition, it was demonstrated that a mixture of ligands **2** and **5** (Scheme 1) reacts with a solution of Cu$^+$ and Ni^{2+} to form only the homoleptic double- and triple-stranded helicates, respectively.[14a]

The degree of self-recognition in self-assembly processes may have practical importance as it implies, at least theoretically, that well-defined supramolecular systems could be generated from preexisting mixtures of instructed components.[14] To further examine the notion of self-recognition in helicates' self-assembly, we have prepared a series of double-stranded helicates from structurally related ligands such as **6**, **2**, **7**, and **8** (Scheme 2). Recently, the effect of the spacer structure on self-assembly of trinuclear copper helicates was reported.[14b] There both homoleptic and heteroleptic helicates were observed.[14b]

Scheme 2



Our approach was first to prepare the ligands, study their homoleptic double-stranded complexes under identical conditions, and then prepare and study the complexes formed from mixtures of these ligands. Interestingly, we found that although **6**, **2**, and **7** form homoleptic double-stranded complexes, no heteroleptic double-stranded copper complexes were formed from the mixtures of **7** with either **6** or **2**. When the starting solution consists of a mixture of ligands **6** and **2**, the distribution of the helicates formed seems to follow simple statistics. Comparative cyclic voltammetry performed on the homoleptic double-stranded complexes enabled to determine the relative affinity of each binding site.

Results and Discussion

Ligand Preparation. Ligand **6** was prepared by reacting 2 equiv of 6-methyl-6′-(bromomethyl)-2,2′-bipyridine (**10**) with 1 equiv of the dilithium salt of 2,9-bis(hydroxymethyl)-1,10-phenanthroline (**9**) in dry THF. Ligands **2**,[7a] **7**, and **8** were prepared using a similar procedure by reacting 2 equiv of the lithium salt of 6-methyl-6′-(hydroxymethyl)-2,2′-bipyridine (**11**) with 1 equivt of 6,6′-bis(bromomethyl)-2,2′-bipyridine (**12**), 5,5′-bis(bromomethyl)-2,2′-bithiophene (**13**), or 3,3′-bis(bromomethyl)biphenyl (**14**), respectively.

The 500 MHz ^{1}H NMR spectra of ligands **6**, **7**, and **8** in DMSO-d_6 and that of **2** in CD$_2$Cl$_2$ are shown in Figure 1. The complete assignment of the ^{1}H NMR spectra of **6**, **2**, **7**, and **8** was accomplished using the long-range COSY (LR-COSY) experiment, which emphasizes $^4J_{HH}$ and $^5J_{HH}$. In these NMR experiments, the cross-peaks between the methyl and the methylene protons of the bridges and their neighboring aromatic protons were identified al-

---

(7) For selected examples of double-stranded helicates, see: (a) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565. (b) Lehn, J.-M.; Rigault, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1095. (c) Garrett, T. M.; Koert, U.; Lehn, J.-M.; Rigault, A.; Meyer, D.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 557. (d) Koert, U.; Harding, M. M.; Lehn, J.-M. *Nature* **1990**, *346*, 339. (e) Schoentjes, B.; Lehn, J.-M. *Helv. Chim. Acta* **1995**, *78*, 1. (f) Marquis-Rigault, A.; Dupont-Gervais, A.; Van Dorsselaer, A.; Lehn, J.-M. *Chem. Eur. J.* **1996**, *2*, 1395. (g) Constable, E. C.; Drew, M. G. B.; Ward, M. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1600. (h) Constable, E. C.; Ward, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 1256. (i) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruna, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4422. (j) Constable, E. C.; Walker, J. V. *J. Chem. Soc., Chem. Commun.* **1992**, 884. (k) Constable, E. C.; Heirtzler, F. R.; Neuburger, M.; Smith, D. R.; Zehnder, M. *J. Chem. Soc., Chem. Commun.* **1996**, 933. (l) Chotalia, R.; Constable, E. C.; Neuburger, M.; Smith, D. R.; Zehnder, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4207. (m) Greenwald, M.; Wesseley, D.; Goldberg, I.; Cohen, Y. *New J. Chem.* **1999**, 337.

(8) For selected examples of triple-stranded helicates, see: (a) Libman, J.; Tor, Y.; Shanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 5880. (b) Williams, A. F.; Piguet, C.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1490. (c) Bernardinelli, G.; Piguet, C.; Williams, A. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1622. (d) Kramer, R.; Lehn, J.-M.; DeCian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 703. (e) Piguet, C.; Bernardinelli, G.; Bunzli, J.-C. G.; Petoud, S.; Hopfgartner, G. *J. Chem. Soc., Chem. Commun.* **1995**, 2575.

(9) (a) Constable, E. C. *Tetrahedron* **1992**, *48*, 10013 and references therein. (b) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005 and references therein.

(10) For selected examples of heteronuclear helicates, see: (a) Constable, E. C.; Edwards, A. J.; Raithby, R.; Walker, J. V. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1465. (b) Funeriu, D. P.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1997**, *3*, 99. (c) Piguet, C.; Rivera-Minten, E.; Bernardinelli, G.; Bunzli, J.-C. G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **1997**, 421.

(11) (a) Zelikovich, L.; Libman, J.; Shanzer, A. *Nature* **1995**, *374*, 790. (b) Piguet, C. *Chimia* **1996**, *50*, 144 and references therein.

(12) (a) Smith, V. C.; Lehn, J.-M. *Chem. Commun.* **1996**, 2733. (b) Hasenknopf, B.; Lehn, J.-M.; Baum, G.; Fenske, D. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 1397.

(13) Williams, A. *Chem. Eur. J.* **1997**, *3*, 15.

(14) (a) Kramer, R.; Lehn, J.-M.; Marquis-Rigault, A. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 5394. (b) Funeriu, D.-P.; He, Y.-B., Bister, H. J.; Lehn, J.-M. *Bull. Soc. Chim. Fr.* **1996**, 133, 673. (c) Caulder, D. L.; Raymond, K. N., *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1440. (d) Albrecht, M.; Schneider, M.; Rottele, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 557.

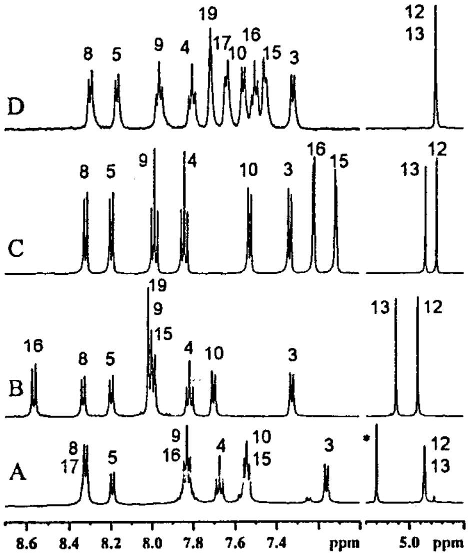


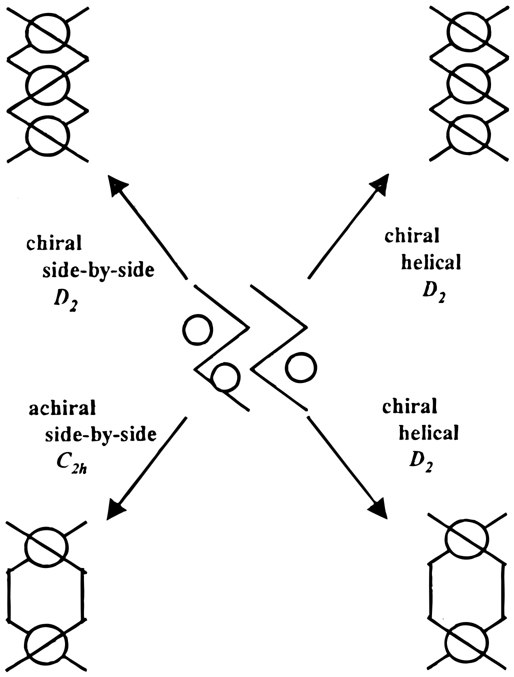
Figure 1. 500 MHz, ^{1}H NMR spectra at 25 °C of (A) **2** in CD$_2$Cl$_2$, (B) **6** in DMSO-d_6, (C) **7** in DMSO-d_6, and (D) **8** in DMSO-d_6. Only the aromatic and the methylene bridges regions are depicted. The signal * indicates the peak of residual protonated methylene chloride.

lowing an unequivocal assignment of all protons. As an example, the LR-COSY ^{1}H NMR specrum of **8** is shown in Figure 2. The protonated carbons were sequentially assigned by the HMQC NMR experiment.[15] The ^{1}H and ^{13}C NMR spectral parameters of ligands **6**, **7**, and **8**, and the ^{1}H NMR parameters of **2** are summarized in the Experimental Section.

Preparation and Characterization of the Homoleptic Double-Stranded Complexes. The Cu$^+$ complexes of ligands **6**, **2**, and **7** were prepared, by reacting 3 equiv of tetrakis(acetonitrile)copper(I) hexafluorophosphate [Cu(CH$_3$CN)$_4$PF$_6$][16] with 2 equiv of **6**, **2**, or **7**, respectively, in acetonitrile. The copper complexes of **8** were obtained by the same procedure from a reaction mixture having a 1:1 stoichiometry. The reaction involved a simple mixing of the components at room temperature, and only few minutes were needed to obtain the final products. When the reactions were carried out in deuterated solvents, the double-stranded complexes were the only products identified by the 500 MHz NMR spectrometer in each reaction. The isolated yields of the complexes were in the range of 80–97%. Scheme 3 shows the most probable structures of di- and trinuclear double-stranded complexes that can be obtained from tetrahedral metals and ligands such as **2**, **6**, **7**, and **8**. It should be noted, however, that when the starting solution contains more than one ligand one can, in principle, expect the formation of both homoleptic and heteroleptic double-stranded complexes.

The 500 MHz ^{1}H NMR spectra of the copper complexes of **6**, **2**, **7**, and **8** in DMSO-d_6 are shown in Figure 3. In all of the studied systems, significant changes in the ^{1}H NMR spectra were observed upon complex formation. The most informative change is in the hyperfine structure of the methylene protons of the –CH$_2$OCH$_2$– bridges. In the double-stranded complexes, the two geminal protons of each methylene in the –CH$_2$OCH$_2$– group are rendered diastreotopic and their hyperfine structure changes: from sharp singlets in the ligands to AB systems in the complexes. In the ^{1}H NMR spectra of the copper complexes of **6** and **2** only the expected two AB systems are found. In the case of **7** four AB systems are observed, while in the case of the copper complexes of **8** at least four AB systems can be identified. From these spectra one can conclude that both **6** and **2** each form a single double-stranded helicate having the structure of [(**L**)$_2$Cu$_3$]$^{3+}$ whose average solution structures, on the NMR time scale, are of D_2 symmetry. Ligand **7** forms a mixture of two double-stranded complexes, and on the basis of their electrochemistry (vide infra), these seem to have also the [(**7**)$_2$Cu$_3$]$^{3+}$ structure.[17] Ligand **8** forms, as expected, complexes having the [(**8**)$_2$Cu$_2$]$^{2+}$ stoichiometry, but it seems that in this case more than two different complexes are obtained. In this respect, ligands **7** and **8** seem to behave similarly to the series of double-stranded complexes recently prepared by Harding et al.[18] There it has been proposed that the doubling of the signal in the ^{1}H NMR spectra originates from the formation of mixtures of helical and side-by-side double-stranded complexes (Scheme 3).[18]

Scheme 3



Among the aromatic protons, positions 9 and 10 should be the most sensitive to the anisotropic ring current effect of the central unit in the different ligands. The changes in the ^{1}H and the ^{13}C chemical shifts ($\Delta\delta^{1}$H and $\Delta\delta^{13}$C, respectively) of positions 9 and 10 (see numbering in Scheme 2) upon the complex formation with ligands **6**, **2**, **7**, and **8** are shown in Table 1. From Table 1 it is clear that $\Delta\delta^{1}$H for H-9 and H-10 upon formation of the copper helicate of ligand **6** are substantially larger than those found for the formation of the helicates of **2** and the double-stranded complexes of **7** and **8**. In contrast to that, Table 1 shows that there are only very small changes in the ^{13}C chemical shifts of these carbons upon complex

---

[15] Muller, J. *J. Am. Chem. Soc.* **1979**, *101*, 4481.

[16] Kubas, G. J. *Inorg. Synth.* **1990**, *26*, 68.

[17] Greenwald, M.; Eassa, M.; Katz, E.; Willner, I.; Cohen, Y. *J. Electroanal. Chem.* **1997**, *434*, 77.

[18] (a) Bilyk, A.; Harding, M. M. *J. Chem. Soc., Dalton Trans.* **1994**, 77. (b) Bilyk, A.; Harding, M. M.; Turner, P.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1994**, 2783.

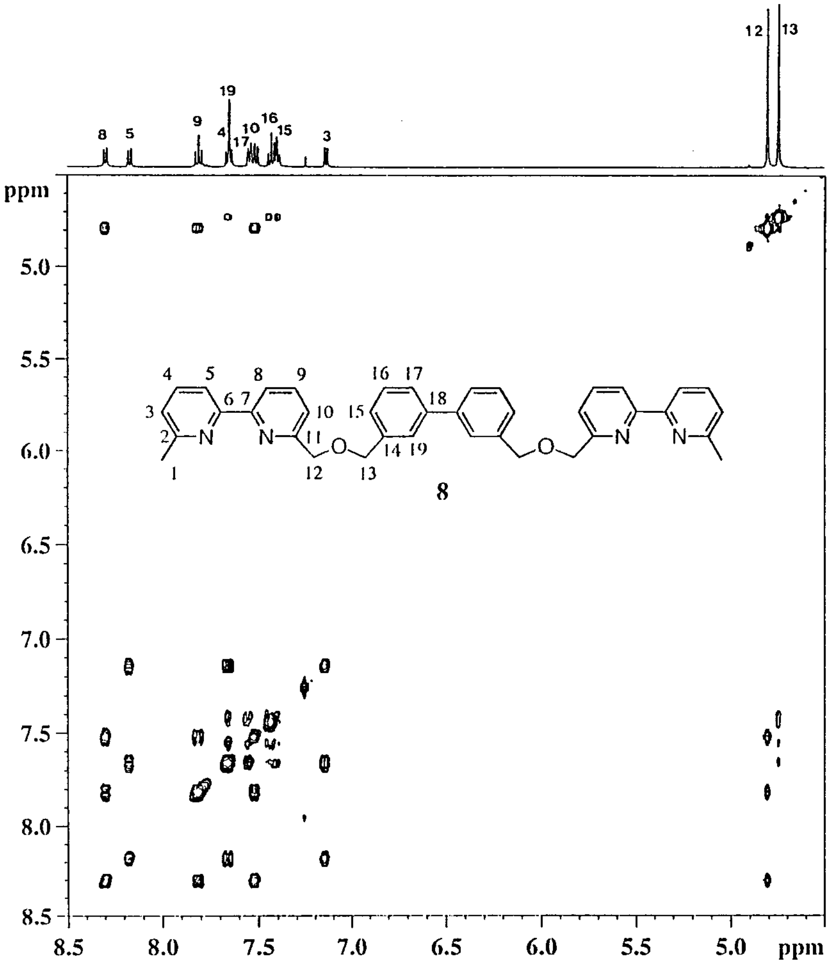


Figure 2. 500 MHz ^{1}H LR-COSY NMR spectrum of ligand **8** in $CDCl_3$. Only the aromatic and the methylene bridges regions are depicted.

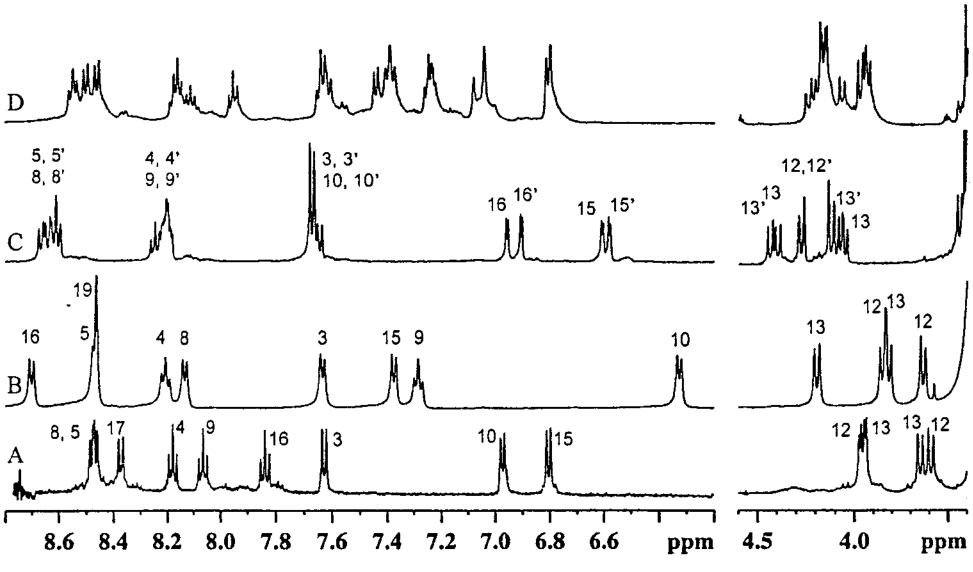


Figure 3. 500 MHz ^{1}H NMR spectra in DMSO-d_6 at 25 °C of the copper complexes of (A) **2**, (B) **6**, (C) **7**, and (D) **8**. Only the aromatic and the methylene bridges regions are depicted.

formation in all systems. This suggests that these changes do not originate from variation in the electronic distributions but rather represent anisotropic contributions due to the ring current effect. It is to be expected that the most pronounced ring current effect would originate from the central phenanthroline unit, as is found experimentally in $[(\mathbf{6})_2Cu_3]^{3+}$. Another possible explanation for the above observation may be the fact that in $[(\mathbf{6})_2Cu_3]^{3+}$ the average distances between the bipyridine units and the central phenanthroline units is shorter than the average distance between the bipyridine units in $[(\mathbf{2})_2Cu_3]^{3+}$. However, at least from the crystal

Table 1. Changes in the Proton and Carbon Chemical Shifts in ppm ($\Delta\delta^1$H and $\Delta\delta^{13}$C, Respectively) upon Formation of the Copper Complexes ($\Delta\delta = \delta$(Helicate) − δ(Ligand))[a]

	$\Delta\delta^1$H		$\Delta\delta^{13}$C	
system	position 9	position 10	position 9	position 10
2[b]	0.24	−0.57	−0.2	1.6
6	−0.72	−1.37	−0.4	0.9
7[c]	0.26	0.14	1.0	2.2
8[c]	0.14	0.12	ND[d]	ND[d]

[a] The data of both the parent compound and the copper helicate were recorded in DMSO$_{d6}$ unless it is specified otherwise. [b] Ligand data was recorded in CD_2Cl_2, copper helicate data was recorded in DMSO$_{d6}$. [c] The largest absolute values are depicted. [d] Not determined as the ^{13}C NMR spectrum of the complexes could not be assigned.

structure of the two helicates, no clear evidence could be found to support this interpretation.[7a,m]

The formation of double-stranded complexes was corroborated also by fast atomic bombardment mass spectrometry (FAB-MS).[19] The FAB-MS spectra of these complexes showed each a well-defined isolated peak at *m*/*z* of 1689, 1639, 1453, and 1429 with the relative intensities of 10%, 2.3%, 13%, and 5%, respectively. These peaks correspond to $[(\mathbf{6})_2Cu_3(PF_6)_2]^+$, $[(\mathbf{2})_2Cu_3(PF_6)_2]^+$, $[(\mathbf{7})_2Cu_2(PF_6)]^+$, and $[(\mathbf{8})_2Cu_2(PF_6)]^+$, respectively. Ligand **7** was also reacted with $CuCF_3SO_3$ in an acetonitrile solution. The product of this reaction showed an isolated peak at *m*/*z* of 1669 that corresponds to $[(\mathbf{7})_2Cu_3(CF_3SO_3)_2]^+$; however, its intensity was only 1% of that of the strongest peak in the FAB-MS spectrum.[19] The electrochemical results of the above series of helicates afford the best evidence for the formation of a $[(\mathbf{L})_2Cu_3]^{3+}$-type copper complexes for ligand **7** (vide infra).

Electrochemistry of the Homoleptic Double-Stranded Complexes. The cyclic voltammograms of the four double-stranded complexes in DMF at ambient temperature are shown in Figure 4. Two quasireversible redox waves having a 2:1 ratio were observed for $[(\mathbf{7})_2Cu_3]^{3+}$ (Figure 4A), $[(\mathbf{2})_2Cu_3]^{3+}$(curve b in Figure 4B), and $[(\mathbf{6})_2Cu_3]^{3+}$ (curve c in Figure 4B), while only one redox wave is observed for $[(\mathbf{8})_2Cu_2]^{2+}$ (curve a in Figure 2B). To better resolve the redox potentials of the copper complexes of **2** and **6**, and in order to prove the existence of only one redox wave for **8**, differential pulse voltammetry was applied to analyze the electrical responses of $[(\mathbf{6})_2Cu_3]^{3+}$, $[(\mathbf{2})_2Cu_3]^{3+}$, and $[(\mathbf{8})_2Cu_2]^{2+}$, as shown in Figure 5. From these experiments, the formal potentials, $E°$, of the redox waves for the Cu^+/Cu^{2+} process in the above complexes were determined (Table 2). In the case of **2**, a strong overlap of the peaks exists and computer deconvolution was used to extract the different $E°$ values (Figure 5B). These data show that all complexes have a similar redox wave at a formal potential of about +0.50 V vs SCE, attributed to the redox process of the copper cations positioned between the off-center bipyridine units of these complexes. These similar redox potentials and the fact that the two copper cations coordinated to the two off-centered bipyridine units in each complex show only one redox potential suggest that there is no significant electrical interaction between the different copper cations in these complexes. In $[(\mathbf{8})_2Cu_2]^{2+}$, where the central unit is a spacer and no interaction is expected between the two coppers, the formal potential is very similar to those of the other complexes. This result further supports the nonsignificant interaction between the different metal centers in these double-stranded complexes (Table 2). This conclusion agrees well with the relatively large distances between the different copper cations in $[(\mathbf{6})_2Cu_3]^{3+}$ and $[(\mathbf{2})_2Cu_3]^{3+}$, which were found by X-ray crystallography to be about 6−6.3 Å.[7a,m] Electrochemical interactions between metal cations was documented in copper helicates in which the distance between the copper cations was significantly shorter than in $[(\mathbf{6})_2Cu_3]^{3+}$ and $[(\mathbf{2})_2Cu_3]^{3+}$.[20a−c] However, it should be noted that the distance between the metal centers is not the only factor which determine such interaction. For

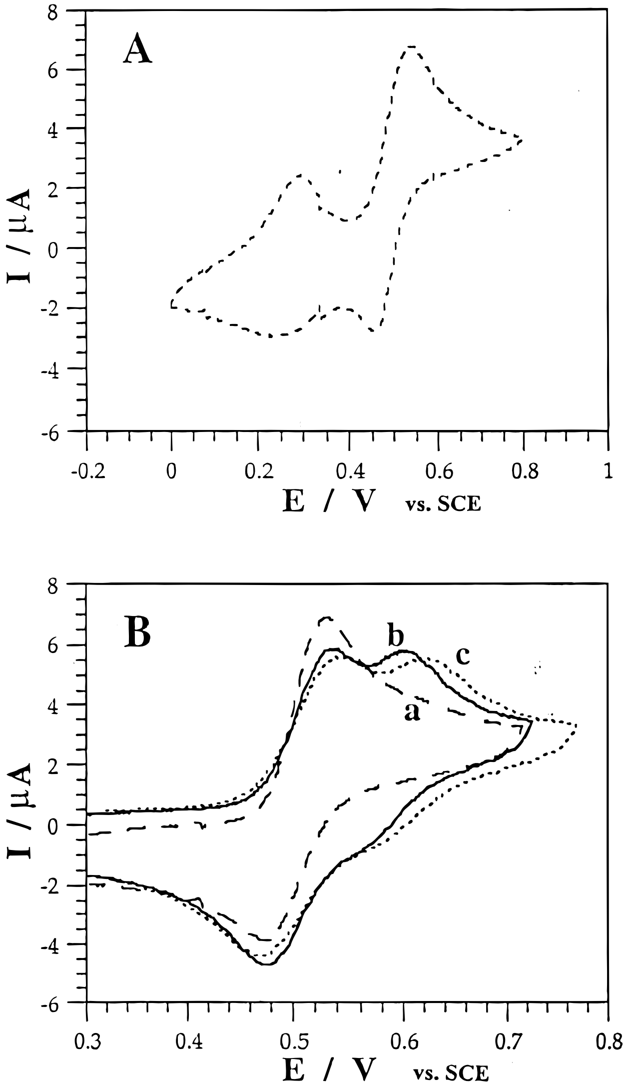


Figure 4. Cyclic voltammograms of the copper complexes of (A) **7** and (B) **8** (curve a), **2** (curve b), and **6** (curve c) using an Au electrode. All complexes were measured in background of 50 mM TBATFB in DMF under argon at ambient temperature. Potential scan rate was 20 mV s^{-1}. The potentials are given vs SCE.

---

(19) For a discussion on the different MS techniques used for helicate characterization see ref 9b pp 2047−2050 and references therein.

(20) (a) Gisselbrecht, J.-P.; Gross, M.; Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R.; Piccini-Leopardi, C.; Arrieta, J.-M.; Germain, G.; Van Meerrssche, M. *Nouv. J. Chim.* **1984**, *8*, 661. (b) Potts, K. T.; Keshevaz-K, M.; Tham, F. S.; Arbuna, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4450. (c) Boulas, P. L.; Gomez-Kaifer, M.; Echegoyen, L. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 216 and references therein. (d) Hanan, G. S.; Volkmer, D.; Schubert, U. S.; Lehn, J.-M.; Baum, G., Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1842.

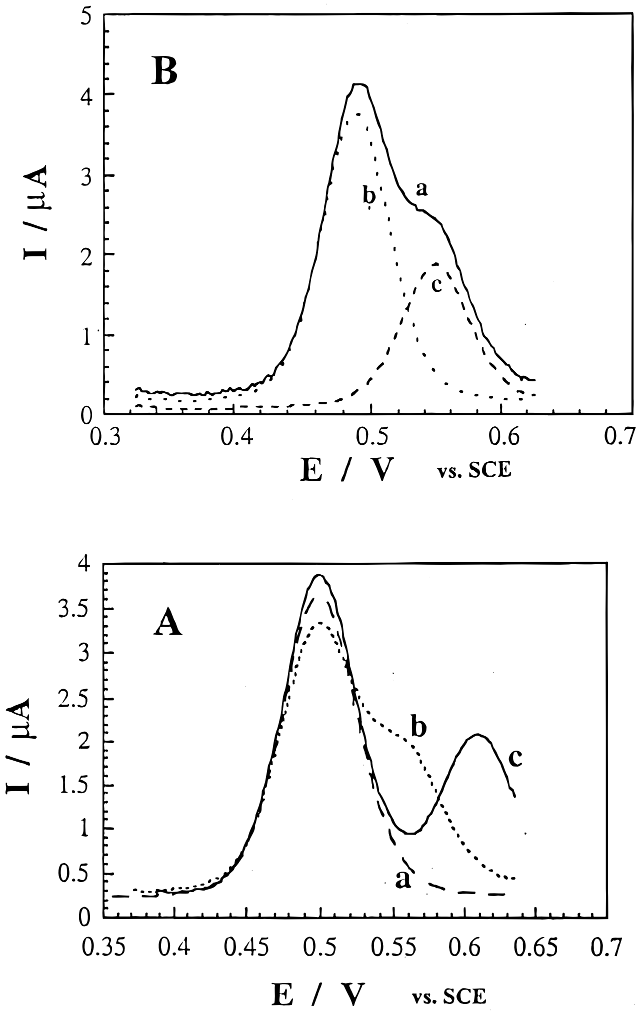


Figure 5. Differential pulse voltammetry of the copper complexes (A) **8** (curve a), **2** (curve b), and **6** (curve c) using an Au electrode under argon at ambient temperature. All complexes were measured in a background of 50 mM TBATFB in DMF. Potential scan rate was 20 mV s^{-1}. The potentials are given vs SCE. (B) Experimental differential pulse voltammogram of the copper complex of **2** (curve a) and its computer deconvolution (curves b and c).

Table 2. Formal Potentials, E^0, and Potential Shift, ΔE^0, of the Different Copper Complexes (2, 6, 7 and 8), as Obtained from Cyclic Voltammetry and Differential Pulse Voltammetry[a]

system	$E°$ (V)		$\Delta E°$ (V)[b]		$\Delta\Delta E°$[d] (mV)	(K_{cent}/K_{bip})[e]
	$E°_{bip}$	$E°_{cent}$	$\Delta E°_{bip}$	$\Delta E°_{cent.}$		
2	0.497[c]	0.555[c]	0.247	0.305	−58	10
6	0.497	0.615	0.247	0.365	−118	100
7	0.497	0.263	0.247	0.013	+234	10^{-4}
8	0.497		0.247			

[a] All data are reported vs SCE electrode. [b] Relative to the Cu^+/Cu^{2+} process in Cu_2SO_4 under the same experimental conditions: Ambient temperature/ 50 mM TBATFB in DMF/ scan rate of 20 mV s^{-1}. [c] Based on computer deconvalution of the differential pulse voltammogram (see Figure 5B). [d] $\Delta\Delta E° = \Delta E°_{bip} - \Delta E°_{cent}$. [e] Calculated according to eq 1 (see ref 23a).

example, in the Co^{2+} 2 × 2 grid prepared by Lehn et al. a significant interaction between the cation was found by cyclic voltammetry although the $Co^{2+}-Co^{2+}$ distances were about 6.5 Å.[20d]

The 2:1 ratios of the quasireversible redox waves of the copper complexes of **6**, **2**, and **7** and the observation of only one redox wave for the copper complexes of **8** support the formation of $[(\mathbf{L})_2Cu_3]^{3+}$-type complexes in the case of **7**, indicating that the bithiophene units participate in the complexation. This result is surprising since it is known that thiophene is a very poor ligand for Cu^+ [21] and since no complexation was observed between 5,5′-dimethyl-2,2′-bithiophene (**15**) and Cu^+ under the reaction conditions used for the preparation of double-stranded complexes of **7**. There is, however, only a small difference between $E°$ for the Cu^+/Cu^{2+} redox process attributed to the copper cation bound to the bithiophenes as compared to free copper (Table 2). This indicates that the interaction between the bithiophenes and the copper cation is weak. The above results suggest that, although isolated bithiophene units do not bind copper, bithiophene units that are part of a larger preorganized ligand can bind, although weakly, the copper(I) cation. In other words, one can conclude that the bithiophene units in ligands **7** are predisposed toward copper complexation. This represents, in our opinion, an additional example of the well-known preorganization principle.[22]

It is interesting to note that the change in the formal potential of the redox wave for the Cu^+/Cu^{2+} process upon complex formation ($\Delta E°$, Table 2) reflects very nicely the binding affinity of the different binding sites toward the copper cation. From these data it is clear that the binding affinity of the central binding unit in ligand **2** is larger than that of the same unit when placed at the edges of the ligand. One can use the difference between the redox potentials of the off-centered bipyridine units ($\Delta E°_{bip}$) and that of the central unit ($\Delta E°_{cent}$), $\Delta(\Delta E°)$, to obtain the relative association constant of these sites to copper(I). This can be calculated from eq 1:[23a]

$$\Delta(\Delta E°) = \Delta E°_{bip} - \Delta E°_{cent} = (RT/nF)\ln(K_{bip}/K_{cent}) \tag{1}$$

The value of RT/nF is 25.67 mV, and K_{bip} and K_{cent} are the association constants of the off-centered bipyridine unit and the central unit, respectively. From the values of $\Delta(\Delta E°)$ we find that the ratios of K_{cent}/K_{bip} are ca. 10^2, 10^1, and 10^{-4} for systems **6**, **2**, and **7**, respectively. This means that, in this type of helicates, the association constant of copper(I) to the central $(\text{bipyridine})_2$ site is around 10 times higher than that of the off-centered $(\text{bipyridine})_2$ site. In addition, we found that the association constant of copper(I) to the central $(\text{phenanthroline})_2$ site is 10 times that of the central $(\text{bipyridine})_2$ site and 10^6 times that of the central $(\text{bithiophene})_2$ site. These results are expected, as it is known that 1,10-phenanthroline is the strongest complexant in this series.[23b]

Self-Recognition in Self-Assembly. Self-assembly provides the opportunity of constructing large supramolecular entities by mixing simple building units in a modular way. It can therefore be used for the construction of nanoscale molecular structures.[24] To improve the capabilities of supramolecular engineering, it is impor-

---

(21) (a) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1975; Vol. 2, p 236. (b) Cotton, F. A.; Wilkenson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 533. Recently, the formation of a ruthenium complex containing a N,N,S-bound Ru^{2+} was reporeted. See: Constable, E. C.; Dunne, S. J.; Rees, D. G. F.; Schmitt, C. X. *J. Chem. Soc., Chem. Commun.* **1996**, 169.

(22) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 9.

(23) (a) Please note that eq 1 is a derivation of eq 12 found in: Heyrovsky, J.; Kuta, J. In *Principles of Polarography*; Academic Press: New York, 1966; p 150. (b) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1975; Vol. 2, p 252.

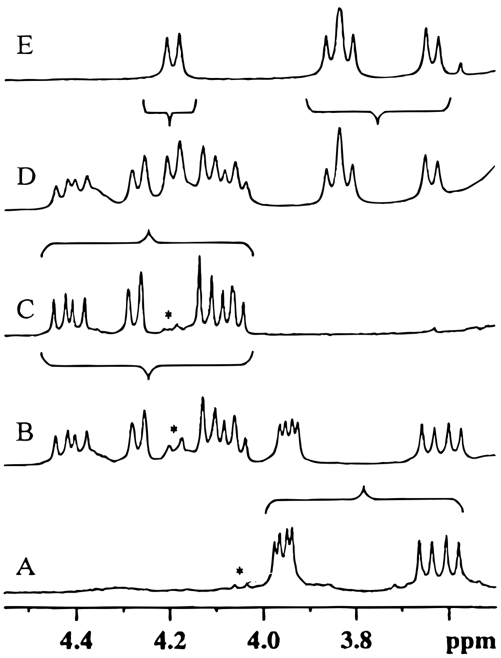


Figure 6. 500 MHz ^{1}H NMR spectra in DMSO-d_6 at 25 °C of the bridges region of the copper complexes obtained from a starting solution of (A) **2** , (B) a mixture of **2** and **7**, (C) **7**, (D) a mixture of **7** and **6**, and (E) **6**. * indicates inpurities.

tant to better understand the basic principles that control the self-recognition and self-assembly processes. For example, a better understanding of the notion of self-recognition in self-assembly processes should, in principle, increase our ability to construct well-defined supramolecular systems from mixtures of ligands rather than from a unique purified material. This should increase the future ability to prepare new functional nanoscale supramolecular assemblies.[14a]

As ligands **2**, **6**, **7**, and **8** all formed double-stranded homoleptic complexes, we thought to use these compounds to challenge the notion of self-recognition. This has been accomplished by performing a series of competition experiments in which the starting solutions consist of different mixtures of the above ligands. Figure 6 shows the ^{1}H NMR spectra of the bridges regions of the homoleptic double-stranded copper complexes of **2**, **7**, and **6** (Figure 6A,C,E, respectively) along with that of the copper complexes obtained from the mixtures of **2**/**7** and **6**/**7** (Figure 6B,D, respectively). Interestingly, we find that when mixtures of **2** and **7** or **6** and **7** were the starting composite solutions, no heteroleptic double-stranded complexes were detected. In those two cases, the ^{1}H NMR spectra obtained (Figure 6B,D) are each a clear superposition of the ^{1}H NMR spectra of the two homoleptic complexes. No extra peaks are observed in those 500 MHz ^{1}H NMR spectra. In contrast, when the starting mixture contained ligands **2** and **6** the ^{1}H NMR spectra did show additional peaks in addition to the peaks attributed to the homoleptic double-stranded complexes of **2** and **6** (compare Figure 7B with Figure 7A,C). These extra peaks were attributed to the hetroleptic double-stranded copper complexes of the $[\mathbf{6}/\mathbf{2}\mathrm{Cu}_3]^{3+}$ type. The NMR results are corroborated by the FAB-MS. Indeed, the FAB-MS spectrum of the sample shown in Figure 7B contained three peaks with *m*/*z* of 1641, 1665, and 1689, which correspond to $[(\mathbf{2})_2\mathrm{Cu}_3(\mathrm{PF}_6)_2]^+$, $[(\mathbf{2}/\mathbf{6})\mathrm{Cu}_3(\mathrm{PF}_6)_2]^+$, and $[(\mathbf{6})_2\mathrm{Cu}_3(\mathrm{PF}_6)_2]^+$, respectively. Figure 8 shows the high-field peaks in the aromatic regions of the ^{1}H NMR spectra of the copper complexes obtained from different mixtures of **2** and **6** in which the **2**/**6** ratios were ~1/1.25, ~1/1.5, and ~1/0.2 (Figure 8A,B,C, respectively). Analysis shows that helicate distributions are very close to those expected from simple statistics.

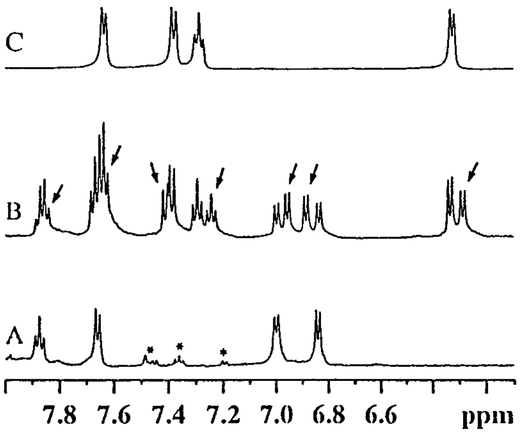


Figure 7. 500 MHz ^{1}H NMR spectra in DMSO-d_6 at 25 °C of the high-field part of the aromatic region the copper helicates obtained from a starting solution of (A) **2**, (B) a mixture of **2** and **6**, and (C) **6**. The arrows indicate signals attributed to the heteroleptic helicate $[(\mathbf{2}/\mathbf{6})\mathrm{Cu}_3]^{3+}$; * indicates inpurities.

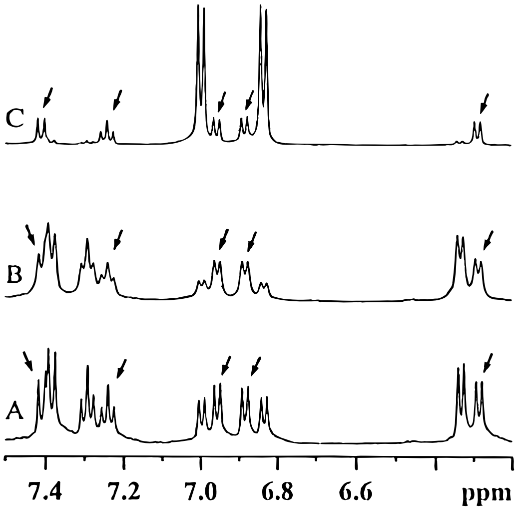


Figure 8. 500 MHz ^{1}H NMR spectra in DMSO-d_6 at 25 °C of the high-field part of the aromatic region of the copper helicates obtained from mixtures of **2**/**6** with the following ratios: (A) ~1:1.25, (B) ~1:1.5, and (C) ~1:0.2. The arrows indicate signals attributed to the heteroleptic helicate $[(\mathbf{2}/\mathbf{6})\mathrm{Cu}_3]^{3+}$.

When helicates were prepared from mixtures of these ligands, our results show examples in which only homoleptic double-stranded helicates were formed and examples in which both homoleptic and heteroleptic could be detected. At first glance, it seems that our results contradict those obtained by Lehn et al,.[14a] who reported the formation of only homoleptic helicates from mixtures of oligo(2,2′-bipyridine). However, Lehn's systems (see Scheme 1) differed in several structural parameters such as their length and number of binding sites. Consequently both the principle of "maximal occupancy" and the entropy factor, which favors the formation of the largest number of product species, could preclude the

---

(24) Stang, P. J.; Fechtenkotter, A.; Olenyuk, B. *J. Chem. Soc., Dalton Trans.* **1998**, 1707.

formation of the heterodimers in these systems.[13] In addition, it has been commented there[14a] that the methyls in these systems could bring about steric interactions when, for example, two strands of **BP2** approach a **BP4** strand. However, in systems **6**, **2**, and **7** the only significant difference is the nature of the binding sites. Both the number and the total length of these ligands are very similar. Consequently, there are no additional steric interactions when a heteroleptic double-stranded helicate is formed between **7** and **2** or **6**. Moreover, the entropic factor[13] for systems **2**, **6**, and **7** is the same. If one accepts the formation of an $[(\mathbf{L})_2\mathrm{Cu}_3]^{3+}$-type complex for **7**, the "maximal occupancy" principle would predict no stability differences between the homoleptic and the heteroleptic complexes, contrary to the experimental results. Therefore, this complete self-discrimination seems strange at first glance, since it implies that the central copper cation "prefers" to be associated to two weak 2,2′-bithiophene ligands rather than to one weak 2,2′-bithiophene and one strong ligand (the 2,2′-bipyridine or 1,10-phenanthroline binding sites). It should be noted that since the copper helicates are kinetically labile, helicates distribution reflects the relative thermodynamic stability of these helicates.[7m]

The fact that no heteroleptic complexes such as $[(\mathbf{2}/\mathbf{7})\mathrm{Cu}_3]^{3+}$ and $[(\mathbf{6}/\mathbf{7})\mathrm{Cu}_3]^{3+}$ are formed may be attributted also to the geometrical differences imposed by the central 5,5′-bithiophene unit as compared to the central 2,2′-bipyridine and 1,10-phenanthroline units. It should be noted, however, that the "simbiotic effect",[25] which is probably less important than the geometrical differences, also will not favor the formation of heteroleptic double-stranded complexes between ligands **7** and **2** or between ligands **7** and **6**. The geometrical factors imposed by the central units, the difference in the binding affinity, and the simbiotic effect all imply that the heteroleptic double-stranded complexes will be less favorable. The results indeed show that, when there are large differences in the binding affinities of the different binding sites, like in the **6**/**7** or the **2**/**7** pairs, no heterodimer can be detected. In contrast, for the **6**/**2** pair where the binding affinities are similar, as are all the other characteristics of the ligands, the product distribution follows statistical expectations. In other words, one can say that ligands **6** and **2** are not "sufficiently instructed" to avoid cross reaction between these ligands, and therefore, an heteroleptic helicate is also formed. Heteroleptic complexes were recently found also in trinuclear copper helicates that differed only in their spacers.[14b] Caulder and Raymond have also shown complete self-recognition in self-assembly of gallium(III) bis-catecholamine triple helices.[14c] However, there rigid ligands of very different length were used so the result is not very surprising. Contrary to that, very recently Albrecht et al. have demonstrated that alkyl-bridged bis(catechol) titanium helicates that differ by one carbon atom in their bridges did form homoleptic and heteroleptic helicates.[14d] It seems therefore that more work will be needed to increase our ability to obtain specific supramolecular systems from a large number of similar ligands.

Conclusions

Ligands **2**,[7a] **6**, **7**, and **8** were shown to self-assemble into double-stranded complexes upon addition of Cu^+. In the case of **6**, like in the case of **2**, a single helicate of the $[(\mathbf{L})_2\mathrm{Cu}_3]^{3+}$ type is formed, while in the cases of **7** and **8** mixtures of double-stranded complexes are formed. Electrochemistry corroborates the formation of $[(\mathbf{L})_2\mathrm{Cu}_3]^{3+}$ type complexes even in the case of **7**. In addition, from the differences in the potential shifts ($\Delta E°$, and $\Delta\Delta E°$), it can be concluded that the association constants to copper(I) of the central 1,10-phenanthroline site is 10 times that of a central 2,2′-bipyridine site and 10^6 times that of the central 2,2′-bithiophene site.

From the complexation experiments performed with mixtures of ligands **2**, **6**, and **7** examples of self-and non-self-recognition systems were observed. The **2**/**7** and **6**/**7** pairs show complete self-recognition, and no heteroleptic complexes could be detected by NMR spectroscopy. However, in the case of the **2**/**6** pair the resulting complex distributions seems to follow simple statistical consideration. It may be concluded that ligands **2** and **6** are not "sufficiently self-instructed" to preclude the formation of heteroleptic helicates.

Experimental Section

Compounds **9**,[27] **10**−**12**,[7a] **14**,[29] and **15**[28] were prepared according to previously published procedures and gave the correct melting points and ^{1}H and ^{13}C NMR spectra.

5,5′-Dibromomethyl-2,2′-bithiophene (13). The previous procedure was modified.[26] A suspension of NBS (2.77 g, 15.6 mmol) in $\mathrm{CCl_4}$ (60 mL) was refluxed for 4 min. Then heating was removed, and 45 mg of azo-bis-isobutylnitrile was added to the solution. After an additional 3 min, a solution of 5,5′-dimethyl-2,2′-bithiophene (**15**)[28] (1.39 g, 7.8 mmol) in 20 mL of $\mathrm{CCl_4}$ was added, and the reaction mixture was gently heated back to reflux. When an exothermic reaction began the external heating was removed. The reaction mixture was stirred for additional 20 min, the last 10 under gentle external heating. The reaction mixture was cooled to 40 °C and filtered. The filtrate was cooled further, and **13** (1.69 g, 59%) was collected by filtration and washed with cold ether. Compound **13** was obtained as flat almost transparent crystals, which were found to decompose within hours. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): 7.02 (d, 3.7, 2H), 6.98 (d, 3.7, 2H), 4.71 (s, 4H). ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$) δ: 139.9, 138.6, 128.9, 123.9, 26.8.

Ligand Synthesis. 2,9-Bis[(6-methyl-2,2′-bipyridin-6′-yl)methylenoxymethylenyl]-1,10-phenanthroline (6). Compound **9**[27] (364 mg, 1.5 mmol) was dissolved in dry THF (30 mL) under inert atmosphere and cooled to −70 °C. Butyllithium 1.6 M (2.1 mL, 3.3 mmol) was added dropwise to the stirring solution of **9** at −70 °C. The colored reaction mixture was stirred for additional 0.5 h and then allowed to reach room temperature. At this point, compound **10**[7a] (837 mg, 3.2 mmol) was added in one portion, and the reaction mixture was refluxed for 5 days. The crude product was filtered and washed with THF (~20 mL) and then with warm chloroform. The obtained solids was dissolved in 5 mL of methanol from which ligand **6** precipitated. After drying (~50 °C, 20 mbar), 130 mg of white powder of **6** was obtained. Evaporation of the filtrates followed by recrystallization from methanol or chromatography [alumina, dichloromethane/MeOH (100:0 to 99:1)] gave an additional 183 mg of white powder having a mp of 103 °C (total yield ~34%). ^{1}H NMR (500 MHz, DMSO-d_6): 8.56 (d, 8.5, H-16, 2H), 8.33 (d, 7.6, H-8, 2H), 8.20 (d, 7.7, H-5, 2H), 8.02, 8.01, 8.00 (s,t,d, 7.5, 8.5, H-19, H-9, H-15, 6H), 7.82 (t, 7.7, H-4, 2H), 7.70 (d, 7.6, H-10, 2H), 7.32 (d, 7.7, H-3, 2H), 5.12 (s, H-13, 4H), 4.92 (s, H-12, 4H), 2.59 (s, H-1, 6H). ^{13}C NMR (125 MHz,

---

[25] Jensen, W. B. *The Lewis Acid−Base Concepts, An Overview*; John Wiley & Sons: New York, 1976; pp 305−309.

[26] Gronowitz, S.; Pedaja, P. *Tetrahedron* **1978**, *34*, 587.

[27] Chandler, C. J.; Deady, L. W.; Reiss, J. A. *J. Heterocycl. Chem.* **1981**, *18*, 599.

[28] Compound **15** was synthesized by coupling 2-bromo-5-methylthiophene based on the procedure of: Deschamps, E.; Ricard, E.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1158. Mp: 63 °C (lit. mp 67 °C; see: Steinkopf, W.; Leitsmann, R.; Muller, A. H.; Wilhelm, H. *Ann.* **1939**, *541*, 271).

[29] Wenner, W. *J. Org. Chem.* **1952**, *17*, 523.

DMSO-d_6): 158.5, 157.6, 157.5, 154.8, 154.4, 144.6, 137.8 (C-9), 137.3 (C-4), 137.0 (C-16), 127.8, 126.2 (C-19), 123.5 (C-3), 121.7 (C-10), 121.0 (C-15), 119.2 (C-8), 117.6 (C-5), 73.7 (C-13), 73.4 (C-12), 24.2 (C-1). FAB-MS (DMSO, NBA): 649 (**6**K$^+$, 1.7), 627 (**6**Na$^+$, 6), 611 (**6**Li$^+$, 14), 605 (**6**H$^+$, 23).

6″,6‴-Bis[(6-methyl-2,2′-bipyridin-6′-yl)methyleneoxymethylen-yl]-2″,2‴-bipyridine (2). Compound **2**, known also as BP$_3$, was prepared according to the literature [7a] and gave the expected ^{1}H spectra. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): 8.32 (d, 7.7, H-8,17, 4H), 8.19 (d, 7.7, H-5, 2H), 7.83 (t, 7.7, H-9, 16, 4H), 7.68 (t, 7.7, H-4, 2H), 7.54 (d,7.7, H-10 or H-15, 2H), 7.52 (d, 7.7, H-10 or H-15, 2H), 7.16 (d, 7.7, H-3, 2H), 4.85 (s, H-12 and H-13, 8H), 2.58 (s, H-1, 6H). Mp: 232−233 °C (lit.[7a] mp 227−229 °C).

5,5′-Bis[(6-methyl,-2,2′-bipyridin-6′yl)methyleneoxymethylen-yl]-2,2′-bithiophene (7). Compound **11** [7a] (1.20 g, 6.0 mmol) was dissolved in dry THF (100 mL) under inert atmosphere and cooled to −70 °C. Butyllithium (4 mL, 6.4 mmol) was added dropwise, and the reaction mixture became deep brown. The reaction mixture was warmed gradually to room temperature, freshly prepared **13** (850 mg, 2.4 mmol) was added, and the reaction mixture was then refluxed for 18 h. The solvent was evaporated, and impurities and unreacted **11** were removed by trituration with MeOH yielding 0.7 g of a red solid (50%). Ligand **7** was crystallized from ethanol giving light orange-yellow powder. Mp: 140−141 °C. ^{1}H NMR (500 MHz DMSO-d_6): 8.32 (d, 7.9, H-8, 2H), 8.20 (d, 7.7, H-5, 2H), 7.99 (t, 7.9, H-9, 2H), 7.84 (t, 7.7, H-4, 2H), 7.53 (d, 7.9, H-10, 2H), 7.33 (d, 7.7, H-3, 2H), 7.22 (d, 3.6, H-16, 2H), 7.11 (d, 3.6, H-15, 2H), 4.85 (s, H-13, 4H), 4.75 (s, H-12, 4H), 2.59 (s, H-1, 6H); ^{13}C NMR (125 MHz DMSO-d_6): 157.5, 154.8, 154.4, 140.2, 137.8 (C-9), 137.4 (C-4), 136.7, 127.8 (C-15), 123.5 (C-3), 123.4 (C-16), 121.5 (C-10), 119.2 (C-8), 117.6 (C-5), 72.3 (C-12), 66.6 (C-13), 31.3 (C-1).

6,6′-Bis[(6-methyl-2,2′-bipyridin-6′-yl)methyleneoxymethylen-yl]-2,2′-biphenyl (8). Compound **11**[7a] (690 mg, 3.45 mmol) was dissolved in dry THF (30 mL) under inert atmosphere and cooled to −65 °C. BuLi 1.6 M (2.2 mL, 3.5 mmol) was added dropwise to the stirring solution, and the temperature was allowed to reach −20 °C over a period of 1 h. Compound **14** [29] (558 mg, 3.64 mmol) dissolved in THF (10 mL) was added dropwise, and then the temperature was allowed to reach 20 °C over a period of 30 min. The reaction mixture was then refluxed gently for 48 h and then cooled to rt and filtered, and the filtrate was evaporated giving a foamy solid. The crude product was recrystalized from methanol to give 565 mg (62%) of pale yellow powder. Pure white powdered **8** could be obtained by additional recrystalliztion from methanol. Mp: 110−112 °C. ^{1}H NMR (500 MHz, DMSO-d_6): 8.30 (d, 7.6, H-8, 2H), 8.17 (d, 7.7, H-5, 2H), 7.97 (t, 7.6, H-9, 2H), 7.80 (t, 7.7, H-4, 2H), 7,72 (s, H-19, 2H), 7.64 (d, 7.6, H-17 or H-15, 2H), 7.56 (d, 7.6, H-10, 2H), 7.51 (t, 7.6, H-16, 2H), 7.45 (d, 7.6, H-17 or H-15, 2H), 7.32 (d, 7.7, H-3, 2H), 4.76 (s, H-12, H-13, 8H), 2.62 (s, H-1, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): 157.9, 157.6, 154.8, 154.5, 140.2, 139.0, 137.9 (C-9), 137.4 (C-4), 129.1 (C-16), 126.9 (C-15), 126.0 (C-17 and 19), 123.6 (C-3), 121.6 (C-10), 119.2 (C-8), 117.6 (C-5), 72.7 and 71.9 (C-12, C-13), 24.2 (C-1). FAB-MS (MeOH): 579 (M$^+$, 100).

Preparation and Characterization of Homoleptic Complexes: [(6)$_2$Cu$_3$(PF$_6$)$_3$]. A solution of Cu(CH$_3$CN)$_4$PF$_6$[16] (46 mg, 123 μmol) in acetonitrile (2 mL) was added to a suspension of **1** (50 mg, 83 μmol) in acetonitrile (1 mL). The red solution obtained was stirred overnight. The solution was filtered over Celite through a Pasteur pipet and concentrated by evaporation. Diethyl ether was added until the complex precipitated completely. The solvent was removed by decantation, and the product was washed successively with diethyl ether/dichloromethane solution (9:1), diethyl ether/acetonitrile solution (95:5), and diethyl ether. Finally, the product was filtered and dried (50 °C, 25 mbar) affording 66 mg of red powder (yield 87%). The product was recrystallized from an acetonitrile solution by slow diffusion of diethyl ether to give fine red needles having a mp of 252 °C (285 °C dec). These crystals were found to be suitable for X-ray crystallography.[7m] ^{1}H NMR (500 MHz, DMSO-d_6): 8.70 (d, 8.1, H-16, 4H), 8.50 (d, 7.7, H-5, 4H), 8.50 (s, H-19, 4H), 8.21 (t, 7.7, H-4, 4H), 8.14 (d, 7.7, H-8, 4H), 7.64 (d, 7.7, H-3, 4H), 7.38 (d, 8.1, H-15, 4H), 7.29 (t, 7.7, H-9, 4H), 6.33 (d, 7.7, H-10, 4H), 4.20:3.82 (AB, 13.4, H-13−13′, 8H), 3.86:3.64 (AB, 13.4, H-12,12′, 8H), 2.10 (s, H-1, 12H). ^{13}C NMR (125 MHz, DMSO-d_6): 156.5, 154.9, 154.1, 150.7, 150.0, 141.4, 138.4 (C-4), 137.8 (C-16), 137.4 (C-9), 128.2, 126.9 (C-19), 126.0 (C-3), 123.4 (C-15), 122.6 (C-10), 120.6 (C-8), 119.8 (C-5), 71.5 (C-13), 70.8 (C-12), 24.6 (C-1). FAB-MS (DMSO, NBA): 1689 ([(**6**)$_2$Cu$_3$(PF$_6$)$_2$]$^+$, 10), 667 ([**6**Cu]$^+$, 100).

[(2)$_2$Cu$_3$(PF$_6$)$_3$]. This helicate was prepared according to Lehn et al.[7a] and gave the expected ^{1}H and ^{13}C NMR spectra and FAB-MS spectrum. ^{1}H NMR (500 MHz, DMSO-d_6): 8.48, 8.47 (d, d, 7.8, H-8, H-5, 8H), 8.37 (d, 7.9, H-17, 4H), 8.18 (t, 7.8, H-4, 4H), 8.07 (t, 7.8, H-9, 4H), 7.84 (t, 7.9, H-16, 4H), 7.63 (d, 7.8, H-3, 4H), 6.97 (d, 7.8, H-10, 4H), 6.81 (d, 7.9, H-15, 4H), 3.94, 3.92 (d, d, 13.4, H-12, H-13, 8H), 3.62, 3.57 (d, d, 13.4, H-13, H-12, 8H), 2.14 (s, H-1, 12H). ^{13}C NMR (125 MHz, DMSO-d_6): 156.4, 154.4, 154.3, 150.9, 150.1, 149.9, 138.6 (C-9), 138.3 (C-4, C-16), 125.9 (C-3), 123.6 (C-10), 123.2 (C-15), 121.4, 119.7 (C-5, 8), 121.1 (C-17), 70.8 (C-12, C-13), 24.6 (C-1). FAB-MS (DMSO, NBA): 1639 ([(**2**)$_2$Cu$_3$(PF$_6$)$_2$]$^+$, 2.3), 643 ([**2**Cu]$^+$, 89). Mp: ~215 °C dec.

[(7)$_2$Cu$_3$(PF$_6$)$_3$]. This complex was obtained by mixing 2 mL of a CH$_2$Cl$_2$ solution of **7** (50 mg, 85 μmol) with 2 mL of a CH$_3$CN solution of Cu(CH$_3$CN)$_4$PF$_6$ (47.3 mg, 127 μmol). The reaction was stirred overnight at room temperature, and then the solvent was evaporated. The obtained red powder was dissolved in a small amount of acetonitrile and precipitated using slow diffusion of diethyl ether. The red precipitate was ground into powder and washed first with ether/acetonitrile solution, then with ether/CH$_2$Cl$_2$ solution, and finally with ether. The red powder was then dried under vacuum at 45 °C.[17] ^{1}H NMR (500 MHz, DMSO-d_6): 8.67 (d, 8.0, 2H), 8.64 (d, 8.0, 2H), 8.62 (d, 8.0, 2H), 8.60 (d, 8.0, 2H), 8.25 (t, 8.0, 2H), 8.20 (m, 6H), 7.67 (d, 8.0, 6H), 7.64 (d, 8.0, 2H), 6.96 (d, 3.5, 2H), 6.91 (d, 3.5, 2H), 6.61 (d, 3.5, 2H), 6.58 (d, 3.5, 2H), 4.43 (d, 13.5, 2H), 4.39 (d, 13.5, 2H), 4.28 (d, 13.5, 4H), 4.12 (d, 13.5, 4H), 4.08 (d, 13.5, 2H), 4.05 (d, 13.5, 2H), 2.16 (s, 12H); ^{13}C NMR (50 MHz, DMSO-d_6): 156.9, 156.1, 151.4, 150.7, 138.8 (C-4), 138.8 (C-9), 138.7, 136.7, 127.5 (C-15), 126.2 (C-3), 123.7 (C-10), 123.1(C-16), 121.4 (C-8), 120.0 (C-5), 71.2 (C-12), 66.5 (C-13), 24.5 (C-1). Anal. Calcd for [Cu$_3$(**7**)$_2$(PF$_6$)$_3$] ($C_{86}H_{60}N_8O_4S_4P_3F_{18}Cu_3$): C, 45.2; H, 3.35; N, 6.20. Found: C, 44.9; H, 3.54; N, 6.21. Mp: 150 °C dec. FAB-MS (DMSO, NBA): 1453 ([(**7**)$_2$Cu$_2$(PF$_6$)]$^+$, 13), 653 ([**7**Cu]$^+$, 69).

[(8)$_2$Cu$_2$(PF$_6$)$_3$]. A solution of Cu(CH$_3$CN)$_4$PF$_6$[16] (31.8 mg, 84.6 μmol) in acetonitrile (2 mL) was added to a solution of **8** (49 mg, 84.6 μmol) in chloroform (2 mL). The red solution was stirred overnight, and then the solvents were evaporated. The complex was redissolved in actonitrile (1 mL), and diethyl ether (~7 mL) was added until a red gummy solid was obtained. The orange solution was decanted, and the procedure was repeated until the material completely solidified. The diethyl ether phase was decanted, and the complex was then washed with diethyl ether/CH$_3$CN (95:5, 2 mL), diethyl ether/CH$_2$Cl$_2$ (9:1, 2 mL), and diethyl ether (2 × 2 mL) and finally refluxed in diethyl ether for 1 h. After drying (30 mbar, 45 °C), 57 mg of red powder was obtained (85%). Mp: 228−230 °C (dec ~245 °C). ^{1}H NMR (500 MHz, DMSO-d_6): 8.56, 8.54 8.50, 8.46 (d, d, d, d, 7.7, 8H), 8.18 and 8.16 (t, t, 7.7, 4H), 8.11 (t, 7.7, 2H), 7.95 (t, 7.7, 2H), 7.65, 7.63 and 7.61 (d, d, d, 7.7, 6H), 7.44, 7.40, and 7.38 (d, d, d, 7.8, 6H), 7.25 (m, 4H), 7.08 (s, 2H), 7.04 (s, 2H), 6.81(d, 7.8, 4H), 4.24−4.07 (m, 16H), 2.14 (s,12H). FAB-MS (DMSO, NBA): 1429 ([(**8**)$_2$Cu$_2$PF$_6$]$^+$, 5), 725 ([**8**H$_2$PF$_6$]$^+$, 24), 641 ([(**8**)Cu]$^+$, 100).

Competition Experiments. A typical procedure for the competition experiment was as follows: a 1:1 mixture of **2** (7.0 mg, 12.05 μmol) and **6** (7.3 mg, 12.05 μmol) was carefully weighed and dissolved in chloroform (6 mL) with the aid of an ultrasonic device and heat. Cu(CH$_3$CN)$_4$PF$_6$[16] (13.5 mg, 36.15 μmol) in acetonitrile (3 mL) was added, at room temperature, to the chloroform solution, and this was stirred overnight. The solvents were evaporated, and the obtained solid was dissolved completely in DMSO-d_6 and analyzed by NMR spectroscopy, without any purification.

JO991469J