JOC Article

Exo- and Endo-Receptors in One. A Novel Class of Supramolecular Structures Housing Transition-Metal-Binding Bi- and Terpyridine Units alongside Lithium Ion-Selective Trispirotetrahydrofuranyl Components

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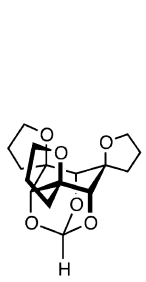
Received December 5, 2003

The preparation of bipyridine and terpyridine ligands covalently linked via acetylenic and alkoxy tethers to rigid inositol orthoformate platforms is described. The constitution of compounds **3**−**6** is such that latent exo- and endo-receptor properties are simultaneously present with specific binding sites for Li^+ and transition-metal ions. The 2-fold complexation in different regions is not dependent on prior molecular association. To gauge this unprecedented property, the model systems **11**−**14** were synthesized and their response to CuCl and $FeCl_2$ probed by UV−vis and MS techniques. In a similar fashion, the ability of **3**−**6** to ligate lithium ions chemoselectively was evaluated by electrospray methods. The introduction of controlled amounts of both types of cation followed, and conversion to insoluble oligomeric products presumed to result from integral incorporation of the different metal ions in the expected fashion was achieved.

The past 30 years have been witness to the development of chemosensors for potential use in many applications, including most notably those of relevance to biology, medicine, materials chemistry, and environmental science.[1] These conceptually fascinating advances have centered around a considerable array of ions ranging from those in the alkali metal family to the many transition-metal candidates. Supramolecular chemistry has emerged as the defining descriptor for the operation of noncovalent interactions in chemical entities where two or more intermolecular forces operate.[2] Current trends in this field suggest that the proper integration of multiple binding sites offers the potential for providing more powerful sensing capabilities than those available to single receptor systems.[3] Although there has been extensive work carried out in connection with multiple cationic binding,[4] little research has been dedicated to a ligand's ability to selectively bind two different metal ions predictably in dissimilar regions of the same molecule.[5] The concept of multiple heterocationic binding *without* cooperativity is of significant interest as it represents a new consideration in metalloreceptor chemistry and has biological relevance, for example, in the co-transport of dissimilar cations across liquid membranes.

We have recently described the synthesis and complexation properties of **1** and its homoditopic dimer **2**.[6] The rigid inositol ortho ester platform is particularly well suited to strong ionophoric interaction with the lithium ion. This property, and particularly the demonstrated preference of **1** for formation of a 2:1 complex with Li^+, is shared by **2**, which readily forms a rodlike ionic polymer upon treatment with $LiClO_4$ or $LiBF_4$. The spirotetrahydrofuran triad is particularly conducive to lithium ion affinity. Smaller ring sizes bind less effectively, presumably because of the differing polarizabilities of the nonbonded electron pairs.[7]



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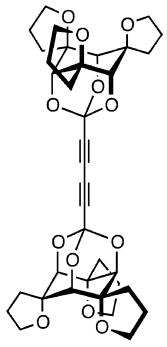

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Herein, we describe synthetic approaches to the four supramolecular ligands **3**−**6** and their behavior regarding co-complexation with Li^+ and several transition-metal ions. One site is the stereodefined and conformationally constrained spiro ether structural arrangement related directly to **1** and **2**. The second locale consists of a bi- or terpyridine building block, for which ample precedent is

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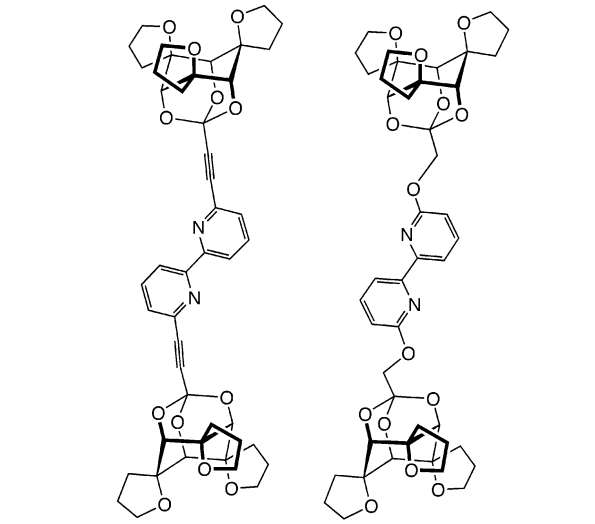
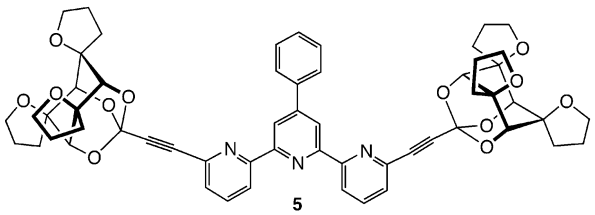
10.1021/jo030373t CCC: $27.50
Published on Web 03/26/2004



3 **4**



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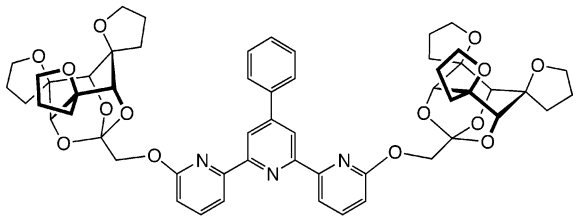
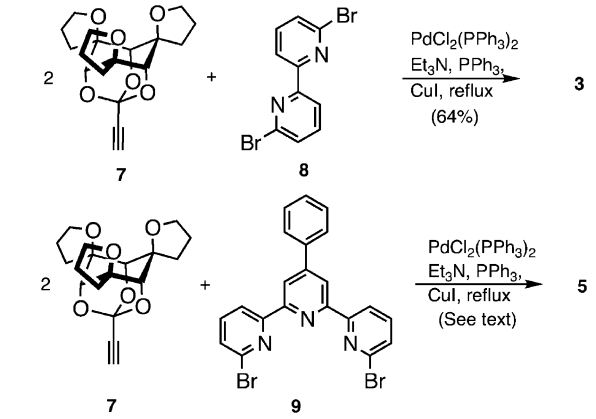


6

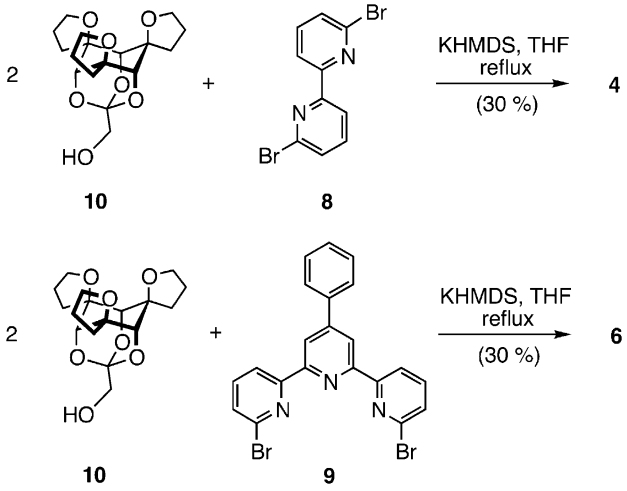
available regarding their heightened capacity for binding to Cu^{+} and Fe^{2+} ions.[8] Complexation of the transition metals occurs selectively on the "inside" portion of the molecule, thereby generating "endoreceptor" characteristics akin to the binding pocket of a protein.[2] When the lithium ion binds specifically to the inositol site, it protrudes out from the ionophoric region, thus giving rise to an "exoreceptor" arrangement.[5–7] The two distinctive regions of molecular association are interlinked by acetylenic or ether bridges.

The present investigation provides a unique look into heterometallic-specific binding under conditions where the binding of one metal ion is not necessary to achieve the second binding.[9] Our analysis of the chemical events in operation is derived from mass spectroscopy and UV–vis analysis of simplified versions of the anticipated supramolecular structures.[10]

SCHEME 1



SCHEME 2



Results and Discussion

The synthesis of **3**–**6** was achieved by two reaction types. Initial attempts at effecting the Sonagashira coupling of the previously reported alkyne **7**[6] with the dibromides **8**[11] and **9**[12] were uniformly unsuccessful at first. Since parallel palladium-catalyzed reactions[13] involving phenylacetylene proceeded smoothly (see below), the major complication was obviously derived from **7**. Ultimately, the Vasella protocol,[14] which involves the coaddition of triphenylphosphine, triethylamine, copper(I) iodide, and the dichloropalladium bistriphenylphosphine complex, gave indication of very modest levels of coupling (Scheme 1). Further improvisation was necessary to achieve reasonable yields of **3** and **5**. These reactions must be performed at reflux temperature under a septum-capped condenser while blanketed with N_2 and with total exclusion of oxygen. Under these conditions, **9** is transformed into **5** (22%) and the monosubstitution product (47%). Alternative heating in a sealed tube resulted in no conversion to product and limited recovery of **7**. Although both **7** and the dibromide of choice are essentially insoluble in triethylamine, decomposition ensues

(5) (a) Kocian, O.; Mortimer, R. J.; Beer, P. D. *Tetrahedron Lett.* **1990**, *31*, 5069. (b) Nabeshima, T.; Inaba, T.; Furukawa, N.; Hosoya, T.; Yano, Y. *Inorg. Chem.* **1993**, *32*, 1407. (c) Kobuke, Y.; Sumida, Y.; Hayashi, M.; Ogoshi, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1496. (d) Nabeshima, T.; Inaba, T.; Furukawa, N. *Tetrahedron Lett.* **1987**, *28*, 6211. (e) Habata, Y.; Bradshaw, J. S.; Zhang, X. X.; Izatt, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 7145.

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(8) (a) Constable, E. C. *Adv. Inorg. Chem.* **1989**, *34*, 1. (b) Sleiman, H.; Baxter, P.; Lehn, J.-M.; Rissanen, K. *J. Chem. Soc., Chem. Commun.* **1995**, 715. (c) Harriman, A.; Ziessel, R.; Moutet, J.-C.; Saint-Amon, E. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1593.

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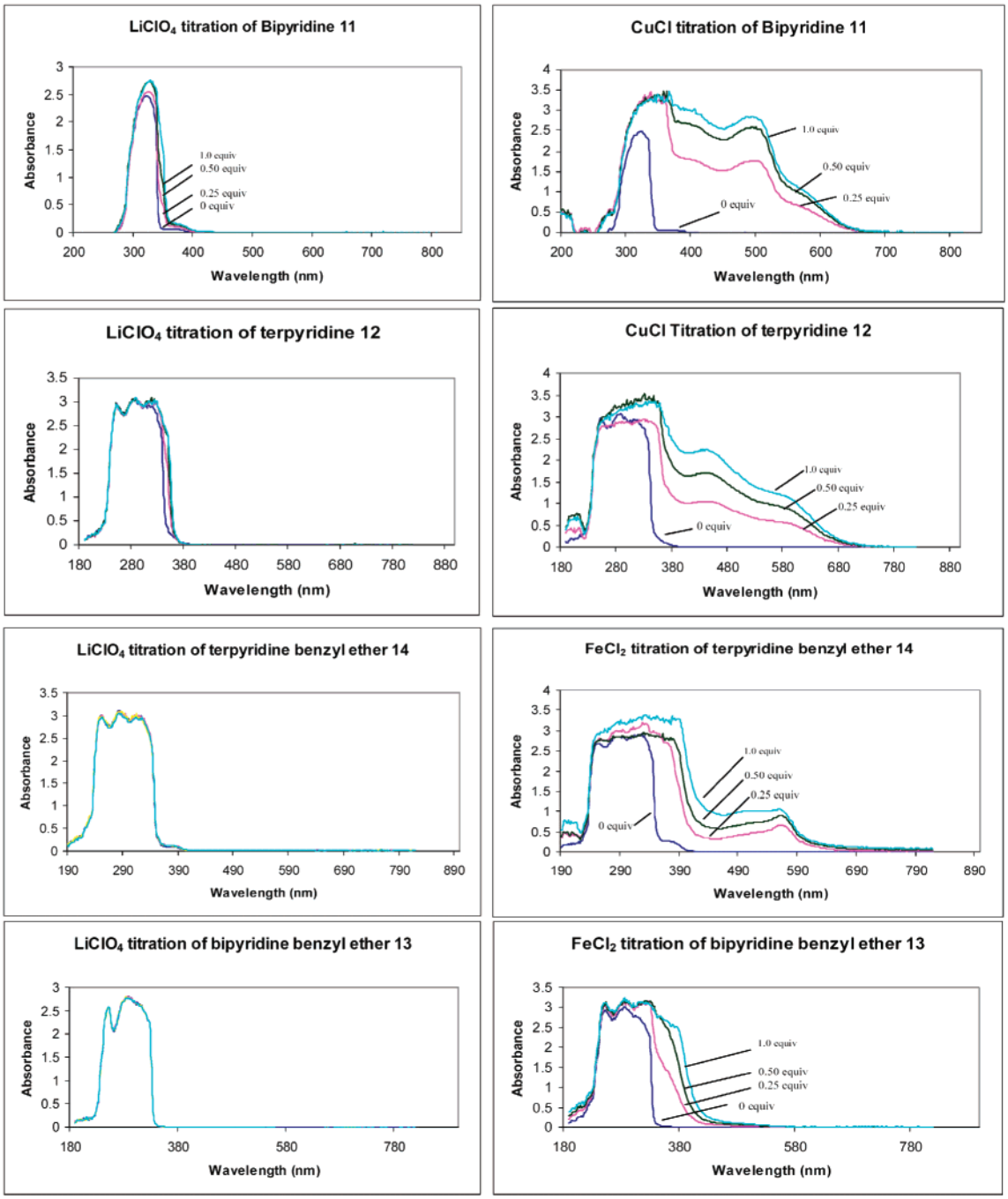

FIGURE 1. Titration curves for **11**, **13**, and **14** as monitored by UV−vis spectroscopy.

if a cosolvent such as acetonitrile or dimethylformamide is added. Finally, during the course of the aqueous workup, it is imperative that potassium cyanide be introduced to free the product from its complex with cuprous ion.

Nucleophilic aromatic substitution involving the same pair of dibromides and the potassium alkoxide of carbinol **10**[6] gave **4** and **6** (Scheme 2). The use of Li^+ as a counterion was avoided so as to skirt complexation of the spiro ether oxygens and loss of product upon aqueous workup. Despite these precautions, the yields of **4** and **6** approximated only 30%. No means for enhancing the efficiency of these conversions was found.

Although the four targeted compounds were now in hand, each was available only in milligram quantities. For this reason, simpler prototypes were also secured for use in probing the site selectivity behavior of those metal ions selected for investigation. Although we viewed as intuitive the fact that lithium ions would exhibit little or no tendency to bind to the available bipyridine or terpyridine endoreceptor subunits, examples of such binding to bipyridines accompanied by large shifts in the UV−vis spectrum have been reported.[15] Consequently,

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(11) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organomet. Chem.* **1973**, *56*, 53.
(12) Constable, E. C.; Lewis, J. *Polyhedron* **1982**, *1*, 303.
(13) Ziessel, R. *J. Org. Chem.* **1996**, *61*, 6535.

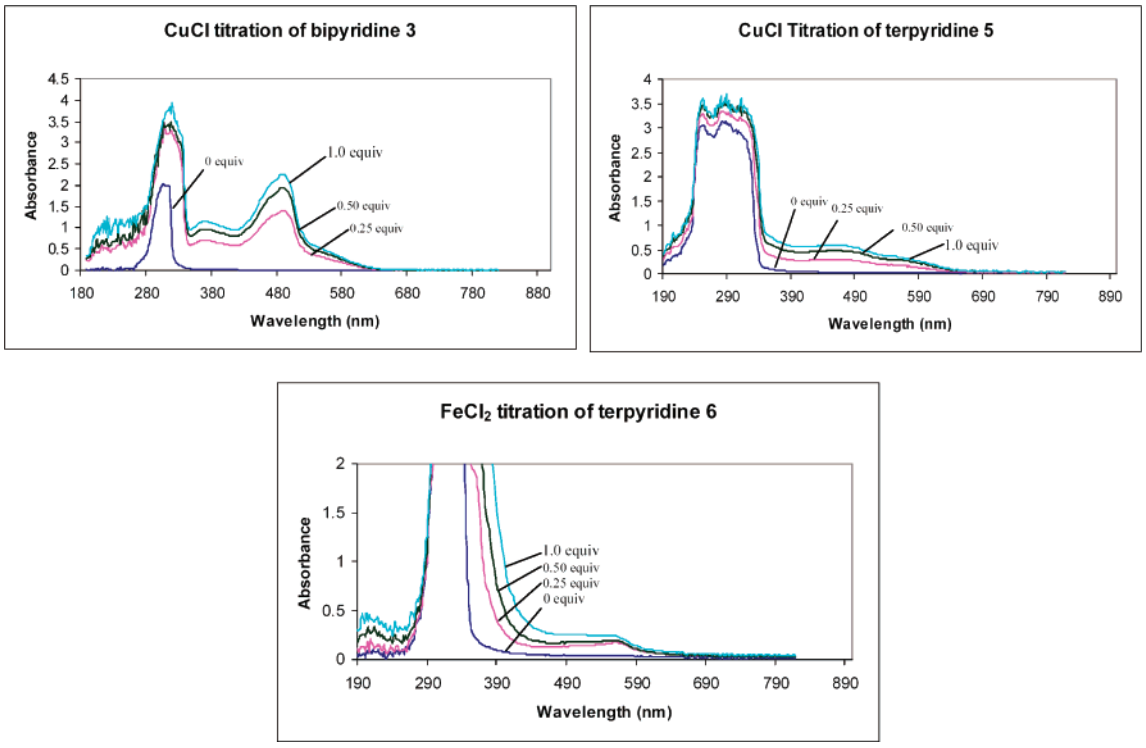
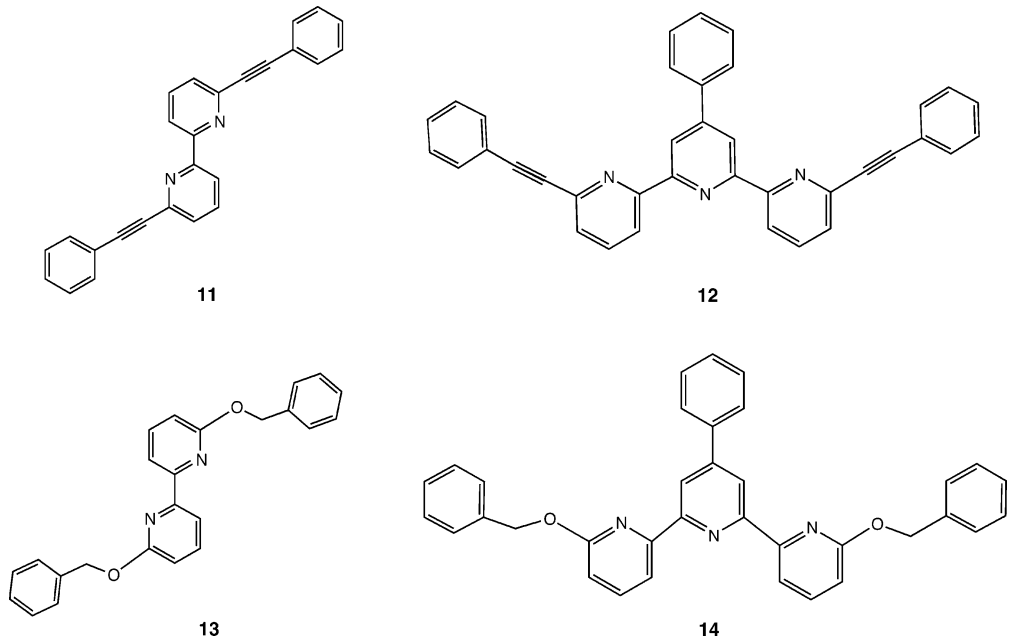


FIGURE 2. Titration curves for **3**, **5**, and **6** as monitored by UV−vis spectroscopy.

CHART 1



the phenylated analogues **11**−**14** (Chart 1) were prepared and subjected to binding studies with $LiClO_4$, CuCl, and $FeCl_2$. Arrival at **11**[16] and **12** was likewise realized by Sonagashira coupling; however, it was not necessary to apply stringently controlled experimental conditions in these cases. This fact and the higher yields observed (75−85%) lend credence to the working principle that the spiro ether triad is a root cause of our difficulties. The acquisition of **13** and **14** was also met with enhanced yields (70%).

In a series of titration experiments, solutions of the Li^+, Fe^{2+}, and Cu^+ salts were added in 0.25, 0.50, and 1.0 equiv amounts to solutions of **11**−**14** in 1:1 CH_3CN/$CHCl_3$. The response of each ligand to such treatment was monitored by UV−vis spectroscopy as shown in Figure 1. The presence of $LiClO_4$ clearly has no effect, and no coordinative interaction develops. In contrast, the progressive addition of a copper(I) or iron(II) salt induces

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(15) Ogawa, S.; Uchida, T.; Uchiya, T.; Hirano, T.; Saburi, M.; Uchida, Y. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1649.
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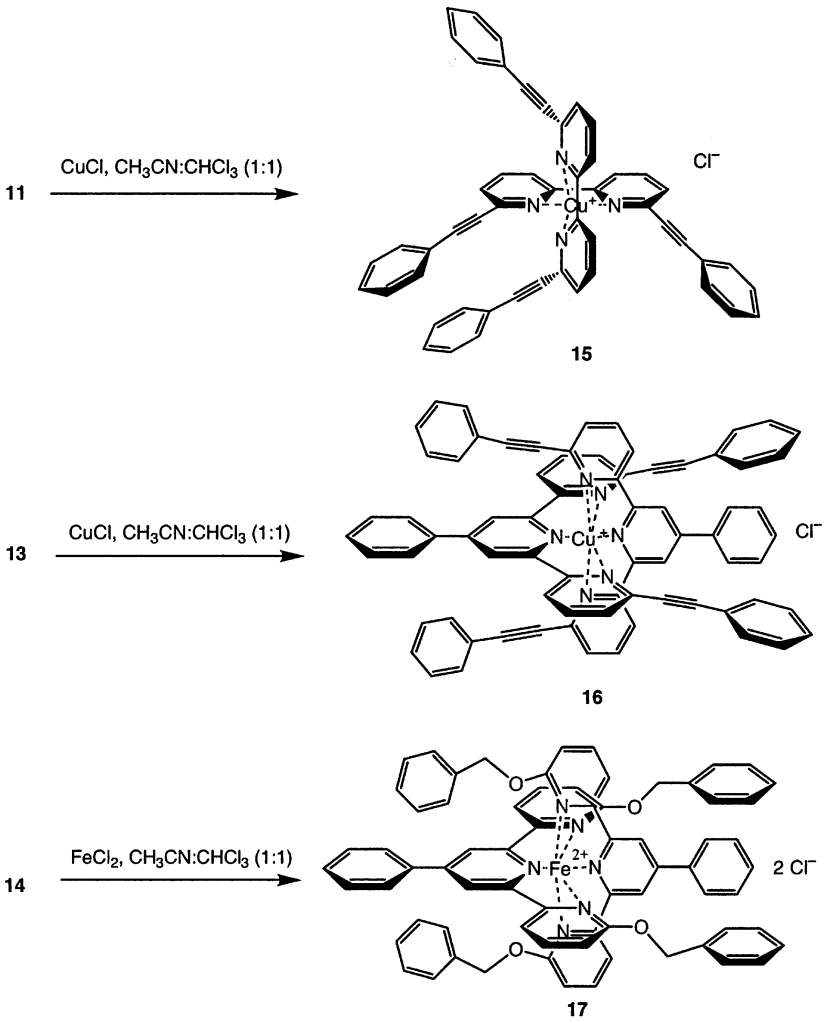
SCHEME 3



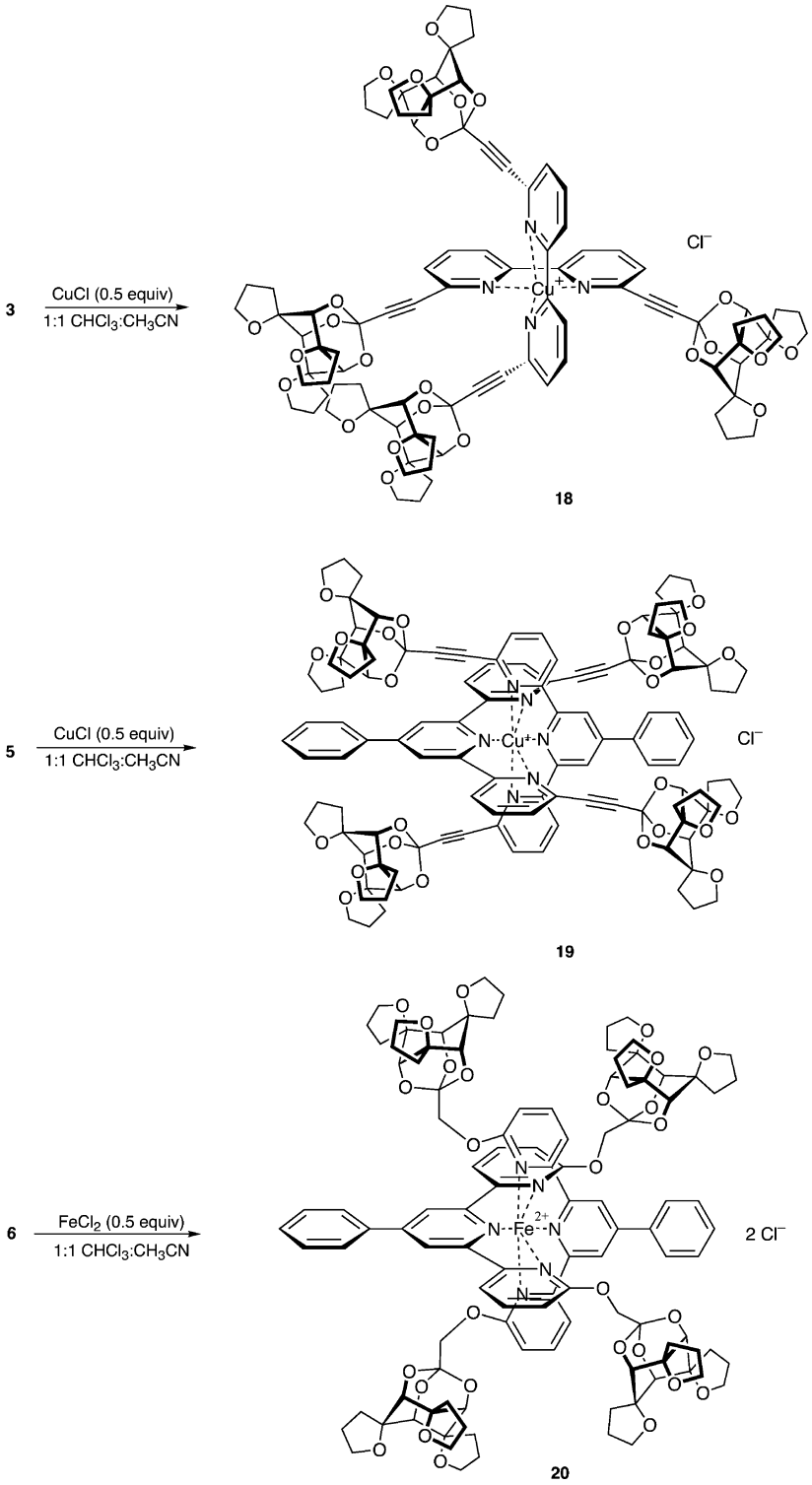
appreciable absorption shifts toward the visible region in at least three of the examples. The generation of **15**−**17** is presumably responsible for these phenomena, as confirmed by electrospray mass spectral analysis of the solids obtained following introduction of 0.5 equiv of the transition metal salt (Scheme 3). The results recorded for **12** are regarded to be inconclusive. Extensive efforts to record ^{1}H NMR spectra for **15**−**17** were to no avail because of substantial line broadening.

Following upon these calibration experiments, ligands **3**, **5**, and **6** were examined for their binding preferences (Figure 2). Particularly notable was the response of **3** and **5** to the presence of CuCl (0.5 equiv). Confirmation that conversion to **18** and **19** had materialized was again derived from spectroscopic and mass spectral measurements. While the complexation of terpyridine **6** to $FeCl_2$ (0.5 equiv) was met with the same reactivity pattern to give **20**, the response of bipyridine **4** was less definitive and therefore probed no further (Scheme 4).

We next addressed the admixture of **3**−**6** with 0.5 equiv of $LiClO_4$ in the same solvent system. The solids produced from these experiments were identified as **21**−**24** by electrospray mass spectroscopy (Chart 2). In light of these observations, double-complexation experiments were performed with **3** and **5**. In the first instance, 0.5 equiv of CuCl was added in advance of 1.0 equiv of $LiClO_4$. The first step was accompanied with the customary color change from water-white to red-orange. The second stage induced the slow precipitation of a gelatinous-like material from the 1:1 $CH_3CN/CHCl_3$ medium, which ultimately gave rise to a pale orange-brown solid in quantitative yield following solvent evaporation. No phenomenological differences were noted if the proportion of $LiClO_4$ was increased to 2.0 equiv. The sequence in which the metal ions were introduced was reversed for **5**. Immediately following admixture with 0.5 equiv of $LiClO_4$, a comparable level of CuCl was introduced. In this instance, colloid formation was initially observed with concomitant orange coloration. However, after solvent removal under reduced pressure, an orange solid again resulted (100%). As expected, both end products proved to be highly insoluble in a variety of solvents, thus precluding their more definitive characterization by mass spectral methods (particularly MALDI).

These results correlate well with the generation of dispersed oligomeric supramolecular structures under these circumstances. There are no options other than ligation of the Cu^+ ions in endo receptor fashion to the bi- and terpyridine nitrogen atoms with concurrent strong coordination of the lithium ions to the spirocyclic oxygen triads. The exo receptor quality of the binding to this alkali metal ion, as rigorously demonstrated in a number of

SCHEME 4

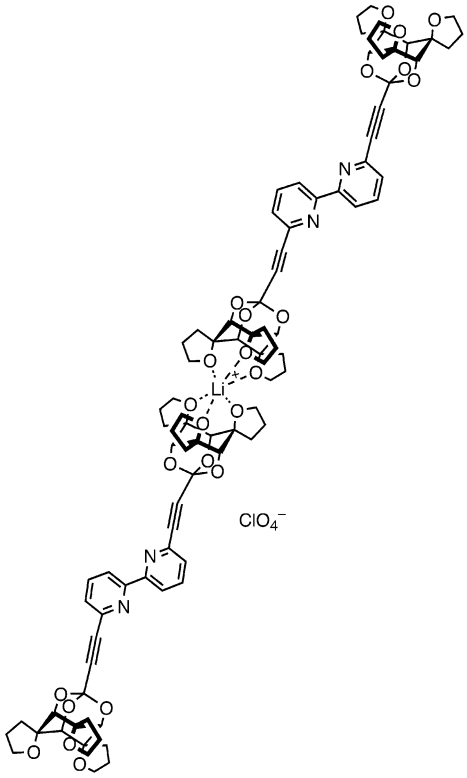


simpler prototypes, is considered to be operative here as well. In keeping with these trends, the resulting polymers are viewed to result from multiple heterocationic binding in dissimilar regions of the same molecule. Since chain length is not a controllable option, the materials generated here are necessarily nonhomogeneous in molecular weight.

Experimental Section

Bipyridine 3. A mixture of dibromide **8** (17.8 mg, 0.057 mmol), $PdCl_2(PPh_3)_2$ (2.4 mg, 3 mol %), CuI (3 mg, 14 mol %), and triphenylphosphine (2.4 mg, 8 mol %) was treated with triethylamine (0.4 mL) and deoxygenated. Alkyne **7** (40 mg, 0.12 mmol) was introduced, and heating at the reflux temperature under an attached condenser with N_2 blanketing was maintained for 48 h. After cooling, the solvent was evaporated and the residue was chromatographed on silica gel. Elution with 5% methanol in CH_2Cl_2 afforded a small amount of **3**. Passage of aqueous KCN solution (Caution!) through the column freed the remainder of **3**, which was isolated upon resumption of the chromatography. A total of 30 mg (64%) of **3** was isolated as a white solid: mp > 270 °C; IR (neat, cm^{-1}) 2950, 2875, 1062; ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, $J = 7.0$ Hz, 2 H), 7.83 (t,

CHART 2



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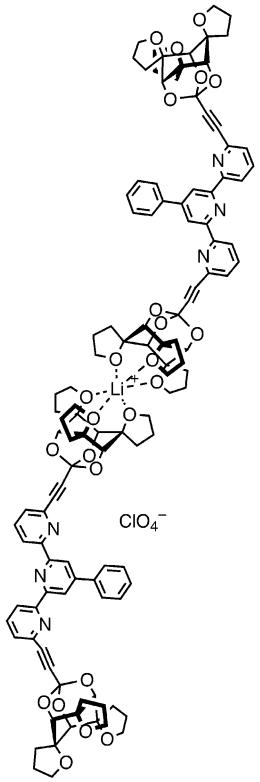

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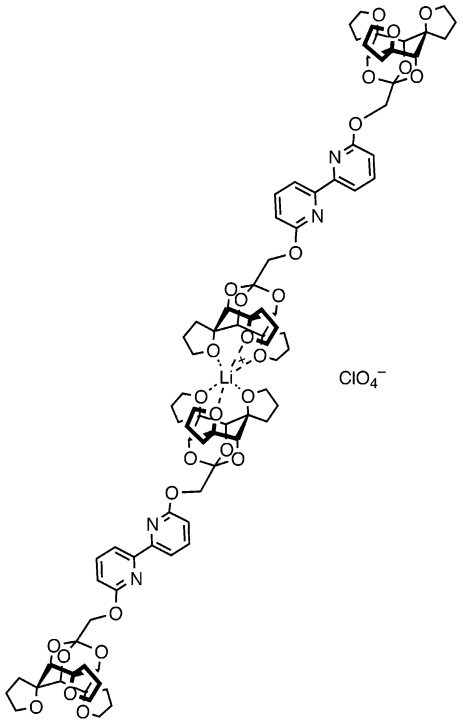

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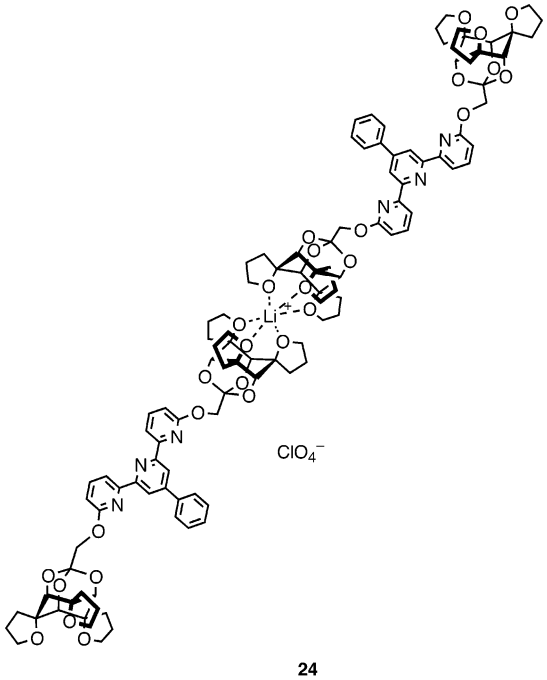

24

J = 7.8 Hz, 2 H), 7.56 (d, J = 7.8 Hz, 2 H), 4.01 (t, J = 6.8 Hz, 12 H), 3.72 (s, 6 H), 2.41 (t, J = 7.8 Hz, 12 H), 1.95 (quintet, J = 7.3 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 140.9, 137.4, 128.6, 122.3, 103.1, 81.6, 81.0, 80.1, 78.0, 70.1, 37.0, 24.4; ES HRMS m/z $(M + Na)^+$ calcd 843.3099, obsd 843.3124.

Terpyridine 5. A mixture of dibromide **9** (28 mg, 0.060 mmol), $PdCl_2(PPh_3)_2$ (2.4 mg, 3 mol %), CuI (3 mg, 14 mol %), and triphenylphosphine (2.4 mg, 8 mol %) was treated with triethylamine (0.4 mL) and deoxygenated. Alkyne **7** (40 mg, 0.12 mmol) was introduced and heating at the reflux temperature under an attached septum-capped condenser with N_2 blanketing was maintained for 48 h. After cooling, the above workup was applied to provide 13 mg (22%) of **5** alongside 20 mg (47%) of the monosubstitution product.

For **5**: white solid; mp 207−210 °C; IR (neat, cm^{-1}) 2940, 1340, 1065; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 2 H), 8.63

(d, J = 8.0 Hz, 2 H), 7.90 (d, J = 7.8 Hz, 2 H), 7.84 (t, J = 7.8 Hz, 2 H), 7.58 (m, 5 H), 4.00 (t, J = 6.8 Hz, 12 H), 3.70 (s, 6 H), 2.42 (t, J = 7.4 Hz, 12 H), 1.93 (quintet, J = 7.0 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 154.9, 150.8, 142.0, 136.9, 129.1, 128.9, 128.1, 127.6, 126.2, 121.6, 120.0, 102.7, 81.2, 80.7, 79.7, 77.5, 69.7, 36.6, 24.0; ES HRMS m/z $(M + Na)^+$ calcd 996.3678, obsd 996.3604.

Bipyridine 4. A solution of **10** (40 mg, 0.12 mmol) in dry THF (2 mL) was treated at rt with potassium hexamethyldisilazide (0.25 mL of 0.5 M in toluene). After 10 min, dibromide **8** (19 mg, 0.06 mmol) was introduced, and the reaction mixture was refluxed overnight, cooled, quenched with water, and extracted with CH_2Cl_2 (5×). The volume of the combined organic phases was reduced to the 10% level by evaporation under reduced pressure, and the residue was chromatographed on silica gel (elution with 5% methanol in CH_2Cl_2) followed by recrystallization from CH_2Cl_2 gave **4** as a white solid: mp > 270 °C (15 mg, 30%); IR (neat, cm^{-1}) 2946, 1072; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.4 Hz, 2 H), 7.67 (t, J = 7.8 Hz, 2 H), 6.84 (d, J = 8.1 Hz, 2 H), 4.45 (s, 4 H), 4.00 (t, J = 6.9 Hz, 12 H), 3.65 (s, 6 H), 2.35 (t, J = 7.3 Hz, 12 H), 1.91 (quintet, J = 7.5 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 152.9, 139.3, 114.2, 111.4, 107.0, 80.0, 76.3, 69.6, 66.2, 36.3, 23.9; ES HRMS m/z $(M + Na)^+$ calcd 855.3311, obsd 855.3271.

Terpyridine 6. Reaction of **10** (50 mg, 0.15 mmol) in dry THF (2.5 mL) sequentially with potassium hexamethyldisilazide (0.30 mL of 0.5 M in toluene) and dibromide **9** (34.4 mg, 0.073 mmol) in a manner paralleling that described above furnished 21 mg (30%) of **6** as a white solid: mp 191−193 °C; IR (neat, cm^{-1}) 2944, 2874, 1581, 1074; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 2 H), 8.32 (d, J = 7.4 Hz, 2 H), 7.85 (d, J = 7.2 Hz, 2 H), 7.80 (t, J = 7.9 Hz, 2 H), 7.60 (t, J = 7.2 Hz, 2 H), 7.53 (t, J = 7.4 Hz, 1 H), 6.94 (d, J = 8.1 Hz, 2 H), 4.56 (s, 4 H), 4.01 (t, J = 6.4 Hz, 12 H), 3.67 (s, 6 H), 2.37 (t, J = 7.4 Hz, 12 H), 1.91 (quintet, J = 7.4 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 156.0, 153.8, 150.9, 139.9, 139.8, 129.5, 129.2, 127.9, 119.4, 115.2, 112.1, 107.6, 80.4, 76.8, 70.0, 66.5, 36.7, 24.4; ES HRMS m/z $(M + Na)^+$ calcd 1008.3889, obsd 1008.3842.

Bipyridine 11. To a mixture of **8** (0.25 g, 0.80 mmol), CuI (18 mg, 12 mol %), and $PdCl_2(PPh_3)_2$ (37 mg, 6 mol %) was added triethylamine (10 mL) under N_2. Phenylacetylene (0.18 mL, 1.67 mmol) was introduced dropwise, and overnight stirring was maintained prior to quenching with water. The aqueous layer was extracted with CH_2Cl_2, and the combined organic phases were dried and concentrated. The residue was chromatographed on silica gel (elution with 1:1 CH_2Cl_2/hexanes) to provide 210 mg (74%) of **11** as a white solid: mp 194−195 °C (lit.[16] mp 195.8−196.2 °C); IR (neat, cm^{-1}) 2357, 1567; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, J = 7.9 Hz, 2 H), 7.81 (t, J = 7.8 Hz, 2 H), 7.64 (m, 4 H), 7.56 (d, J = 7.7 Hz, 2 H), 7.39 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 142.8, 137.1, 132.0, 128.9, 128.3, 127.5, 122.3, 120.8, 89.0, 88.9.

Terpyridine 12. To a mixture of **9** (0.25 g, 0.54 mmol), CuI (12 mg, 12 mol %), and $PdCl_2(PPh_3)_2$ (23 mg, 6 mol %) was added triethylamine (10 mL) under N_2. After the dropwise introduction of phenylacetylene (0.29 mL, 2.6 mmol), the reaction mixture was processed in the above manner to give 190 mg (70%) of **12** as a white solid: mp 219−220 °C; IR (neat, cm^{-1}) 3060, 2360, 1575, 1400; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 2 H), 8.62 (d, J = 7.9 Hz, 2 H), 7.93 (d, J = 7.1 Hz, 2 H), 7.87 (t, J = 7.8 Hz, 2 H), 7.67 (m, 4 H), 7.59 (d, J = 7.4 Hz, 2 H), 7.45 (m, 3 H), 7.39 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 155.0, 150.7, 146.9, 142.8, 138.1, 137.0, 132.1, 129.0, 128.9, 128.4, 127.5, 127.4, 122.4, 120.6, 119.7, 89.1, 89.0; ES HRMS m/z $(M + Na)^+$ calcd 532.1784, obsd 532.1782.

Bipyridine 13. A cold (0 °C) solution of **8** (0.20 g, 0.64 mmol) in dry THF (15 mL) was treated with potassium hexamethyldisilazide (5.1 mL of 0.5 M in toluene) and stirred for 20 min prior to the introduction of benzyl alcohol (0.26 mL, 2.55 mmol). The reaction mixture was heated to reflux for 3 h and quenched with water. The product was extracted into CH_2Cl_2, and the combined organic phases were dried and evaporated. The residue was chromatographed on silica gel (elution with 1:1 CH_2Cl_2/hexanes) to furnish 0.17 g (72%) of **13** as a white solid: mp 174−175 °C; IR (neat, cm^{-1}) 1574, 1435; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 7.3 Hz, 2 H), 7.72 (t, J = 7.5 Hz, 2 H), 7.53 (d, J = 6.8 Hz, 4 H), 7.39 (m, 6 H), 6.82 (d, J = 8.2 Hz, 2 H), 5.53 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 153.3, 139.4, 137.6, 128.5, 128.1, 127.8, 113.9, 111.3, 67.4; ES HRMS m/z $(M + Na)^+$ calcd 391.1417, obsd 391.1418.

Terpyridine 14. Reaction of **9** (0.20 g, 0.43 mmol) with benzyl alcohol (0.18 mL, 1.7 mmol) according to the predescribed protocol resulted in the isolation of 0.11 g (50%) of **14** as a white solid: mp 158−159 °C; IR (neat, cm^{-1}) 3064, 1582, 1266; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 2 H), 8.27 (d, J = 7.5 Hz, 2 H), 7.79 (m, 4 H), 7.55 (m, 7 H), 7.39 (m, 6 H), 6.88 (d, J = 8.2 Hz, 2 H), 5.56 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 155.8, 153,6, 150.0, 141.0, 139.5, 137.8, 129.1, 129.0, 128.5, 128.0, 127.8, 127.3, 118.8, 114.3, 111.6, 67.7; ES HRMS m/z $(M + Na)^+$ calcd 544.1995, obsd 544.2013.

General Procedure for Complexation Experiments Involving 11, 13, or 14 with CuCl or $FeCl_2$. Approximately 1.0 mg of the ligand was dissolved in ∼0.5 mL of a 1:1 mixture of CH_3CN and $CHCl_3$. To this solution was added the proper quantity of a 0.04 or 0.08 M solution of CuCl in the same solvent system or of $FeCl_2$ in methanol. After the addition, the red or yellow solutions were evaporated in a stream of N_2 to furnish the complex in quantitative yield.

For **15**: orange solid; ES HRMS m/z (M^+) calcd 775.2017, obsd 775. 2015.

For **16**: pale orange solid; ES HRMS m/z (M^+) calcd 1081.3174, obsd 1081.3180.

For **17**: red solid; ES HRMS m/z ($M^{+2}/2$) calcd 549.1772, obsd 549.1778.

General Procedure for Complexation Experiments Involving 3, 5, and 6 with CuCl or $FeCl_2$. Approximately 1.0 mg of the ligand was dissolved in ∼0.5 mL of a 1:1 mixture of CH_3CN and $CHCl_3$. To this was added the proper μL quantity of a 0.04 or 0.08 M CuCl in the same solvent system or of $FeCl_2$ in methanol. Subsequently, the red or yellow solutions were freed of solvent under a stream of N_2 to give the complex in quantitative yield.

For **18**: orange solid; ES HRMS m/z (M^+) calcd 1704.5839, obsd 1704.5736.

For **19**: orange solid; ES HRMS m/z (M^+) calcd 2010.6996, obsd 2010.7003.

For **20**: red solid; ES HRMS m/z ($M^{+2}/2$) calcd 1013.8683, obsd 1013.8723.

General Procedure for Recording UV−vis Absorption Curves. A specific weight of 1−5 mg of the ligand was dissolved in 1:1 $CH_2CN/CHCl_3$ (1−5 mL). These solutions were scanned in the region from 190 to 890 nm. These solutions were individually treated with 0.25, 0.50, and 1.0 equiv of $LiClO_4$, CuCl, or $FeCl_2$ solutions defined above. Scanning was repeated at every stage.

General Procedure for Complexation Experiments Involving 3−6 with $LiClO_4$. Approximately 1.0 mg of ligands **3**−**6** was dissolved in ∼0.5 mL of a 1:1 mixture of CH_3CN and $CHCl_3$. To each solution was added the proper microliter quantity of 0.235 or 0.176 M $LiClO_4$ in the same solvent system. After the addition, either the solid that precipitates or the resulting solution was freed of solvent under a stream of N_2 to provide the complex in quantitative yield.

For **21**: obtained from **3** as a white solid that precipitates immediately; ES HRMS m/z for $C_{92}H_{96}LiN_4O_{24}^+$ calcd 1648.6603, obsd 1648.6749.

For **22**: obtained as a white solid after solvent evaporation; ES HRMS m/z for $C_{114}H_{110}LiN_6O_{24}Na^{+2}$ calcd 988.8826, obsd 988.8888.

For **23**: obtained as a white solid after solvent evaporation; ES HRMS m/z for $C_{88}H_{104}LiN_4O_{28}Na^{+2}$ calcd 847.3442, obsd 847.3429.

For **24**: obtained as a white solid after solvent evaporation; ES HRMS *m*/*z* for $C_{110}H_{118}LiN_6O_{28}Na^{+2}$ calcd 1000.9037, obsd 1000.9046.

Double Complexation Experiments. A. Involving Ligand 3. To a solution of **3** (1.0 mg, 1.2 μmol) in 1:1 $CH_3CN/CHCl_3$ (0.5 mL) was added a solution of CuCl in the same solvent system (9.3 μL of 0.0652 M). Following the color change to orange, 1.0 equiv of $LiClO_4$ (3.5 μL of 0.176 M in the same solvent) was introduced. The precipitation of a gelatinous-like material ensued. Solvent evaporation gave in quantitative yield a light orange solid that proved totally insoluble in all solvents examined.

B. Involving Ligand 5. To a solution of **5** (1.0 mg, 1.03 μmol) in 0.5 mL of 1:1 $CH_3CN/CHCl_3$ was added 0.5 molar equiv of $LiClO_4$ from a 0.176 M solution in the same solvent. Immediately thereafter, 0.5 equiv of CuCl from a 0.0535 M solution of 1:1 $CH_3CN/CHCl_3$ was introduced. No precipitation was evident. However, subsequent solvent removal gave rise in quantitative yield to an orange solid that proved totally insoluble in all solvents examined.

Supporting Information Available: Copies of the ^1H NMR and ^{13}C NMR spectra of compounds **3**−**6** and **12**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO030373T