

Bipyridine: The Most Widely Used Ligand. A Review of Molecules Comprising at Least Two 2,2'-Bipyridine Units

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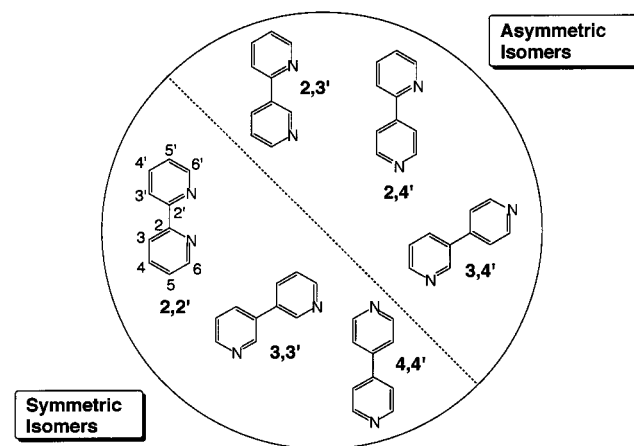
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I. Introduction

The purpose of the present review is to present the diverse variety of molecules comprising at least two 2,2'-bipyridine units in the form of an exhaustive database. Rather than concentrate on a particular class of application, the aim here is to provide an overall view on the most explored chelate system in coordination chemistry. The intended audience is, on one side, researchers already active in the area and, on the other, those who might be newcomers to it. This review will hopefully be useful to readers in verifying whether a targeted ligand has been previ-

Scheme 1. Symmetrical and Asymmetrical Isomers of Bipyridine



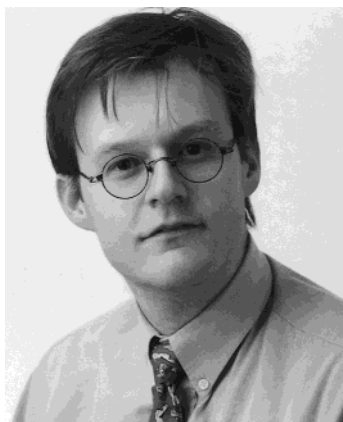
ously prepared and in finding the relevant literature associated with its synthesis. Since the 2,2'-bipyridine unit has been used in a variety of approaches dealing with structural coordination chemistry and/or functional systems based on 2,2'-bipyridine metal complexes, an article dealing with the organic synthetic strategies employed to prepare the ligand system, the synthetic approaches to form their metal complexes, and physical properties of metals chelated by 2,2'-bipyridine ligands would have been too broad a theme for a single review. Therefore, in the present contribution, we mainly focus on structural as well as synthetic features. However, when feasible, we do also indicate the functional context guiding the design of the ligand systems reported.

Since its discovery at the end of nineteenth century,¹ the bipyridine ligand has been used extensively in the complexation of metal ions. It is possible to distinguish (Scheme 1) the symmetrical isomers of bipyridine (2,2', 3,3', and 4,4') from the asymmetrical ones (2,3', 2,4', and 3,4'), and of these, only the 2,3'- and the 3,3'-bipyridines are found to be naturally abundant in certain varieties of tobacco.^{2–4}

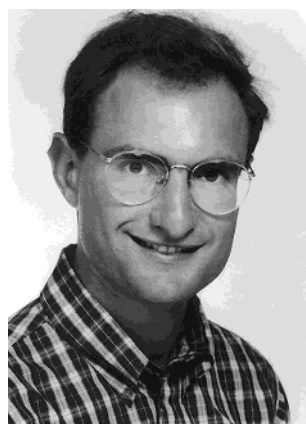
The 2,2'-bipyridine ligand has been extensively used as a metal chelating ligand due to its robust redox stability and ease of functionalization. In contrast to other ligands, such as catechol, which is dianionic, and derivatives of the acetylacetonate ion, which are monoanionic, 2,2'-bipyridine is a neutral ligand. It thus forms charged complexes with metal cations, and this property has been exploited in the

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Christian Kaes was born in Luxembourg in 1970. He graduated in chemistry at the Université Louis Pasteur, Strasbourg. After completing his Ph.D. in 1998 under supervision of Professor M. Wais Hosseini at the Université Louis Pasteur, Strasbourg, he joined the Goodyear Technical Centre in Luxembourg as a staff-engineer.



Alexander Katz was born in Minsk, Republic of Belarus, and raised in Minneapolis, Minnesota. He graduated Cum Laude in chemical engineering at the University of Minnesota and performed research there with Professor Michael D. Ward, during which time he developed a piezoelectric microrheometer for polymer films. Alexander received a Master of Science in Chemical Engineering from the University of Minnesota in 1994 and was subsequently awarded a Fannie and John Hertz Foundation Graduate Fellowship. He pursued doctoral studies in the rational design of catalytic materials at Caltech with Professor Mark E. Davis. Upon finishing his Ph.D. in 1998, Alex was awarded a NSF International Awards Fellowship to investigate the use of supramolecular chemistry in the design and synthesis of materials, as a postdoctoral researcher in the Organic Coordination Chemistry Laboratory of Professor M. Wais Hosseini at the Institut Le Bel, Université Louis Pasteur, in Strasbourg, France. Currently, he is an Assistant Professor of Chemical Engineering at University of California at Berkeley, where his interests are in the design and synthesis of materials for chemical engineering applications.

design and synthesis of metal–bipyridine complexes. Here the various major classes and syntheses of molecules are summarized comprising at least two 2,2'-bipyridine units (units that cannot be classified as higher oligopyridines such as terpyridines, quaterpyridines, quinquopyridines, etc.), which are connected in different positions around the aromatic ring (3, 4, 5, and 6) by covalent bonds. Molecules containing metal–coordination interactions (such as ferrocene-based ligands containing bipyridine) are included here only if the bipyridine moieties are attached to the molecule following the creation of the coordination bonds that hold the molecule together (polymeric metal complex networks containing bipyridine⁵ are therefore not included here).

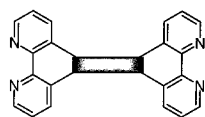


Mir Wais Hosseini was born in 1955 in Kabul, Afghanistan. In 1972 he moved to Strasbourg, France. He was mainly educated at the Université Louis Pasteur, Strasbourg, where he obtained his Ph.D. degree in 1983 working with Jean-Marie Lehn. In 1981 he joined the French National Research Centre as a permanent member. After a postdoctoral fellowship spent in 1985 with Kenneth Raymond at Berkeley, he returned to Strasbourg where he continued to work with Jean-Marie Lehn. In 1990 he was appointed as a Professor of Organic Chemistry at the Université Louis Pasteur. In 1992 he was nominated for a period of five years at the Institut Universitaire de France. He was an invited professor at the University of Western Australia at Perth, University of Geneva, The Institut of Materials and Chemical Research, Tsukuba, Japan, and University of Tokyo. His main research interests are in the area of molecular architectures in chemistry, biology, and physics and range from molecular receptors and catalysts to molecular networks and molecular materials.

Ligands containing two or more 2,2'-bipyridine units can in principle be used as bridges to interconnect metal centers in a well-defined spatial arrangement. The uses of such ligands as precursors for helical assembly,⁶ chiral molecular recognition,^{7,8} luminescent devices,^{9,10} and other applications in photonics and optoelectronics^{11,12} and electrochemistry¹³ have been reviewed elsewhere. The classes of molecules containing two or more 2,2'-bipyridine units can be categorized as (a) molecules having units connected in positions 3 and 3', (b) nonmacrocylic molecules having units connected in positions 4 and 4', (c) macrocyclic molecules having units connected in positions 4 and 4', (d) nonmacrocylic molecules having units connected in positions 4,4' and 5,5', (e) nonmacrocylic molecules having units connected in positions 5 and 5', (f) macrocyclic molecules having units connected in positions 5 and 5', (g) nonmacrocylic molecules having units connected in positions 6 and 6', (h) macrocyclic molecules having units connected in positions 6 and 6', (i) asymmetrically connected units, and (j) polymers containing 2,2'-bipyridine. Tables containing illustrations of the ligands are labeled according to their corresponding category.



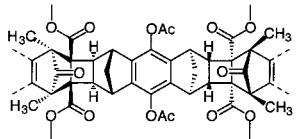
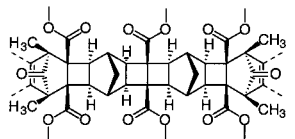
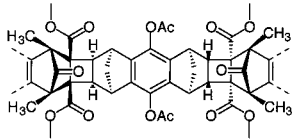
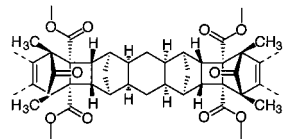
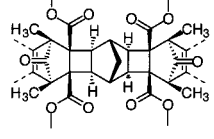
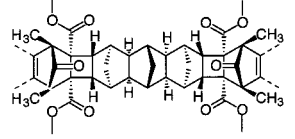
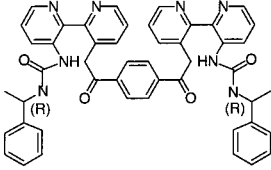
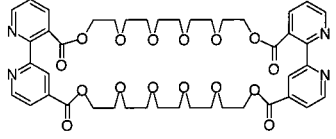
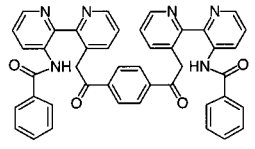
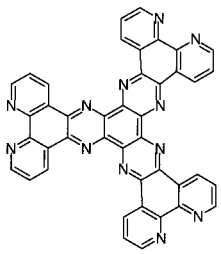
II. Ligands with 2,2'-Bipyridine Connected in Positions 3 and 3'

Ligand **1a**^{14–17} was obtained in three steps from 1, 10-phenanthroline, by oxidation of the latter with KMnO_4 to give 4,5-diazafluorenone, which subsequently dimerizes to give **1a** (Table 1).¹⁶ The subsequent dehydrogenation of **1a** yields **2a**,¹⁵ which has also been obtained via a reductive coupling strategy.¹⁷ Ligand 5,5'-bis(1,10-phenanthroline) **3a** has been

Table 1

Number		Reference	Number		Reference
1a		16	18a		34
2a		15, 17	19a		34
3a		18	20a		35
4a		14	21a		35
5a		20	22a		36
6a		22	23a		36
7a		20	24a		36
8a		21	25a		36
9a		23	26a		37
10a		24	27a		37
11a		25			
12a		28			
13a		29			
14a		30			
15a		30			
16a		30			
17a		32			

Table 1 (Continued)

Number		Reference	Number		Reference
28a		37	31a		37
29a		37	32a		37
30a		37	33a		37
Number	Ligand	Reference	Number	Ligand	Reference
34a		38	36a		39
35a		38	37a		40

synthesized by two successive Skraup reactions for the purpose of forming a compound with chelating ability for Fe(II) and Cu(I).¹⁸ Dimers **4a**,^{14,19} **5a**,²⁰ and **6a**^{21,22} have been obtained by starting from 9-diazo-4,5-diazafluorene, and compounds **7a**²⁰ and **8a**²¹ have been synthesized by starting from 2-diazo-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthrene. The reduction of 5-nitro-1,10-phenanthroline by NaBH₄ drives to the formation of 5,5'-azo-1,10-phenanthroline **9a** (among other byproducts).²³ The ligand bis-(1,10-phenanthroline) **10a** has been synthesized by starting from 5-amino-1,10-phenanthroline and formaldehyde, and its interactions with DNA have been investigated.²⁴ Lehn and co-workers prepared a trinuclear Ru–Pd–Ru complex²⁵ by utilizing ligand **11a**, which is a larger homologue of ligand **12a**. Ligand **11a** has been synthesized in the form of its mononuclear complex with Ru(II), by reacting 11,12-diamino-dipyrido[3,2-a:2',3'-c]phenazine with the complex [Ru(phen)₂(phen-5,6-dione)]²⁺.²⁵ Macrocyclic **12a** can be synthesized by two different methods: the condensation of 5,6-dione-1,10-phenanthroline with 5,6-diamino-1,10-phenanthroline and the reaction of 5,6-dione-1,10-phenanthroline with MeCO₂NH₄. The luminescence properties and X-ray crystallographic structure of the dinuclear complex of **12a** with Ru-

(II) have been investigated.^{26–28} The same ligand has been used to construct a Ru(II)-based coordination polymer.²⁷ Ligand **13a** has been synthesized by following the same type of reaction as for **11a**, i.e., a condensation of the complex [Ru(phen or bipy)₂(phen-5,6-dione)]²⁺ with 3,3',4,4'-tetraamino-biphenyl, and a large association constant of the binuclear Ru(II) complex of ligand **13a** to DNA has been reported.²⁹

Ligands **14a–16a** have been obtained by the condensation of 4,5-diazafluoren-9-one with various diamines. Because of sp² hybridization of the bridging nitrogen atom, protons in the two pyridines comprising each bipyridine unit are nonequivalent, and this is manifested in shifts in their proton NMR behavior.³⁰ The binuclear ruthenium complexes of ligands **14a–16a** have been reported and give rise to metal-to-ligand charge transfer absorptions and intraligand transitions in the ultraviolet spectrum, as well as to a short-lived emission.³¹

Ligands **17a–19a** represent larger homologues of **11a** and **12a**. Although attempts to synthesize **17a** starting from 5,6-diamino-1,10-phenanthroline and tetraketopyrene in a manner analogous to **12a** were not successful due to solubility problems, an alternative synthetic route was used that involved successive functionalization of precursor complexes. Thus reac-

tion of 6-amino-5-nitro-1,10-phenanthroline, which was obtained by nucleophilic amination of 5-nitro-1,10-phenanthroline, with $\text{Ru}(\text{bipy})_2\text{Cl}_2\cdot\text{H}_2\text{O}$ gave the corresponding amino–nitro complex in high yield, which was subsequently reduced by hydrazine hydrate over Pd/C to yield a diamino-containing ruthenium–bipyridine complex. Condensation of this complex with tetraketopyrene yielded **17a**.³² Ligand **17a** provided the first example of supramolecular dimerization of a binuclear metallic complex maintained only by π – π stacking interactions; however, electrochemical and spectroscopic studies of the binuclear complex have shown that the various parts of this dimer remain noninteracting, despite the extended aromaticity of the complexed bridging ligand dimer.³³ Ligands **18a** and **19a** were prepared as their diruthenium complexes by coupling benzoyl-substituted phenazine units with corresponding diamines.³⁴ The anthraquinone spacer in **19a** was shown to efficiently quench emission processes relative to ligand **18a**.³⁴

Dimer **20a** of 7,8-diazaphencyclone has been used as a source of 1,10-phenanthroline, in order to stereoselectively attach the latter over a rigid “molrac”-type system.³⁵ In complexing the phenanthroline of this “molrac” system by $\text{Ru}[(\text{bipy})_2(\text{CF}_3\text{SO}_3)_2]^{2+}$, diads are obtained which can be studied for their intramolecular charge transfer processes. The heating of **20a** to a temperature of 100 °C drives isomerization to **21a**.³⁵ Ligand **20a** and 9-diazo-4,5-diazaphenylene have also been used as phenanthroline sources to synthesize a “molrac”-type system containing two 1,10-phenanthroline units in ligands **22a**, **23a**, **24a**, **25a**, and **26a**.^{36,37} Alternatively 6,7-diazaphencyclone can be used as a phenanthroline source to produce ligands **27a**–**33a** in Diels–Alder-based reaction involving ring-strained alkenes.³⁷

Ligands **34a** and **35a** are linear oligobipyridines and were synthesized from 3,3'-diamino-2,2'-bipyridine for NMR and circular dichroism-based investigations of intramolecular hydrogen bonding.³⁸ The coronand **36a** has been synthesized by reacting the cesium salt of 3,3'-dicarboxy-2,2'-bipyridine with a dichloro derivative of poly(ethylene glycol).³⁹ Finally the disk **37a**,⁴⁰ which belongs to the same family of ligands as **11a**–**12a** and **17a**, has been synthesized by reacting 5,6-dione-1,10-phenanthroline with hexaminobenzene.

III. Ligands with 2,2'-Bipyridine Connected in Positions 4 and 4'

A. Nonmacrocylic 2,2'-Bipyridine Molecules Connected in Positions 4 and 4'

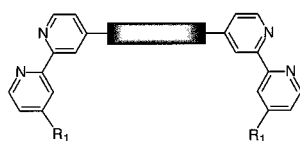
Derivatives of 2,2'-bipyridine that bear functional groups in the 4 and 4' positions have been shown to complex metals in square-planar, tetrahedral, and octahedral coordination geometries. Approximately two decades ago, several investigators observed that the lowest energy excited state of several Ru(II) and Os(II) (octahedral coordination) complexes had sufficiently long lifetimes in solution to allow for energy transfer processes to occur. It was furthermore reported that Ru(II) and Os(II) polypyridine complexes were suitable reagents for energy and electron

transfer processes due to their reversible redox behavior. Since then, investigators have prepared multimetallic systems in order to further elucidate the above-mentioned processes. One method of synthesizing such systems is to covalently link two or more 2,2'-bipyridines in positions 4 and 4' (or similarly in positions 5 and 5') by a bridge, which can be either saturated or unsaturated. The first compound **1b** (Table 2) prepared along these lines comprised a dimethylene bridge and was originally synthesized by Elliott and co-workers with an oxidative addition reaction, by reacting the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine with 1,2-dibromoethane, which served as the oxidant in the reaction scheme.⁴¹ Furue and co-workers later synthesized the same compound **1b** by alternatively reacting the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine with 4-bromomethyl-4-methyl-2,2'-bipyridine.⁴² Compounds possessing bridges $(\text{CH}_2)_3$ **2b**,⁴² $(\text{CH}_2)_4$ **3b**,⁴³ $(\text{CH}_2)_5$ **4b**,⁴⁴ $(\text{CH}_2)_7$ **5b**,⁴⁵ $(\text{CH}_2)_{10}$ **6b**,⁴⁶ and $(\text{CH}_2)_{12}$ **7b**⁴⁴ have all been synthesized by reacting 1 equiv of the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine with the corresponding dibromo derivative. Elliot and co-workers have also synthesized bis(4-(4'-methyl-2,2'-bipyridyl)methyl)ether **8b** and bis(4-(4'-methyl-2,2'-bipyridyl)methyl)sulfide **9b**.⁴⁷ Using a similar synthetic approach, ligand **10b**, 1,3-bis(4'-methyl-2,2'-bipyridin-4-yl)-2-propanol, was synthesized by reacting the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine with ethyl formate with an overall yield of 20%.⁴⁸

By performing a Wittig condensation between (4-(4'-methyl-2,2'-bipyridyl)methyl)triphenylphosphonium bromide and 4-formyl-4'-methyl-2,2'-bipyridine, Meyer and co-workers synthesized *trans*-1,2-bis(4-methyl-2,2'-bipyridin-4-yl)ethylene **11b**.⁴⁹ A Wittig condensation was also used in the synthesis of 1,4-bis(4'-methyl-2,2'-bipyridin-4-yl)buta-1,3-diene **12b**.⁵⁰ The butadiene ligand was subsequently transformed via a Diels–Alder addition using diethyl fumarate to give the diester product **13b**.⁵⁰ Hydrolysis of the latter with KOH followed by a double decarboxylation yielded ligand 1,4-bis(4'-methyl-2,2'-bipyridin-4-yl)benzene **14b**.⁵⁰ Both ligands **14b** and **15b** have the potential to serve as rigid bridging ligands for redox and photoactive applications. Ligand **16b** was independently synthesized by the groups of Beer⁵¹ and Schmehl,⁵² and both reacted the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine with terephthalaldehyde in their synthetic procedure to first produce the diol **17b**, which was dehydrated to **16b**. Ligand **18b** was synthesized by reacting the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine with α,α' -dibromo-*p*-xylene,⁴⁴ and it has been used in investigating energy transfer processes between different metal centers.⁵³

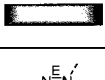
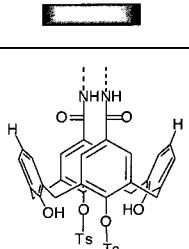
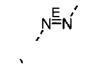
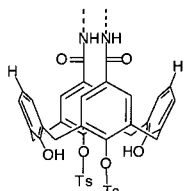
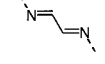
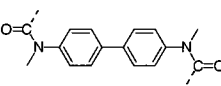
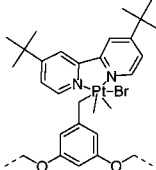
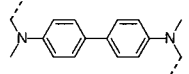
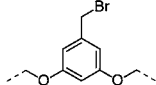
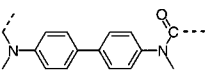
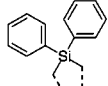
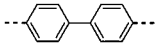
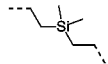
Elliott investigated the photoinduced electronic transfer properties of the different Ru(II) dinuclear complexes of various bipyridine ligands that are connected by bridges in which the number of connections remained fixed but where the steric environment varied (ligands **19b**, **20b**, **21b**, **22b**, **23b**, **24b**).⁵⁴ The nucleophilic substitution of the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine on

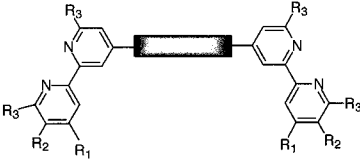
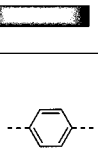
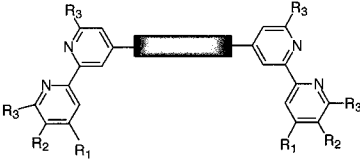
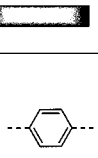



Table 2



Number		Functional Groups	Reference	Number		Functional Groups	Reference
1b		R ₁ = CH ₃	41, 42	27b		R ₁ = CH ₃	55
2b		R ₁ = CH ₃	42, 43	28b		R ₁ = CH ₃	55
3b		R ₁ = CH ₃	43	29b		R ₁ = CH ₃	51
4b		R ₁ = CH ₃	44	30b		R ₁ = CH ₃	51
5b		R ₁ = CH ₃	45	31b		R ₁ = CH ₃	51
6b		R ₁ = CH ₃	46	32b		R ₁ = CH ₃	51
7b		R ₁ = CH ₃	44	33b		R ₁ = CH ₃	56
8b		R ₁ = CH ₃	47	34b		R ₁ = CH ₃	57
9b		R ₁ = CH ₃	47	35b		R ₁ = CO ₂ Et	58
10b		R ₁ = CH ₃	48	36b		R ₁ = CO ₂ Et	58
11b		R ₁ = CH ₃	49	37b		R ₁ = CO ₂ Et	58
12b		R ₁ = CH ₃	50	38b		R ₁ = CO ₂ Et	58
13b		R ₁ = CH ₃	50	39b		R ₁ = Me	58
14b		R ₁ = CH ₃	50	40b		R ₁ = H	59
15b		R ₁ = H	69	41b		R ₁ = H	59
16b		R ₁ = CH ₃	51, 52	42b		R ₁ = H	60
17b		R ₁ = CH ₃	51, 52	43b		R ₁ = H	61
18b		R ₁ = CH ₃	44				
19b		R ₁ = CH ₃	54				
20b		R ₁ = CH ₃	54				
21b		R ₁ = CH ₃	54				
22b		R ₁ = CH ₃	54				
23b		R ₁ = CH ₃	54				
24b		R ₁ = CH ₃	54				
25b		R ₁ = CH ₃	46				
26b		R ₁ = CH ₃	46				

Table 2 (Continued)

Number		Functional Groups	Reference	Number		Functional Groups	Reference
44b		R ₁ = H	62	50b		R ₁ = H	67
45b		R ₁ = NH ₂	63	51b		R ₁ = CH ₃	68
46b		R ₁ = CH ₃	64	52b		R ₁ = CH ₃	68
47b		R ₁ = CH ₃	64	53b		R ₁ = CH ₃	68
48b		R ₁ = CH ₃	65	54b		R ₁ = H	69
49b		R ₁ = CH ₃	66				

Number		Functional Groups	Reference	Number		Functional Groups	Reference
55b		R ₁ = R ₂ = H R ₃ = COOH	69	57b		R ₁ = H R ₂ = R ₃ = CH ₃	70
56b		R ₁ = R ₂ = H R ₃ = COOH	69	58b		R ₁ = R ₂ = CH ₃ R ₃ = H	71
				59b		R ₁ = R ₃ = CH ₃ R ₂ = H	71

1,4-cyclohexanedione gives a mixture of *cis* **23b** and *trans* **24b** conformations of 1,4-bis((4'-methyl-2,2'-bipyridin-4-yl)methyl)cyclohexane-1,4-diol. Dehydration of this diol mixture with sulfuric acid in acetic acid gives a mixture of different dienes containing bis((4'-methyl-2,2'-bipyridin-4-yl)methyl)cyclohexa-1,4-diene **19b**.⁵⁴ Rearomatization of this diene with 5% Pd/C finally yields α,α' -bis(4'-methyl-2,2'-bipyridin-4-yl)-*p*-xylene **20b**.⁵⁴ The *cis* **21b** and *trans* **22b** derivatives were obtained upon hydrogenation of the diene mixture.⁵⁴

By grafting two fragments of 4-formyl-4-methyl-2,2'-bipyridine onto 3,3'-diamino-*N*-methyl-dipropylamine and 1,8-diaminooctane, ligands **25b** and **26b**, respectively, were synthesized, and the dinuclear Ru(II) complexes of these ligands have been studied as potential candidates for double intercalation with DNA.⁴⁶ Ligand **27b** was synthesized by reacting 2 equiv of the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine with 1 equiv of bis(hydroxymethyl)-2,2'-bipyridine methylsulfonate.⁵⁵ The unsaturated

homologue **28b**,⁵⁵ which possesses two *trans* double bonds, was synthesized from the addition of 2 equiv of 4-((diphenylphosphinoyl)methyl)-4'-methyl-2,2'-bipyridine (synthesized from the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine and chlorodiphenylphosphane) with 1 equiv of 6,6'-diformyl-2,2'-bipyridine. Similarly structured ligands **29b** and **30b**, comprising a 2,2'-bipyridine-type bridge connected in positions 4 and 4', have been synthesized by Beer and co-workers.⁵¹ Upon adding 2 equiv of the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine to 1 equiv of 4,4'-diformyl-2,2'-bipyridine, the diol **29b** was obtained, which upon dehydration yielded ligand **30b**. Using the same reaction sequence, compounds **31b** and **32b**, possessing bridges of the coronand type, have also been synthesized, and their Ru(II) complexes have been prepared.⁵¹

An elegant method of grafting a porphyrin between two 2,2'-bipyridines has been developed by Therien. In this synthesis, the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine was transformed into an



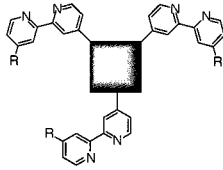
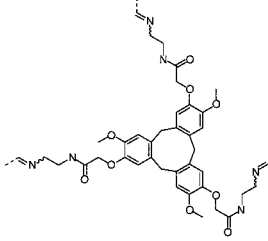
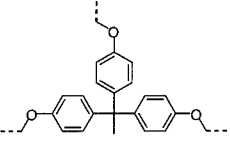
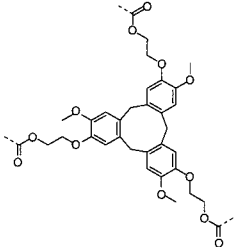
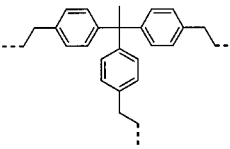
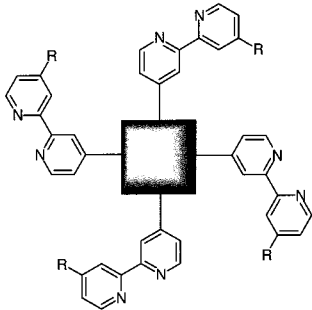


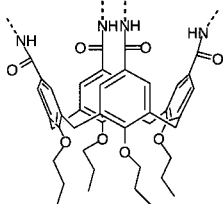
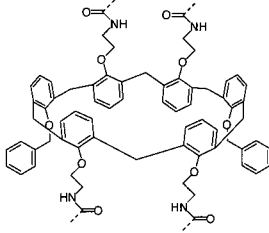
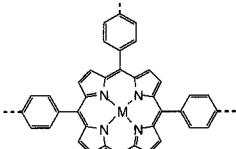
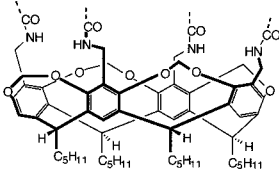
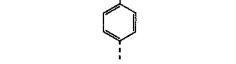
organotin derivative with tributyltin chloride.⁵⁶ A coupling reaction of this derivative with 5,15-dibromo-10,20-diphenylporphyrin was performed to give ligand **33b**.⁵⁶

The dinuclear Ru(II) complex of **34b**, possessing a conjugated pentene-type spacer, has been reported to show an electronic coupling following excitation, despite the relatively large distance between the metals in this case.⁵⁷ This ligand was synthesized using a Wittig reaction between 4-((diphenylphosphino)methyl)-4'-methyl-2,2'-bipyridine and 2,7-diformyl-2,4,6-octatriene.⁵⁷ The Ru(II), Rh(II), and Os(II) complexes of ligands **35b**, **36b**, **37b**, **38b**, and **39b** have been synthesized, and the stability constants of the reversible complexes have been measured with different halogen anions and H_2PO_4^- .⁵⁸ These constants have been shown to vary significantly depending on the nature of the spacer.⁵⁸ Bridges of the ethyne type **40b** and diethyne type **41b** have been grafted between two 2,2'-bipyridines.⁵⁹ The synthesis begins from 4-bromo-2,2'-bipyridine and consists of grafting the trimethylsilylacetylene in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ and $n\text{-PrNH}_2$. Upon repeating the same reaction sequence following deprotection of the TMS moiety with a weak base (K_2CO_3 or KF), the compound **40b** possessing an ethyne-type bridge is obtained. Compound **41b**, which has a diethyne-type bridge, is prepared by a coupling reaction between two identical molecules (CuCl , TMEDA, and O_2). The reaction of 4-ethynyl-2,2'-bipyridine with *trans*- $[\text{Pt}(\text{P}^n\text{Bu}_3)_2\text{Cl}_2]$ using a CuI catalyst and HNi-Pr_2 as base leads to the organometallic compound **42b**.⁶⁰ Beer et al. have grafted 2 equiv of 4-chloro-carbonyl-2,2'-bipyridine on a diamine derivative of calix-[4]-arene in synthesizing **43b** for anion recognition applications.⁶¹ Ligand **44b**, which has shown application potential as a molecular switch, requires that an azo-type bridge connect two 2,2'-bipyridines and was synthesized by reductive coupling starting from 4-nitro-2,2'-bipyridyl-1-oxide using NaBH_4 and Pd-C.⁶² Imine **45b** has been synthesized by the stoichiometric addition of 4,4'-diamino-2,2'-bipyridine to glyoxal and has been used as a model compound in reference to polymeric ligands prepared via the same synthetic condensation sequence.⁶³ Ligand **46b** has been obtained by an oxidative addition on the C-Br bond of **47b** over $[\text{PtMe}_2(\text{t}^{\text{bu}}_2\text{bpy})]$ ($\text{t}^{\text{bu}}_2\text{bpy}$: 4,4'-di(*tert*-butyl)-2,2'-bipyridine); **46b** and **47b** serve as starting compounds for the step-by-step synthesis of organometallic dendrimers.⁶⁴ The silane-containing bridging ligands **48b**⁶⁵ and **49b**⁶⁶ have been synthesized by our group, by reacting the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine with corresponding silyl derivatives. The binuclear Ru(II) complex of calix-[4]-arene **50b** is an anion binding element that possesses selectivity for the H_2PO_4^- anion.⁶⁷ Ligand **51b** was synthesized by amide formation between dimethyldibenzidinium dichloride, which was synthesized from benzidine via a protection/alkylation/deprotection strategy, and 4'-methyl-2,2'-bipyridine-4-carboxylic acid using bromotripyrrolidinophosphonium hexafluorophosphate as the coupling reagent.⁶⁸ Dimethyldibenzidinium dichloride

was also used to synthesize ligand **52b** via coupling with 4-bromomethyl-4'-methyl-2,2'-bipyridine using cesium carbonate, in an attempt to prepare a ligand with a greater redox potential relative to **51b**.⁶⁸ For the same purpose, ligand **53b** was synthesized by substitution of *N,N*-dimethyl-benzidine by 4-bromomethyl-4'-methyl-2,2'-bipyridine followed by amide formation via coupling with 4'-methyl-2,2'-bipyridine-4-carboxylic acid.⁶⁸ Several compounds have been synthesized using precursors containing two pyridines already connected by a bridge and by adding bipyridines by continuation to produce ligands **15b**, **54b**, **55b**, and **56b**.⁶⁹ A similar approach was followed by Rehberg and Krönke in the synthesis of **57b**, which was made in several steps via two Michael addition reactions followed by a double dehydration.⁷⁰ Compounds **58b** and **59b** were obtained by an oxidative addition starting from the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine and an oxidizing agent such as either Br_2 , I_2 , or 1,2-dibromoethane, and their electronic absorption and emission properties have been investigated.⁷¹

A new family of siderophore, which includes compounds **60b** and **61b** (Table 3), has been synthesized by Collet and co-workers by starting from the triamine derivative of cyclotrimeratrylene and 4-formyl-4-methyl-2,2'-bipyridine or starting from the trimethylsilylate derivative of cyclotrimeratrylene and the acid 4-carboxyl-4'-methylcarboxylate-2,2'-bipyridine.⁷² Their iron complexes have been synthesized, and X-ray diffraction has been used to study the spin states coexisting in the iron-complexed ligands.⁷³ As with ligands **46b** and **47b**, **62b** can also be used for the construction of organometallic dendrimers.⁶⁴ Ligand **63b** was synthesized from 4,4'-dimethyl-2,2'-bipyridine and 1,1,1-tris(4-bromomethylphenyl)ethane using diisopropylamine/*n*-butyllithium as coupling reagents.⁷⁴ Its hemicage Ru(II) complex exhibited longer excited-state lifetimes and higher emission quantum yields than corresponding model complexes, which were attributed to a decrease in the rate of nonradiative decay via vibrational deactivation in the more rigid complexes.⁷⁴ Ligand **64b** comprises a tetranuclear Ru(II) complex of calix-[4]-arene which, like ligand **50b**, has been used as an anion binding element that possesses selectivity for the H_2PO_4^- anion.⁶⁷ Ligand **65b** was synthesized using 4-bipyridylbenzaldehyde, which was prepared using a modified Hantzsch pyridine synthesis, by reaction with pyrrole following classic Adler porphyrin synthesis, although reported yields were low with this method.⁷⁵ By treating **65b** with zinc acetate in an acetic acid-water mixture, **66b** was obtained.⁷⁵ Analysis of metal quenching of Cu(II)-bound **66b** was used to illustrate that the presence of multiple metal ion binding sites can be a significant factor in the concentration dependence of metal ion quenching.⁷⁵ Ligand **67b** was synthesized starting from 39,42-bis-(benzyloxy)calix[6]arene, which was converted to the tetracyano and tetramino analogues by treatment with bromoacetonitrile and reduction with diborane, respectively. The tetraamine was quenched with 4 equiv of 2,2'-bipyridine-4-carbonyl chloride to afford **67b** in 55% yield.⁷⁶ Further treatment of ligand **67b**

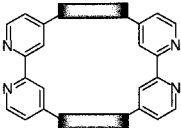


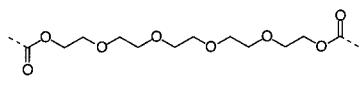
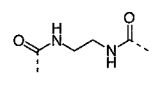
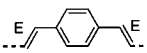
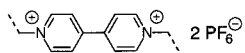
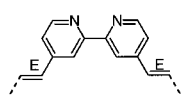
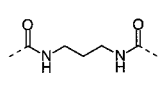
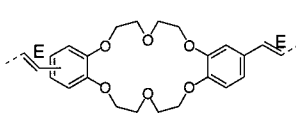
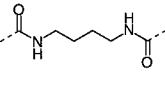
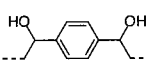
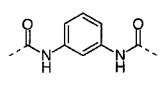
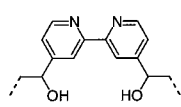
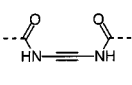
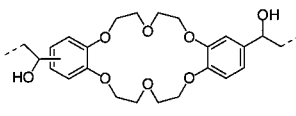

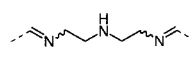

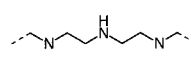


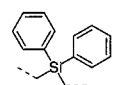
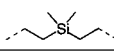
Table 3

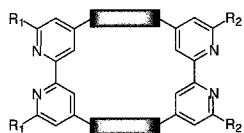
Number		Functional Groups	Reference	Number		Functional Groups	Reference
							
60b		R = CH ₃	72	62b		R = CH ₃	64
61b		R = CO ₂ CH ₃	72	63b		R = CH ₃	74
							
Number		Functional Groups	Reference	Number		Functional Groups	Reference
64b		R = H	67	67b		R = H	76
65b		R = H and M = H ₂	75	68b		R = COOC ₂ H ₅	77
66b		R = H and M = Zn(II)	75				

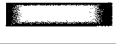
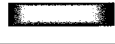






with *cis*- Δ -[Ru(bpy)₂(DMSO)Cl]PF₆ led to the formation of a complex retaining stereochemistry and showing a strong molar circular dichroism spectrum, in comparison with a racemate-treated **67b**, which had an inactive spectrum.⁷⁶ The related **68b**, which is

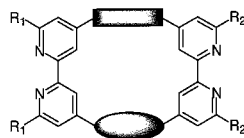
based on resorcinarene chemistry, was synthesized using similar coupling chemistry to **67b**. Ligand **68b** was used to bind chloride, acetate, and benzoate anions and showed a particular preference for carboxylate anions.⁷⁷

Table 4

					
Number		Reference	Number		Reference
1c		78	10c		80
2c		51	11c		81
3c		51	12c		82
4c		51	13c		82
5c		51	14c		82
6c		51	15c		82
7c		51	16c		85
8c		79	17c		84
9c		79	18c		87
			19c		87
			20c		65
			21c		66



Number		Functional Groups	Reference	Number		Functional Groups	Reference
22c		R ₁ = H R ₂ = 	87	23c		R ₁ = R ₂ = 	87
				24c		R ₁ = R ₂ = 	87




Number		Reference
25c		84

Table 4 (Continued)

Number	Ligand	Reference	Number	Ligand	Reference
26c		85			
27c		85	30c		88
28c		86			
29c		88	31c		89
Number		Reference	Number		Reference
32c		90	33c		90

B. 2,2'-Bipyridine Macrocycles Connected in Positions 4 and 4'

By connecting two 2,2'-bipyridines in positions 4 and 4' by different bridges, macrocycles having coordination sites directed toward the exterior of the macrocycle (exoditopic coordination sites) are formed. Most of these ligands have been synthesized so as to make exonuclear complexes with transition metals (from groups VIII, IX, and X). Complexes with transition metals from group VIII have been investigated in particular because of their photoinduced electron transfer behavior, which may be potentially useful for applications dealing with the transformation and storage of solar energy.⁹⁻¹²

Dürr et al. have synthesized the heterocyclic corannulene **1c** (Table 4), which possesses bridges based on poly(ethylene glycol), by reacting the dicesium salt of the acid 4,4'-dicarboxylate-2,2'-bipyridine with dibromopentaethyleneglycol in DMF with an overall yield of 3%.⁷⁸ On a related approach, Beer and co-workers have synthesized macrocycles **2c**, **3c**, and **4c**, which serve as novel chromophores for multielectronic photoredox processes in the form of their polynuclear complexes.⁵¹ Macrocycles **2c**, **3c**, and **4c**,

which all have double bonds, result from the dehydration of the corresponding tetraalcohols with phosphoric acid. Macrocycles **5c**, **6c**, and **7c** have been synthesized by a one-pot synthesis in four steps, by reacting 1 equiv of lithium diisopropylamide with 4,4'-dimethyl-2,2'-bipyridine, followed by the addition of 1/2 equiv of the appropriate aldehyde, 1 equiv of LDA, and finally another 1/2 equiv of aldehyde.⁵¹ The Schiff base **8c** is obtained by reacting 4,4'-diformyl-2,2'-bipyridine and triethylenetriamine in CH₃CN and is reduced by the action of NaBH₄ in methanol to give ligand **9c**.⁷⁹ The resulting cyclophane has been used to investigate mononucleotide (in its monophosphate form) complexation within the cavity of the cycle.⁷⁹ Macrocycle **10c**, synthesized in the form of its dinuclear Ru(II) complex, shows pronounced recognition for chloride anion relative to H₂PO₄⁻ anion.⁸⁰ The synthesis was accomplished in several steps starting by condensing 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine with a *tert*-butoxycarbonyl monoprotected ethylenediamine followed by Ru(bipy)₂Cl₂·2H₂O complexation. The complex thus obtained is deprotected in acidic media and condensed with the Ru(II) complex of bis(chlorocarbonyl)-2,2'-bipyri-

dine.⁸⁰ Cyclophane **11c** was synthesized starting from bis(bromomethyl)-2,2'-bipyridine, which was synthesized from 4,4'-dimethyl-2,2'-bipyridine via oxidation with chromium(VI) oxide in concentrated H₂SO₄, esterification in MeOH and H₂SO₄, reduction to the diol with NaBH₄ in EtOH, and finally bromination in 48% hydrobromic acid.⁸¹ High dilution conditions were then used to react the bis(bromomethyl)-2,2'-bipyridine with 4,4'-bipyridine in two steps to give the target compound **11c** in 25% yield.⁸¹ Beer et al. synthesized ligands **12c–15c** for use in selective anion recognition by equimolar addition of corresponding bis(acid chloride) and diamine in the presence of triethylamine base. These ligands show selective complexes with Cl⁻, H₂PO₄⁻, and OAc⁻ anions depending on ligand topology and receptor cavity size.⁸² In our laboratory, we have synthesized the macrocycles **16c–28c**. Many of these exo-ligands have been used as building blocks for the construction of unidimensional coordination polymers^{83–87} and were synthesized via the monolithium derivative of 4,4'-dimethyl-2,2'-bipyridine. Ligand **17c** was synthesized by the dehydrogenation of **16c**, and its Os(II) homobinuclear diastereomeric complexes were prepared, separated, and characterized by single-crystal X-ray diffraction, cyclic voltammetry, and absorption spectroscopy, which showed the presence of weak metal–metal interactions in this case.⁸⁴ During the course of synthesizing ligands **16c–24c**, we have also been successful in isolating the partially oxidized compound **25c**,⁸⁴ the tritopic homologue compound **26c**,⁸⁵ and the four 2,2'-bipyridine unit homologues of the type **27c**⁸⁵ and **28c**.⁸⁶

The first synthesis of a tritopic polypyridine ligand was performed by Bossmann and Dürr in 1992, using a templated single-step synthesis from Ru(II) complexes of hexacesium-bipyridine-tris-dicarboxylate and the α,ω -oligo-glycol-dichlorides under high dilution conditions to yield ligands **29c** and **30c**.⁸⁸ The Ru(II)-coronates of these ligands were prepared and demonstrated bimolecular electron transfer and relatively high photostabilities.⁸⁸ The bis[2]catenane **31c** incorporating 2,2'-bipyridine ligands was synthesized using a donor/acceptor template-directed synthesis and was used to make a mechanically interlocked coordination polymer bridged with Ag(I) ions.⁸⁹

Cryptand **32c**, possessing coordination sites directed to both the exterior and interior, has been synthesized by a (2 + 3) tripodal-type condensation, by reacting 3 equiv of 4,4'-diformyl-2,2'-bipyridine with 2 equiv of tris(2-aminoethylamine) in dry acetonitrile with an overall yield of 70%.⁹⁰ The Schiff base **32c** can be reduced by NaBH₄ to give cryptand **33c**.⁹⁰

IV. Ligands with 2,2'-Bipyridine Connected in Positions 4,4' and 5,5'

The group of von Zelewsky has conceived “chiragen” (chirality generator) ligands for the design and synthesis of molecular assembly-based structures possessing a predetermined chirality. This has proven especially useful for complexes with transition metals having an octahedral coordination geometry and containing more than one bipyridine in a *cisoid*

Table 5

Number	Ligand	Reference
1d		90
2d		90
3d		90
4d		92
5d		90
6d		90
7d		93
8d		95
9d		95
10d		95
11d		92
Number	Ligand	Reference
12d		94
13d		96
14d		97

configuration. To synthesize enantiomerically pure Ru(II) complexes, von Zelewsky and co-workers have prepared different ligands, which serve as a basis for the synthesis of polynuclear assemblies. Compound **1d** (Table 5) was obtained by an oxidative addition, by reacting the monolithium derivative of (-)-[4,5]-pinene-bipyridine with I₂.⁹⁰ Ligands **2d** and **3d** are

obtained by reacting the monolithium derivative of (-)-[4,5]-pinene-bipyridine with HCOOEt or Me₂-SiCl₂.⁹⁰ The CD spectra of ligands **1d**, **2d**, and **3d** in solution have allowed conformational information to be elucidated.⁹⁰ By preparing the same monolithium derivative and by reacting it with 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, and 1,6-dibromohexane, compounds **4d**,⁹² **5d**,⁹⁰ **6d**,⁹⁰ and **7d**,⁹³ respectively, which have saturated aliphatic chains of different length as spacers, have been synthesized. Many of these ligands have been reported to form stereoselective complexes with metals in which the helical chirality of the resulting complex is completely predetermined by the ligand.^{92,94} "Chiragen" molecules **8d**, **9d**, and **10d**, having xylene-based spacers connected in different positions, have also been synthesized.⁹⁵ In an attempt to increase the number of coordination sites, bis(bromomethyl)-2,2'-bipyridine has been used as a bridge that joins two pinene-bipyridine units in **11d**, which allows, in principle, the synthesis of a trinuclear species.⁹² The "superchiragen" molecule **12d**⁹⁴ has been synthesized by following procedures similar to those reported for ligand **1d**. Ligand **13d**, which is the endomacrocyclic equivalent of **10d**, forms circular helicates upon assembly with Ag(I) ions.⁹⁶ In changing the spacer bridge of this endo ligand from phenyl to naphthyl in **14d**, a polymeric infinite helix (of predetermined helicity) with Ag(I) ions is obtained, thus highlighting the importance of (among others) π -stacking interactions in the supramolecular assembly process.⁹⁷

V. Ligands with 2,2'-Bipyridine Connected in Positions 5 and 5'

A. Nonmacrocyclic 2,2'-Bipyridine Molecules Connected in Positions 5 and 5'

The dimethylene bridge of ligand **1e** (Table 6) results from an oxidative addition of the monolithium derivative of 5,5'-dimethyl-2,2'-bipyridine.⁷¹ The fluorescence emission of **1e**, which shows an intense fluorescence in contrast to the corresponding 2,2'-bipyridine, was suggested to be favored by the linking of the two bipyridines in **1e** to thus provide for the possibility of interaction between one electronically excited part of the molecule with the other part of the molecule in the ground state. Similar fluorescence behavior was observed for ligands **58b** and **59b**.⁷¹ Compound **2e** was obtained by an oxidative addition starting from 3,3'-ethylene dipyridine using a palladium-carbon catalyst.⁹⁸ By heating the sodium salt of 5-sulfonyl-2,2'-bipyridine to a temperature of 500° C under a nitrogen flow, ligand **3e** is obtained, which can be oxidized by K₂Cr₂O₇ to obtain compound **4e**.⁹⁹ Ligand **5e** has been synthesized by reacting 2 equiv of 5-bromomethyl-5'-methyl-2,2'-bipyridine with 1 equiv of *N,N*-dimethylethylenediamine in CH₃CN using K₂CO₃ as the base, and **5e** has been shown to coordinate chloride and bromide anionic guests, which has been investigated using NMR spectroscopy.¹⁰⁰ The reaction of the monolithium derivative of 5,5'-dimethyl-2,2'-bipyridine with diiodomethane leads to **6e** possessing a trimethylene bridge, and the complexation of this ligand with two Fe(II) atoms has

been reported to lead to a mesohelicate.¹⁰¹ Ligand bis-(2,2'-bipyridin-5-yl)ethyne **7e** has been synthesized by reacting 5-bromo-2,2'-bipyridine with 5-ethynyl-2,2'-bipyridine in the presence of diisopropylamine and [Pd(PPh₃)₄].¹⁰² The related bis(2,2'-bipyridin-5-yl)butadiyne **8e** has been synthesized by the oxidative addition of 5-ethynyl-2,2'-bipyridine in the presence of CuCl as a rigid and preorganized ditopic ligand.¹⁰² The reaction of the monolithium derivative of 5,5'-dimethyl-2,2'-bipyridine with 5,5'-bis(bromomethyl)-2,2'-bipyridine leads to ligand **9e**, and the latter in the presence of either Ni(II) or Fe(II), depending on the experimental conditions, gives a triple trinuclear propeller or a circular pentanuclear helix.¹⁰³ Likewise, a similar synthetic coupling procedure was used in the synthesis of ligands **10e** and **11e**.^{65,104} Ligand **10e** has been reported to form flattened tetrahedra with Ag(I) and Cu(II) ions.¹⁰⁴

Ligand **12e**, which is based on a combination of the cation complexing [2,2] macrocycle and two 2,2'-bipyridine units, has been synthesized by the reaction of 5-bromomethyl-2,2'-bipyridine on the crown ether and in the presence of base; however, it showed relatively poor alkali and alkaline earth metal cation extraction capability.¹⁰⁵ Ligand **13e** was also synthesized by alkylation using the same reagent.¹⁰⁶ Other macrocycles containing an amide linkage **14e**–**17e** were synthesized by the condensation of 2 equiv of 5-chlorocarbonyl-2,2'-bipyridine and the corresponding amine-containing crown ether. Titration and electrochemical data from Ru(II) complexes of these ligands suggest that both the crown ether portion and the bipyridine portion of the metal-bound ligand can cooperatively enhance the strength of chloride anion complexation.¹⁰⁷

Ligands **18e** through **20e** were synthesized from the corresponding dibrominated aromatic compound (benzene, naphthalene, and anthracene) with 5-ethynyl-2,2'-bipyridine in *n*-PrNH₂, which served as a general base and solvent, and [Pd⁰(PPh₃)₄] as catalyst, for energy transfer studies using well-defined, rigid molecular architectures.¹⁰⁸ In an attempt to design a system for the transfer of energy or electrons along a single preferred direction and over relatively long distances, Vögtle et al. synthesized the rigid alkyne **21e**.¹⁰⁹ This ligand has been synthesized via bis-alkene (*E,E*) **22e**, which is obtained using a Wadsworth–Emmons reaction. The bromination of the alkene gives the tetrabromo derivative **23e**, and the dehydrobromination of the latter in the presence of an excess of KOH gives the desired diyne **21e**. The Ru(II) and Os(II) complexes of **22e** have been investigated, and each unit displays an independent absorption spectrum and electrochemical properties, regardless of the presence of a second metal attached to the ligand. In the case of the mixed metal complex, quenching of Ru-based luminescence intensity by energy transfer to the Os-based unit has been reported.¹¹⁰ Adamantane-based ligands **24e** and **25e** were synthesized by coupling a bipyridine phosphonate ester with adamantanedicarboxaldehyde and biadamantanedicarboxaldehyde, respectively. Complexes containing Ru(II) and Os(II) metal ions with these ligands were also prepared. As in the case of

Table 6

Number		Functional Groups	Reference	Number		Functional Groups	Reference
1e		R ₁ = R ₂ = CH ₃ R ₃ = H	71	20e		R ₁ = R ₂ = R ₃ = H	108
2e		R ₁ = R ₂ = R ₃ = H	98	21e		R ₁ = R ₂ = R ₃ = H	109
3e		R ₁ = R ₂ = R ₃ = H	99	22e		R ₁ = R ₂ = R ₃ = H	109
4e		R ₁ = R ₂ = R ₃ = H	99	23e		R ₁ = R ₂ = R ₃ = H	109
5e		R ₁ = R ₂ = CH ₃ R ₃ = H	100	24e		R ₁ = R ₂ = R ₃ = H	111
6e		R ₁ = R ₂ = CH ₃ R ₃ = H	101	25e		R ₁ = R ₂ = R ₃ = H	111
7e		R ₁ = R ₂ = R ₃ = H	102	26e		R ₁ = R ₂ = CH ₃ R ₃ = H	112
8e		R ₁ = R ₂ = R ₃ = H	102	27e		R ₁ = R ₂ = R ₃ = H	113
9e		R ₁ = R ₂ = CH ₃ R ₃ = H	103	28e		R ₁ = R ₂ = R ₃ = H	114
10e		R ₁ = R ₂ = CH ₃ R ₃ = H	104	29e		R ₁ = R ₂ = R ₃ = H	114
11e		R ₁ = R ₂ = CH ₃ R ₃ = H	65	30e		R ₁ = R ₂ = R ₃ = H	115
12e		R ₁ = R ₂ = R ₃ = H	105	31e		R ₁ = R ₂ = R ₃ = H	116
13e		R ₁ = R ₂ = R ₃ = H	106	32e		R ₁ = R ₂ = CH ₂ Br R ₃ = H	117
14e		R ₁ = R ₂ = R ₃ = H	107	33e		R ₁ = R ₂ = CH ₂ PPh ₃ Br R ₃ = H	117
15e		R ₁ = R ₂ = R ₃ = H	107	34e		R ₁ = R ₂ = CH ₂ Br R ₃ = H	117
16e		R ₁ = R ₂ = R ₃ = H	107				
17e		R ₁ = R ₂ = R ₃ = H	107				
18e		R ₁ = R ₂ = R ₃ = H	108				
19e		R ₁ = R ₂ = R ₃ = H	108				

Table 6 (Continued)

Number		Functional Groups	Reference	Number		Functional Groups	Reference
35e		$R_1 = R_2 = R_3 = H$	118	38e			119
36e			119	39e		$R_1 = R_2 = R_3 = H$	120
37e			119	40e		$R_1 = R_2 = R_3 = H$	121
				41e		$R_1 = R_2 = R_3 = H$	121

ligand **22e** described above, each unit on the ligand displayed its own absorption spectrum and electrochemical properties, and in the mixed metal units containing Ru(II) and Os(II), electronic energy transfer was reported to occur.¹¹¹ The substitution of bis-(bromomethyl)-2,2'-bipyridine by 5-hydroxymethyl-5'-methyl-2,2'-bipyridine in the presence of base gives ligand **26e**.¹¹² The condensation of 5-ethynyl-2,2'-bipyridine with 5,5'-dibromo-2,2'-bipyridine gives ligand **27e**.¹¹³ In constructing molecules that have anion recognition capability, Beer et al. have synthesized ligands **28e** and **29e**.¹¹⁴ Ligand **28e** is obtained by treating 4,4'-bipyridine with 2 equiv of 5-bromomethyl-2,2'-bipyridine. Ligand **29e** is obtained by a grafting approach in which two 4,4'-bipyridines are attached to 5,5'-bis(bromomethyl)-2,2'-bipyridine followed by the addition of 2 equiv of 5-bromomethyl-2,2'-bipyridine.¹¹⁴ Ligand **30e**, synthesized from 5-carboxy-2,2'-bipyridine, 1,1'-carbonyldiimidazole, and 1,3-diaminopropane, has been reported to autoassemble in the presence of Fe(II) to a dinuclear triple propeller.¹¹⁵ With the goal of constructing molecular structures to transfer energy via photochemical processes, Belser et al. have synthesized ligand **31e** by condensing the acid chloride of 2,2'-bipyridine with a diamine derivative of anthracene.¹¹⁶



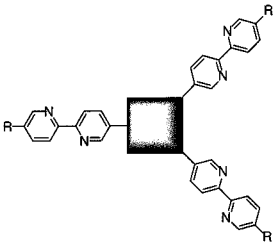
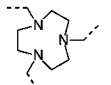
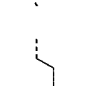
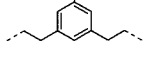
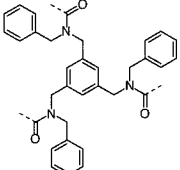
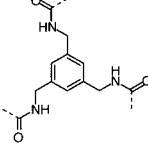
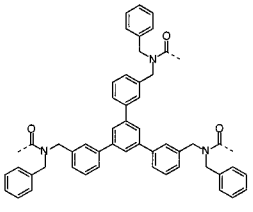
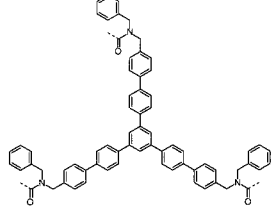
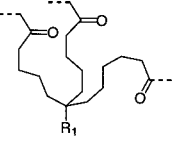
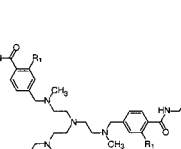

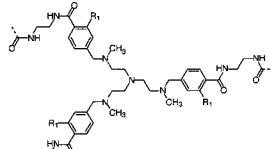
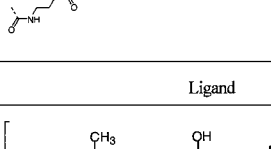
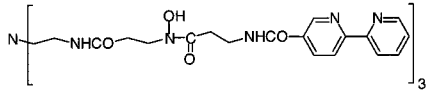
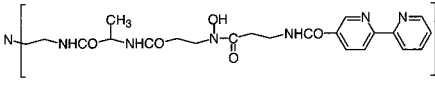
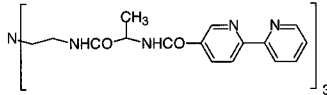
Wasielowski and co-workers synthesized pseudo-conjugated polymers containing chelating ligands that were based on model compounds **32e**, **33e**, and **34e**.¹¹⁷ Ligand **35e** was also synthesized by investigators in the field of bipyridine-containing polymers

as a model compound for comparing photophysical characteristics.¹¹⁸ Ligands **36e**, **37e**, and **38e**, which have been synthesized in several steps by solid-phase peptide synthesis, serve as sensors for the detection of metallic ions.¹¹⁹ These peptide-based complexing agents have been reported to have special fluorescent properties that supposedly result from photoinduced electronic transfer, which is dependent on the presence or absence of metals, with the anthracene group playing the role of acceptor and the dimethoxybenzene that of donor. In the absence of metallic ions there are almost no interactions between the chromophores, probably due to the large distance between acceptor and donor. In this case, a possible role of the metallic ion may be to reduce the distance between donor sites and the acceptors by fixing the conformation of the ligand as a result of complexation.¹¹⁹

In an attempt to synthesize a metalloprotein mimic, a Japanese group has synthesized a derivative of gramicidin containing two units of 2,2'-bipyridine **39e**.¹²⁰ On the basis of the β structure of gramicidin, the two 2,2'-bipyridines in the mimic are predisposed with one facing the other, thus allowing an efficient complexation of transition metals such as Co(II), Ni(II), Cu(II), and Zn(II). Ligands **40e** and **41e** were obtained by peptide coupling procedures using dicyclohexylcarbodiimide as the coupling agent, and Zn(II) binding to **40e** was shown to quench fluorescence emission.¹²¹

Macrocyclic **42e** (Table 7) has been synthesized by reacting 3 equiv of 5-bromomethyl-2,2'-bipyridine

Table 7

Number		Functional Groups	Reference	Number		Functional Groups	Reference
							
42e		R = H	122				
43e		R = CH ₃	123				
44e		R = CH ₃	125				
45e		R = H	127				
46e		R = COOC ₂ H ₅	126				
47e		R = COCl	126				
48e		R = COOH	126				
49e		R = COOC ₂ H ₅	126				
50e		R = H	127				
51e		R = H	127				
52e		R ₁ = CH ₃ ; R = H	128				
53e		R ₁ =  ; R = H	128				
54e		R = COOCH ₂ CH ₃ R ₁ = OH	129				
55e		R = COOCH ₂ CH ₃ R ₁ = OCH ₂ OCH ₃	129				
Number	Ligand	Reference	Number	Ligand	Reference		
56e		130	57e		130		
			58e		130		

with 1,4,7-triazacyclononane,¹²² and it has been reported to be a strong chelate for Ru(II).¹²² A similar synthetic procedure was used to synthesize **43e**, which was used as an Fe(II) chelate, and a Eu(III) complex of the same ligand has been reported to show a high luminescence quantum yield.^{123,124} Another ligand of this type, **44e**, has been synthesized by reacting the monolithium derivative of 5,5'-dimethyl-2,2'-bipyridine with 1,3,5-tri(bromomethyl)benzene. This ligand with its three bipyridine arms has been reported to complex a metal in an octahedral coordination geometry.¹²⁵ The Ru(II) and Os(II) com-

plexes of tripodal ligands **45e**–**51e** have been synthesized so that their electrochemical and luminescence properties could be investigated.^{126,127} In this case it was observed that the efficiency of energy transfer decreases by increasing the size of the spacer between the 2,2'-bipyridine units. Another tripodal ligand of the bipyridine type, **52e**, is reported to gel in toluene by establishing a network of hydrogen bonds (one molecule is supposedly capable of maintaining up to 8000 molecules of toluene within such an organogel).¹²⁸ The other part of this ligand complexes Fe(II) with an enhanced stability constant.

Table 8

Number	R ₁ R ₂ R ₃ R ₄	Reference
59e	R ₁ = R ₂ = R ₃ = R ₄ =	131
60e	R ₁ =R ₄ =	131
61e	R ₁ =R ₄ =	134
62e	R ₁ =R ₄ =	134
63e	R ₁ =R ₄ =	135
64e	R ₁ =R ₄ =	136
65e	R ₁ =R ₄ =	136
66e	R ₁ = R ₂ = R ₃ =	136

However, homologue **53e** does not present this toluene-gelation phenomenon.¹²⁸ Tripodal ligands **54e** and **55e**, containing both soft sites (comprising bipyridine units) and hard sites (comprising salicylamide units), have been investigated as redox molecular switches.¹²⁹ Ligands **56e**, **57e**, and **58e** were synthesized to investigate the effects of bipyridyl and hydroxamate ion binding groups for the development of molecular redox switches.¹³⁰ Treatment of ligands **56e** and **57e** with Fe(II) and ascorbic acid resulted in the oxidation of the metal to Fe(III), which could be reversed back to Fe(II) using ammonium persulfate; in contrast, however, the intermolecular ion translocation involving **58e** and a similar tris-hydroxamate-containing ligand failed to occur under identical conditions, suggesting the necessity of an intramolecular redox process in **56e** and **57e** in this case.¹³⁰

Based on calix-[4]-arene-type spacers, podands **59e** and **60e** have been synthesized¹³¹ for the purpose of forming lanthanide complexes, and their luminescence behavior has been investigated (Table 8).¹³² The bipyridine *N,N*-dioxide analogue of **60e** has also been prepared along with its Eu(III) complex.¹³³ Ligand **61e**, which has been synthesized by starting from intermediate **62e**, has been reported to function as a redox switch that possesses two hard complexation sites (hydroxamate) and two soft complexation sites (bipyridine).¹³⁴ In the presence of a hard metallic ion such as Fe(III), the two sites of the hydroxamate-type bind the metal ion and the two bipyridine units are divergent. Upon reducing Fe(III) to Fe(II), the ligand supposedly rearranges, thus allowing the complex-

Table 9

Number	Ligand	Notes	Reference
67e			137
68e			139
69e			123
70e		Ml ³⁺ = (none)	140
71e		Ml ³⁺ = Eu ³⁺	140
72e		Ml ³⁺ = Tb ³⁺	140
73e		X = Y = and X = Y =	141
74e		X = Y = and X = Y =	141
75e			88

ation of the Fe(II) by the bipyridines while the hard sites remain divergent. In complexing Ru(II) by two bipyridines of the calix-[4]-arene derivative **63e**, a luminescent complexing agent has been reported, which shows intensity variation as a function of pH.¹³⁵ Depending on whether the phenolic units of the free calix-[4]-arene are protonated or not, a photoinduced intramolecular electron transfer or a restoration of the Ru(II) trisbipyridyl luminescence units is reported to be observed in this case.¹³⁵ Ligands **64e** and **65e** were prepared by treating **63e** with ethyl 4-bromobutyrate and *N*-(3-bromopropyl)-pyrrole, respectively, and NaH in DMF. Solid lanthanide complexes of **64e** and **65e** could not be isolated in this study, and this was explained by the steric effect of the appended substituents in forcing the chelating bipyridine units apart.¹³⁶ Ligand **66e** was synthesized starting from propoxycalix-[4]-arene by reaction with NaH and 5-bromomethyl-5'-methyl-2,2'-bipyridine, and its Eu(III), Tb(III), and Gd(III) complexes have been prepared.¹³⁶

Baret et al. synthesized the chiragen-based ligand **67e** (Table 9) in an attempt to prepare enantiopure triple helicates. The key synthetic step in the synthesis of **67e** relies on a Krönke-type reaction between (–)-myrtenal and a pyridinium salt intermediate that originates from 2-acetyl-5-alkoxycarbonylpyridine.¹³⁷ The stereospecific self-assembly of a binuclear Fe(II) triple helicate using **67e** has been reported.¹³⁸ Ligand **68e**, which was synthesized by coupling 5-bromomethyl-2,2'-bipyridine and 1,4,8,11-tetraazacyclotetradecane under basic conditions, was used as a sensor in its Ru(II) complexed form. It was used to extract stability constants and rate data for macrocyclic complexation of Cu(II) and Ni(II) via fluorimetric titration.¹³⁹ The macrocyclic polyamine **69e** was synthesized in a manner similar to **43e**, starting from 5-(bromomethyl)-5'-methyl-2,2'-bipyridine, and it has been characterized by mass spectrometry, UV spectroscopy, and ¹H NMR.¹²³ Ligands **70e** through **72e** possess a β -cyclodextrin scaffold for the organization of six bipyridine moieties. These ligands are synthesized in a one-pot procedure (82% yield) based on a phosphinimine approach, which uses the reactants heptakis-[6-azido]- β -cyclodextrin and an excess of 5-aminomethylene-5'-methyl-2,2'-bipyridine in the presence of triphenyl phosphane.¹⁴⁰ The catenane **73e**, synthesized from amide **74e** by Vögtle and co-workers, possesses 2,2'-bipyridine groups bearing sulfonamide functions, which act to block the free rotation of one of the two macrocycles.¹⁴¹ The bipyridines have been grafted on the catenane by reacting 5-bromomethyl-2,2'-bipyridine with selectively deprotonated sulfonamide functions. Finally, ligand **75e** belongs to the same family as ligands **29c** and **30c**, and it shows high photostability of its Ru(II) complex.⁸⁸

B. 2,2'-Bipyridine Macrocycles Connected in Positions 5 and 5'

Ligand **1f** (Table 10) is in the cryptand family of calix-[4]-barrelands, which has been so named because of its arrangement in the form of a barrel.¹³¹ The macrobicycles **2f** and **3f** result from a 2 + 3

condensation between the tris(2-amino-ethyl)amine and 5,5'-diformyl-2,2'-bipyridine.¹⁴² The binuclear bis-Cu(I) and trinuclear-Ag(I) complexes of ligand **2f** were prepared, their ¹H NMR behavior was investigated, and the crystal structure of the Ag(I) complex of **2f** was determined.¹⁴² The tris(bipyridine) macrobicyclic ligand **3f** allows for the endo-complexation of three Ag(I) ions and has been published jointly by different investigators.¹⁴² Macrobicycle **4f** has been obtained by three 2,2'-bipyridine assemblage units connected in positions 5 and 5' and two spacer benzene units substituted in positions 1, 3, and 5.¹²⁶ This macrobicycle has been reported to bind Fe(II) in the center of the cage with an extraordinarily high stability constant for a ligand of such large size.¹²⁶ Other macrobicycles of even greater size such as **5f**, **6f**, **7f**, and **8f** that possess a conical cavity have been synthesized for the complexation of organic molecules.^{143,144} The calix-[4]-barrel **9f** constitutes another member of the same family as **1f**.¹³¹ Finally, the reaction of the meso-tetra($\alpha,\alpha,\alpha,\alpha$ -*o*-aminophenyl)porphyrin with 5,5'-diformyl-2,2'-bipyridine leads to the bis-porphyrin **10f** which after reduction gives the octaamine compound **11f**.¹⁴⁵ It is interesting to note that the preparation of this sandwich compound does not require high dilution reaction conditions, due to the preorganization of the building blocks and their intermediates.

VI. Ligands with 2,2'-Bipyridine Connected in Positions 6 and 6'

A. Nonmacrocyclic 2,2'-Bipyridine Molecules Connected in Positions 6 and 6'

Ligand **1g**⁷¹ (Table 11) as well as its derivatives having methyl groups either in positions 4 and 4' or in positions 5 and 5' and no methyl substituents **2g**¹⁴⁶ were obtained by oxidative addition starting from the corresponding monolithium derivatives. The product bis(2,2'-bipyridyl)ethylene **3g** has been reported by performing a Wittig–Horner reaction.¹⁴⁷ Ligand **4g** was synthesized from monomer bipyridine units bearing amine and aldehyde functional groups, and it was used to form helicates using Ag(I) and Cu(I) with the potential for displaying self-generation and self-replication processes based on the reversibility of the imine bond.¹⁴⁸ Ligands **5g**¹⁰⁵ through **9g**¹⁶³ containing lateral oligopyridine arms have been synthesized by reacting derivatives of (bromomethyl)- or (chloromethyl)-bipyridines with crown ethers in the presence of a base, and the ¹H NMR behavior of Cu(I) complexes with some of these ligands has been investigated. Liquid membrane transport experiments have revealed that the double-armed crown ethers can exhibit superior cation binding capability relative to the corresponding lariat ethers in these ligand systems.¹⁰⁵ Ligands **10g**, **11g**, and **12g** have been synthesized in a similar manner and formed complexes with Cu(I) in organic solvents,¹⁴⁹ and **11g** and **12g** were shown to selectively extract Zn(II) from solution.¹⁴⁹

Ligands **13g**–**17g** have been reported to provide double recognition of Ag(I) and Cu(I) cations using the combined binding capability of the pseudo-thia-

Table 10

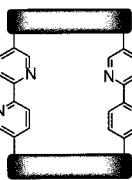


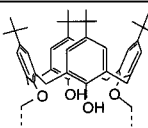
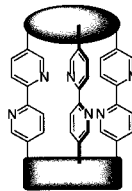





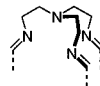
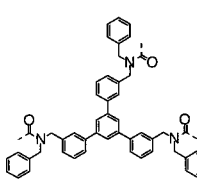
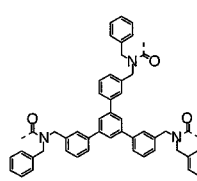
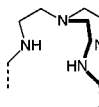
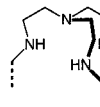
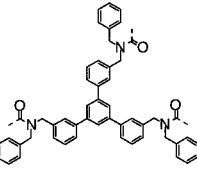
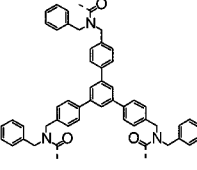
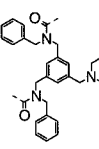
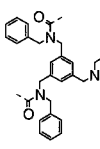
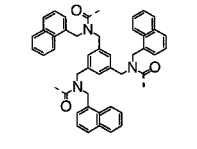
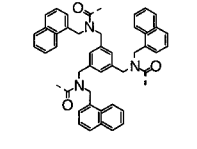
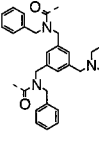
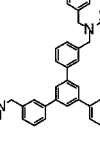
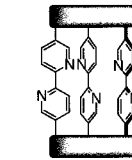


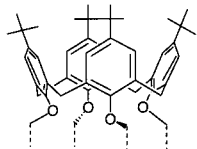
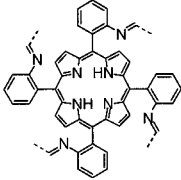
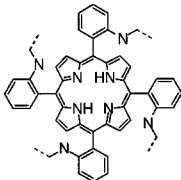
							
Number		Reference	Number		Reference		
1f		131					
							
Number			Reference	Number			Reference
2f			142	6f			143
3f			142	7f			143
4f			126	8f			144
5f			143				
							
Number		Reference	Number		Reference		
9f		131	10f		145		
			11f		145		

Table 11

Number		Functional Groups	Reference	Number		Functional Groups	Reference
1g		R ₁ = CH ₃ R ₂ = R ₃ = H	71	17g		R ₁ = CH ₃ R ₂ = H R ₃ =	150
2g		R ₁ = R ₂ = R ₃ = H	146				
3g		R ₁ = CH ₃ R ₂ = R ₃ = H	147				
4g		R ₁ = CH ₃ R ₂ = R ₃ = H	148				
5g		R ₁ = CH ₂ OCH ₃ R ₂ = R ₃ = H	105	18g		R ₁ = CH ₃ R ₂ = R ₃ = H	151
6g		R ₁ = CH ₃ R ₂ = R ₃ = H	163				
7g		R ₁ = CH ₂ OCH ₂ OCH ₃ R ₂ = R ₃ = H	105				
8g		R ₁ = R ₂ = R ₃ = H	163				
9g		R ₁ = R ₂ = R ₃ = H	163	19g		R ₁ = CH ₃ R ₂ = R ₃ = H	152
10g		R ₁ = CH ₃ R ₂ = H R ₃ =	149				
11g		R ₁ = CH ₃ R ₂ = H R ₃ =	149	20g		R ₁ = CH ₃ R ₂ = R ₃ = H	152
12g		R ₁ = CH ₃ R ₂ = H R ₃ =	149				
13g		R ₁ = CH ₃ R ₂ = H R ₃ =	150	21g		R ₁ = CH ₃ R ₂ = R ₃ = H	152
14g		R ₁ = CH ₃ R ₂ = H R ₃ =	150	22g		R ₁ = R ₂ = R ₃ = H	153
15g		R ₁ = CH ₃ R ₂ = H R ₃ =	150	23g		R ₁ = R ₂ = H R ₃ = SCH ₃	153
16g		R ₁ = CH ₃ R ₂ = H R ₃ =	150	24g		R ₁ = R ₂ = R ₃ = H	154
				25g		R ₁ = R ₂ = H R ₃ = SCH ₃	154
				26g		R ₁ = R ₂ = R ₃ = H	155
				27g		R ₁ = CH ₃ R ₂ = R ₃ = H	156
				28g		R ₁ = CH ₃ R ₂ = R ₃ = H	157

Table 11 (Continued)



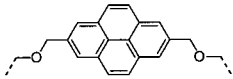
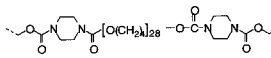
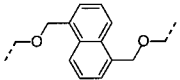
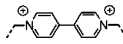
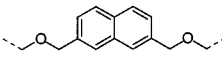
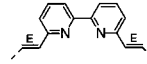
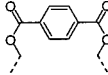
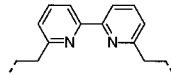
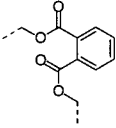

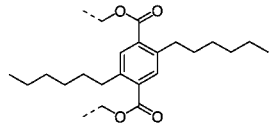
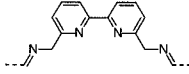
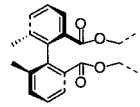
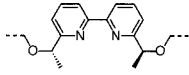
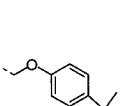
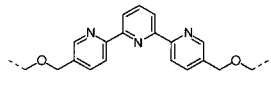
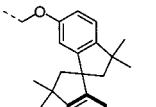
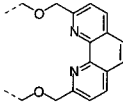
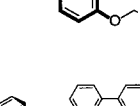
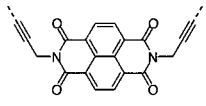
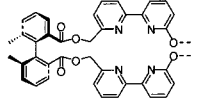
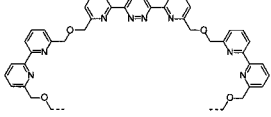
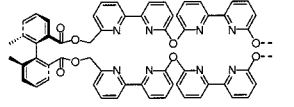
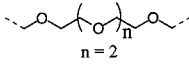
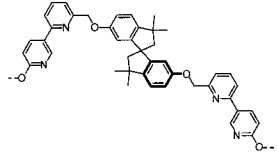
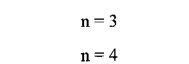
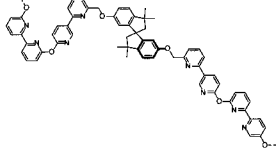
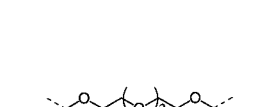

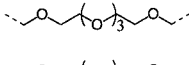
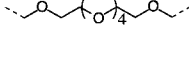





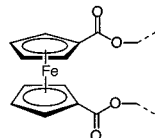
Number		Functional Groups	Reference	Number		Functional Groups	Reference
29g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	157	44g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	162
30g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	158	45g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	163
31g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	158	46g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	164
32g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	159	47g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	164
33g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	159	48g		$R_1 = R_2 = R_3 = \text{H}$	165
34g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	159	49g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	148
35g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	160	50g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	167
36g		$R_1 = \text{CH}_2\text{Br}$ $R_2 = R_3 = \text{H}$	160	51g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	168
37g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	160	52g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	169
38g		$R_1 = \text{CH}_2\text{Br}$ $R_2 = R_3 = \text{H}$	160	53g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	170
39g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	160	54g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	171
40g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	160	55g		$R_1 = \text{CH}_3$ $R_2 = \text{H}$ $R_3 =$	151
41g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	160	56g		$R_1 = \text{CH}_3$ $R_2 = \text{H}$ $R_3 =$	172
42g		$R_1 = \text{CH}_3$ $R_2 = R_3 = \text{H}$	160	57g		$R_1 = \text{CH}_3$ $R_2 = \text{H}$ $R_3 =$	172
43g		$R_1 = R_2 = R_3 = \text{H}$	161	58g		$R_1 = R_2 = R_3 = \text{H}$	172
				59g		$R_1 = R_2 = R_3 = \text{H}$	172
				60g		$R_1 = R_2 = R_3 = \text{H}$	102
				60g		$R_1 = R_2 = R_3 = \text{H}$	102
				61g		$R_1 = \text{H}$ $R_2 = R_3 = \text{CH}_3$	59
				62g		$R_1 = \text{H}$ $R_2 = R_3 = \text{CH}_3$	59
				63g		$R_1 = \text{H}$ $R_2 = R_3 = \text{CH}_3$	174
				64g		$R_1 = R_2 = R_3 = \text{H}$	175

Table 11 (Continued)



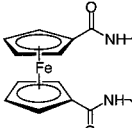
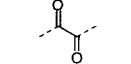
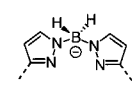
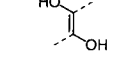
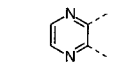
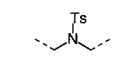
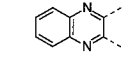
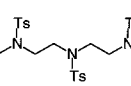
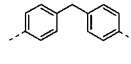
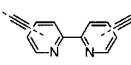
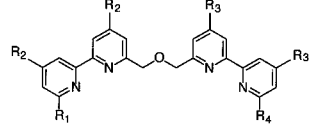
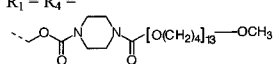
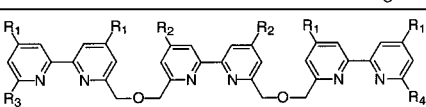
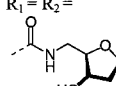
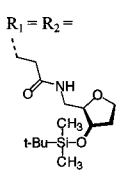
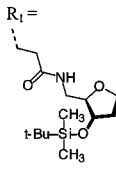


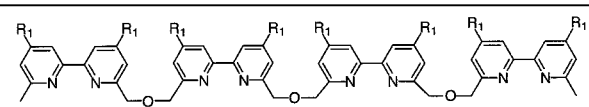
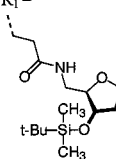
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66g		$R_1 = R_2 = R_3 = H$	177	70g		$R_1 = R_2 = R_3 = H$	180
67g		$R_1 = R_2 = R_3 = H$	180	71g		$R_1 = R_2 = R_3 = H$	163
68g		$R_1 = R_2 = R_3 = H$	180	72g		$R_1 = R_2 = R_3 = H$	163
				73g		$R_1 = R_2 = R_3 = H$	181
				74g		$R_1 = R_3 = H$ $R_2 = CH_3$	102
							
Number	Functional Groups	Reference	Number	Functional Groups	Reference		
75g	$R_1 = R_4 = CH_3$ and $R_2 = R_3 = H$	183	81g	$R_1 = R_4 = CHO$ and $R_2 = R_3 = H$	185		
76g	$R_1 = CH_2OH$, $R_2 = R_3 = H$ and $R_4 = CH_3$	182	82g	$R_1 = CH_3$, $R_2 = R_3 = H$ and $R_4 = CH_2O(CH_2)_4O(t-Bu)$	185		
77g	$R_1 = CH_2Br$, $R_2 = R_3 = H$ and $R_4 = CH_3$	182	83g	$R_1 = CH_3$, $R_2 = R_3 = H$ and $R_4 = CH_2O(CH_2)_4OH$	185		
78g	$R_1 = CH_2Br$, $R_2 = R_3 = CH_2CH_2CO_2(t-Bu)$ and $R_4 = CH_3$	184	84g	$R_1 = R_4 = CH_3$ and $R_2 = R_3 = CONEt_2$	166		
79g	$R_1 = CH_2Br$, $R_2 = H$, $R_3 = CH_2CH_2CO_2(t-Bu)$ and $R_4 = CH_3$	184	85g	$R_1 = R_4 = CH_3$ and $R_2 = R_3 = CO_2(t-Bu)$	166		
80g	$R_1 = R_4 = CH_2OH$ and $R_2 = R_3 = H$	188	86g	$R_1 = R_4 =$ 	$R_2 = R_3 = H$	186	
							
Number	Functional Groups	Reference	Number	Functional Groups	Reference		
87g	$R_1 = R_2 = H$, $R_3 = CH_2Br$ and $R_4 = CH_3$	160	99g	$R_1 = R_2 =$ 	$R_3 = R_4 = CH_3$	184	
88g	$R_1 = R_2 = H$, $R_3 = CH_2OH$ and $R_4 = CH_3$	160	100g	$R_1 = R_2 =$ 	$R_3 = R_4 = CH_3$	184	
89g	$R_1 = R_2 = H$ and $R_3 = R_4 = CH_3$	183	101g	$R_1 =$ 	$R_2 = H$ and $R_3 = R_4 = CH_3$	184	
90g	$R_1 = R_2 = H$, $R_3 = CH_3$ and $R_4 = CH_2O(CH_2)_4O(t-Bu)$	185					
91g	$R_1 = R_2 = CO_2Et$ and $R_3 = R_4 = CH_3$	190					
92g	$R_1 = R_2 = CONEt_2$ and $R_3 = R_4 = CH_3$	166					
93g	$R_1 = R_2 = CO_2(t-Bu)$ and $R_3 = R_4 = CH_3$	166					
94g	$R_1 = CH_2CH_2CO_2(t-Bu)$, $R_2 = H$ and $R_3 = R_4 = CH_3$	166					
95g	$R_1 = R_2 = CH_2CH_2CO_2(t-Bu)$ and $R_3 = R_4 = CH_3$	166					
96g	$R_1 = R_2 = CO_2H$ and $R_3 = R_4 = CH_3$	184					
97g	$R_1 = R_2 = CH_2CH_2CO_2H$ and $R_3 = R_4 = CH_3$	184					
98g	$R_1 = CH_2CH_2CO_2H$, $R_2 = H$ and $R_3 = R_4 = CH_3$	184					
Number		Functional Groups	Reference	Number		Functional Groups	Reference
							

Table 11 (Continued)

Number	Functional Groups	Reference	Number	Functional Groups	Reference
102g	R ₁ = H	166, 182	103g	R ₁ = CONEt ₂	166
			104g	R ₁ = CO ₂ (t-Bu)	166

Number	Functional Groups	Reference	Number	Functional Groups	Reference
105g	R ₁ = R ₂ = R ₃ = H	166, 182	110g	R ₁ = CH ₂ CH ₂ CO ₂ (t-Bu) and R ₂ = R ₃ = H	166
106g	R ₁ = R ₂ = H and R ₃ = CH ₃	167	111g	R ₁ = CH ₂ CH ₂ CO ₂ H and R ₂ = R ₃ = H	184
107g	R ₁ = R ₂ = CONEt ₂ and R ₃ = H	166	112g	R ₁ =  and R ₂ = R ₃ = H	184
108g	R ₁ = R ₂ = CO ₂ (t-Bu) and R ₃ = H	166			
109g	R ₁ = R ₂ = COOEt and R ₃ = H	189			

crown and bipyridine.¹⁵⁰ In this system, Cu(I) is bound to the bipyridine moieties to give the corresponding pseudo-thiacrowns, and Ag(I) is taken into the thiacycrown ring selectively and in a manner showing positive allosterism using Cu(I) as an effector for certain ligands in this series.¹⁵⁰ Ligand **18g** was synthesized in 49% yield by treating pentaethylene glycol with the corresponding bromide compound containing two bipyridines linked via an oxa bridge, and its helical tetrahedral adducts with Cu(I) have been reported, which do not racemize at room temperature, supposedly due to the greater degree of complexation afforded by the four bipyridine moieties present.¹⁵¹ Similar complexation behavior has also been investigated for ligands **19g–21g**, which contain chiral auxiliaries attached to the polyether.¹⁵² The Cu(I) complex of **21g** has been reported to exist as a mixture of two inert diastereomers at room temperature.¹⁵²

Linking two bipyridines with a 1,3-phenylene spacer results in ligands **22g** and **23g**, which spontaneously self-assemble into double helicates upon treatment with Cu(I), Ag(I), Co(II), and Ni(II) ions.¹⁵³ The biphenyl homologues of these ligands, **24g** and **25g**, were also prepared and formed double-helical structures with a range of transition-metal cations in which the observed intermetallic separation distance within the helix increased relative to **22g** and **23g**.¹⁵⁴ It is interesting to note that in the helicate structures obtained with ligands **22g–25g**, π - π stacking interactions do not appear to be of importance in the stabilization of the structures, which is in contrast to linear oligobipyridine systems where these interactions have been shown to be significant (vide supra).¹⁵⁴ The disulfide **26g** was synthesized from 6-(2-aminophenyl)-2,2'-bipyridine by converting the amine to a thiol, and its Cu(I) and Ag(I) complexes were obtained, in which the ligand imposes a relatively rigid pseudo-tetrahedral geometry about the metal centers.¹⁵⁵

In addition to the proven capability of oligopyridine compounds to act as ligands for soft metals, com-

pounds that increase their hard metal binding ability have also been synthesized. Harding and co-workers have incorporated significant steric limitations that act to control the assemblage of binuclear homochiral and heterochiral complexes of the [Zn₂L₂]⁴⁺ type with the bis-bipyridine series comprising **27g**,¹⁵⁶ **28g**,¹⁵⁷ and **29g**.¹⁵⁷ They report ligand **29g** to selectively give the heterochiral complex, ligand **28g** to give approximately 60% helicate, and ligand **27g** to give 48% helicate with Zn(II) in deuterated chloroform solution.¹⁵⁶ These results have been explained by the steric requirements of the bridges, since in the helicate structures, the bridges are positioned closer together than in the nonhelicate structures, and consequently this arrangement is disfavored with bridges that are sterically demanding.¹⁵⁶ The Zn(II) complexes of ligands **28g**, **30g**,¹⁵⁸ and **31g**¹⁵⁸ were synthesized, and the effect of the substitution pattern of the naphthalene spacer was investigated. It was found that **28g** and **31g** formed [2 + 2] complexes, and **30g** formed a [1 + 1] complex in this case.¹⁵⁸ Ligands **32g**, **33g**, and **34g** containing ester linkages have been obtained by reacting different acid chlorides with 6-hydroxymethyl-6'-methyl-2,2'-bipyridine, and they form selective mononuclear complexes in the presence of Ag(I) and Cu(I).¹⁵⁹ By introducing a chiral bridge between the oligopyridines as in compounds **35g–42g**, Siegel and co-workers were able to enantioselectively synthesize a Cu(I)-containing helicate structure.¹⁶⁰ It is interesting to note that the chiral integrity reported in these helicate complexes suggests that stereochemical information may be transmitted over distances of up to 1 nm along a molecular scaffold (as observed in these structures).

The sterically constrained ligand **43g** was synthesized, and its Cu(I) and Cu(II) complexes were characterized by X-ray diffraction.¹⁶¹ Amide-containing polyether **44g** was synthesized from 6-[(chloro-carbonyl)oxy]methyl]-6'-methyl-2,2'-bipyridine and α -[(piperazinylcarbonyl)oxy]- ω -(piperazinylcarbonyl)-poly(oxytetramethylene) containing 28 oxytetramethylene repeat units and was reported to form

double-stranded helices with Cu(I) ions.¹⁶² By reacting 6-bromomethyl-6'-methyl-2,2'-bipyridine with 4,4'-bipyridine in CH₃CN, Beer and co-workers have isolated the viologen **45g**.¹⁶³ The compound **46g** comprising three 2,2'-bipyridine units and an unsaturated bridge has been synthesized by using Wittig-Horner condensation procedures.¹⁶⁴ The corresponding saturated bridging ligand **47g** has been prepared from ligand **46g** by a four-step reaction sequence starting from commercially available compounds. Ligand **47g** has been reported to selectively form a trinuclear double propeller in the presence Cu(I), and **46g** has been reported to give a mixture of several products under the same experimental conditions.¹⁶⁴ More recently, the Ni(II) and Fe(II) complexes of ligand **48g** were obtained, in which the metal cation adopts a distorted octahedral coordination environment only to the 5,5'-disubstituted bipyridine moiety at the bridge, with the 6-monosubstituted bipyridine sidearms unbound in these cases.¹⁶⁵ Ligand **49g** belongs to the same family as **4g**, and its helicates with Ag(I) have also been investigated.¹⁴⁸ The chiral tris(bipyridine) **50g** has been synthesized and was reported to give a trinuclear helicate structure.^{166,167} Ligand **51g** forms heterotopic helicates via a process of autoassembly.¹⁶⁸ Phenanthroline-bridged **52g** was prepared by reacting 1 equiv of the dilithium salt of 2,9-bis(hydroxymethyl)-1,10-phenanthroline with 2 equiv of 6-bromomethyl-6'-methyl-2,2'-bipyridine.¹⁶⁹ Its complexes with Cu(I), Ag(I), and Zn(II) cations were shown to self-assemble into double-stranded helicates, with the Zn(II) helicate being the first trinuclear double-stranded zinc helicate.¹⁶⁹ Ligand **53g** was synthesized in three steps from 6-bromo-6'-methyl-2,2'-bipyridine in the presence of Zn(II) and *o*-dimethoxybenzene, and it assembles into a chiral and helical metallomacrocyle.¹⁷⁰ Ligand **54g** incorporates several functional features that coordinate Cu(I) and has been reported to assemble into large (external diameter of 28 Å and cavity diameter 11 Å) nanocyclic architectures comprising four ligand molecules and nine Cu(I) ions in nearly quantitative yield.¹⁷¹ Ligands **55g**, **56g**, and **57g** were synthesized from 6-(bromomethyl)-6'-methyl-4,4'-bis(4-methoxyphenyl)-2,2'-bipyridine, which was obtained by brominating 6,6'-dimethyl-4,4'-bis(4-methoxyphenyl)-2,2'-bipyridine with *N*-bromosuccinimide, and the corresponding oligoethylene glycol using sodium hydride in refluxing THF, in a fashion similar to that reported for ligands **18g–21g**.^{151,172} Similar synthetic procedures were used in the synthesis of ligands **58g** and **59g**.¹⁷² An interesting observation is the reported K⁺ ion binding selectivity of Cu(I)-bound ligand **57g**, which supposedly is a result of both pseudo-crown ring size and electrostatic repulsion between the bound Cu(I) and K⁺ metal cations.¹⁷² The synthesis of ligands **60g**,¹⁰² **61g**,^{59,102,173} **62g**,^{59,102} and **63g**,¹⁷⁴ comprising ethynyl, diethynyl, and tetraethynyl bridges, has been described for the same bridges in positions 4 and 4' and in positions 5 and 5'. Ligands **64g**¹⁷⁵ and **65g**¹⁷⁶ were prepared by the stoichiometric reaction of 6-(hydroxymethyl)-2,2'-bipyridine and 6-aminomethyl-2,2'-bipyridine, respectively, with chlorocarbonylferrocene, and were both characterized

using cyclic voltammetry. Ligand **64g** has been reported to form a mixed tetranuclear helicate with Cu(I) ions, which has been characterized by X-ray diffraction,¹⁷⁵ and ligand **65g** has been reported to form a complex with H₂PO₄⁻ by utilizing the amide protons in a hydrogen bonding arrangement between host and guest.¹⁷⁶ Ligand **66g** has been reported to form a double propeller via self-assembly in the presence of potassium, and its complexes with K⁺, Cu(II), Gd(III), and Tl⁺ have been synthesized.^{177,178} The combination of coordination and electrostatic interactions afforded by **66g** in the binding of metal ions is similar to the binding afforded by borocryptand systems.¹⁷⁹ The oligo-(2,2'-bipyridyl)pyrazines **67g** and **68g** have been prepared through the intermediate compounds **69g** and **70g**, and their crystal structures were studied using single-crystal X-ray diffraction.¹⁸⁰ Ligand **67g** results from the reaction of 1,2-diaminoethane with **69g** followed by treatment with chloroaniline, and ligand **68g** is obtained by reacting *o*-phenylenediamine with ligand **69g**. Beer and co-workers have synthesized ligands **71g** and **72g** with the spacer groups *p*-toluenesulfonamide and *N,N,N'*-tritosyldiethylenetriamine, respectively.¹⁶³ These two ligands form monometallic complexes in the presence of Ag(I) cation. Ligand **73g**, which contains two 2,2'-bipyridines connected by a diphenylmethane-type spacer, can act either as a *N,N'*-bidentate donor or as a *C,N,N'*-tridentate donor, which leads to a metallocycle.¹⁸¹ These have been complexed with Ru(II), and two coordination modes have been observed in these complexes. The synthesis of tris(bipyridine) **74g** connected by ethynyl-type bridges in positions 4,4' and 5,5' on 2,2'-bipyridine has been described above (vide supra).¹⁰²

In the linear oligopyridine series comprising oxy-(bismethylene) bridges, compound **75g**¹⁸² is the smallest ligand. The Cu(I) complex of **75g** was characterized by NMR and X-ray diffraction and was one of the first examples of double-stranded helix formation with bipyridines, in which two molecular strands wrap around two Cu(I) ions and thus hold the structure together.¹⁸³ Ligands **76g**,¹⁸² **77g**,¹⁸² **78g**,¹⁸⁴ and **79g**¹⁸⁴ serve as intermediates in the synthesis of higher homologues (tri-, tetra-, and penta-bipyridine subunit-containing ligands). Treatment of **80g** with oxalyl chloride in the presence of NEt₃ yields ligand **81g**, which was synthesized as an intermediate for the synthesis of unsymmetrical higher oligobipyridines.¹⁸⁵ The synthesis of ligand **82g** was performed by reacting 6-(hydroxymethyl)-6'-methyl-2,2'-bipyridine, which is available via a *N*-oxidation route, with 6'-(bromomethyl)-6-(4''-tert-butylxytetramethylenoxymethyl)-2,2'-bipyridine.¹⁸⁵ Ligand **83g** was synthesized from **82g** in 94% yield by treatment with 4 N HCl in dioxane under reflux, for the same purpose of unsymmetrical higher oligobipyridine synthesis as for **81g**.¹⁸⁵ Amide and ester functions were introduced onto ligands **84g** and **85g** in an attempt to organize functional groups within the double helical structure already known from unsubstituted **75g**.¹⁶⁶ The polymer **86g** is also synthesized from **80g** and has been reported to form a dinuclear helicate complex in the presence of Cu(I) cation.

Table 12

Number	Ligand	Reference	Number	Ligand	Reference
113g		151	119g		195
114g		105	120g		194
115g		192	121g		195
116g		180	122g		194
117g		193	123g		195
118g		195			

The tris(bipyridines) **87g** and **88g** are intermediates in the synthesis of compounds **39g** and **41g**.¹⁶⁰ Ligand **89g** forms helicates in the presence of Cu(I) or Ag(I) cations.^{183,187} Ligand **90g** is synthesized by treating **77g** with 6-(4'-*tert*-butyloxymethyl)-6'-(hydroxymethyl)-2,2'-bipyridine, which is also a precursor for the synthesis of ligand **82g**.¹⁸⁵ Most of ligands **84g–112g** (with the exception of **86g**,¹⁸⁶ **87g**,¹⁶⁰ **88g**,¹⁶⁰ and **90g**¹⁸⁵) were first synthesized by Lehn and co-workers by employing variations on Williamson condensation between a dibromo-bipyridine-containing compound and a corresponding diol. These ligands provide a basis for demonstrating

selectivity, cooperativity, and self-recognition in supramolecular helicate formation.^{166,167,184,187–190} Their use in the synthesis and design of helicates has been reviewed.¹⁹¹

The unsymmetrical ionophore **113g** (Table 12) belongs to the same ligand family as **57g**. Its Cu(I) complex has been studied using NMR for the purpose of investigating the possibility of molecular chirality as a function of temperature.¹⁵¹ Ligand **114g** is an extension of the concepts introduced in ligands **5g–8g**, and it was shown to preferentially bind Cu(II) and Zn(II) to Ba(II) (reverse selectivity to ligand **8g**).¹⁰⁵ By heating 6-cyano-2,2'-bipyridine with NaH

under an inert atmosphere, tris(2,2'-bipyridyl)pyrazine **115g** is obtained.¹⁹² The compound tetrakis(2,2'-bipyridyl)pyrazine **116g** has been prepared by heating compound **70g** in the presence of an excess of ammonium acetate.¹⁸⁰ The tris(6-(2,2'-bipyridyl))-phosphine **117g** is synthesized by mixing 6-bromo-2,2'-bipyridine with *n*-BuLi followed by the addition of PCl₃.¹⁹³ Other polybipyridine ligands that are based on acyclic polyamine derivatives such as ligands **118g**, **119g**, and **120g** or macrocycles such as ligands **121g**, **122g**, and **123g** have also been reported, and their polynuclear metal complexes with Re(II), Fe(II), and Re(bpy)(CO)₃Cl have been synthesized.^{194,195}

The calix-[4]-arene **124g** (Table 13), obtained by deprotection of **125g** by trifluoroacetic acid, can act as a molecular redox switch with its two hard complexation sites (comprising hydroxamate) and two soft complexation sites (comprising bipyridine).¹³⁴ Ligand **126g** has been synthesized, and its Eu(III) complex showed a high extinction coefficient and luminescence quantum yield (15% reported).¹³² The related ligand **127g** has been reported to extract sodium picrate from the solid to a chloroform phase containing the ligand.¹⁹⁶ In addition the Tb(II) complex of **127g** was reported to show intense metal luminescence.¹⁹⁶ Introduction of a chiral substituent, (*S*)-2-methylbutyl, close to the bipyridine coordination site in ligand **128g** via reaction of the calixarene with (+)-(*S*)-1-bromo-2-methylbutane in the presence of K₂CO₃ resulted in Cu(I) helicates possessing a 30% induced enantiomeric excess.¹⁹⁷ The synthesis of ligands **129g**–**133g** as well as of ligand **134g** has been accomplished by the regioselective O-alkylation of calix-[4]-arene, with the product depending on the base used, and these ligands have been reported to be Cu(I) and Cu(II) complexing agents.^{198–200} Ligands **135g**–**138g** were synthesized in order to obtain luminescent complexes with Eu(II) and Tb(III), by alkylating the calixarene with 6-bromomethyl-2,2'-bipyridine and α -chloro-*N,N*-diethylacetamide under basic conditions.¹⁹⁶ Ligands **135g** and **137g** were reported to sensitize Eu(II) and Tb(II) luminescence.¹⁹⁶ The calix-[4]-resorcinarene **139g** in the form of an "octopus" has been reported to simultaneously complex eight molecules of CoCl₂.²⁰¹

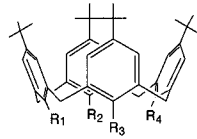
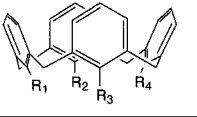
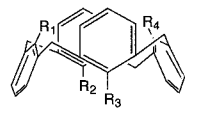
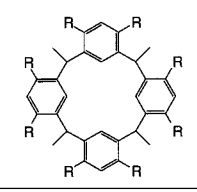
B. 2,2'-Bipyridine Macrocycles Connected in Positions 6 and 6'

One of the first macrocycles connecting two 2,2'-bipyridine units in positions 6 and 6' was ligand **1h** (Table 14), which was synthesized by using a zinc templating effect in 1980. According to this procedure, 6,6'-dichloro-2,2'-bipyridine was mixed with (NH₄)₂-ZnCl₄, and the crude product was demetalated.²⁰² Several years later, the yield for the formation of macrocycle **1h** was improved by reacting 6,6'-dichloro-2,2'-bipyridine with 6,6'-diamine-2,2'-bipyridine in a sealed ampule heated at 230 °C, thus making the 6,6'-dichloro-2,2'-bipyridine react with gaseous ammonia solution under autogenous pressure.²⁰³ This macrocycle has been reported to exist in both the imine and amine form, with the equilibrium between the two forms being sensitive to the

nature of the solvent environment.²⁰² Ligand **2h** has served as a model compound and results from the successive reaction of NaH and *n*-butyl iodide on cycle **1h**.²⁰³ Macrocycle **3h** is synthesized by monoalkylating ligand **1h** with *n*-hexyl bromide and NaOH as base, and its tautomeric structure was investigated and shown to be different in methanol and chloroform solutions.²⁰³ Compound **4h** was accidentally obtained during the preparation of *N,N*-ditosyl-6,6'-bis(aminomethyl)-2,2'-bipyridine, when 6,6'-dichloro-2,2'-bipyridine was mixed with the monosodium salt of tosylamide in absolute ethanol under reflux.²⁰⁴ The detosylation of this ligand in concentrated H₂SO₄ leads to the macrocyclic diamine **5h**,²⁰⁴ which has served as a synthetic starting point for a large number of other macrocycles, simplest among these being **6h**, which was synthesized by *N*-methylation using CH₂O in HCO₂H.²⁰⁵ Macrocycles containing the aza functional group **7h**–**11h** have been studied as a model of ion transport through liquid-phase membranes and have been compared with other types of functional groups.²⁰⁶ Macrocycle **10h** is reported to selectively complex Li⁺ and is synthesized in three steps, starting with the treatment of α -cyanoacetamide in DMF with NaH and the subsequent addition of 6,6'-dibromo-2,2'-bipyridine. The dinitrile macrocycle thus obtained is then alkylated by *n*-butyl iodide in the presence of NaH, leading to the monoalkylated derivative **9h** and the *trans* and *cis* derivatives, **7h** and **8h**, respectively, which can be chromatographically separated.²⁰⁷ By treating the mixture of isomers with sulfuric acid at 70 °C, compound **10h** is obtained, which like ligand **11h** can exist as one of two tautomeric forms.²⁰⁶ Ligand **12h** was synthesized starting from 6,6'-bis(chloromethyl)-2,2'-bipyridine and results from a mixture of glycols generated in situ via a fragmentation process.²⁰⁸ The tetra-*N*-oxide derivative of ligand **13h**²⁰⁹ as well as the macrocycle **14h**²¹⁰ have been synthesized for the purpose of complexing lanthanides and for the investigation of their fluorescence characteristics. Variable temperature NMR-based investigations of **12h** indicate a restricted rotation of the amide bonds at ambient temperature and suggest a fixed syn conformation of this molecule in solution, in which the bipyridines are in a "face-to-face" arrangement on the ligand.²¹¹ Ligands **15h**,²¹² **16h**,²¹³ **17h**,²¹⁴ **18h**,¹⁹⁴ **19h**,²¹³ and **20h**²¹³ have been synthesized by reacting the appropriate halogenated derivatives with macrocycle **5h** in the presence of Na₂CO₃ or NEt₃ (following the addition of the halogenated derivative) in CH₃CN. The macrocyclic polyamine **21h**, which has been characterized by single-crystal X-ray diffraction, has been synthesized by reacting 6,6'-bis(chloromethyl)-2,2'-bipyridine with the sodium salt of *N,N*-ditosylethylene-diamine in DMF with an overall yield of 5%.²⁰⁴ Ligand **22h** has been synthesized in two steps by reacting the corresponding diacid chloride of 2,2'-bipyridine with crown ethers in the presence of NEt₃.²¹⁵

To provide additional experimental confirmation of the strong fluorescence of the lithium complex of ligand **10h**, Ogawa and co-workers synthesized macrocycle **23h**²¹⁶ by condensing 6,6'-diamine-2,2'-bipy-

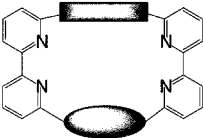
Table 13












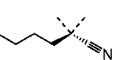

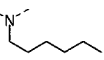

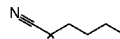
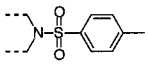
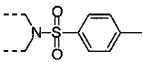









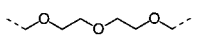
											
Number	R ₁	R ₂	R ₃	R ₄	Reference	Number	R ₁	R ₂	R ₃	R ₄	Reference
124g					134	129g					198
125g					134	130g	R ₁ = R ₄ = OH				199
126g					132	131g	R ₁ = R ₂ = R ₃ =			R ₄ = OH	199
127g					196	132g	R ₁ = R ₂ =			R ₃ = R ₄ = OH	199
128g					197	133g	R ₁ = R ₂ = R ₃ = R ₄ =				199
											
Number	R ₁	R ₂	R ₃	R ₄	Reference	Number	R ₁	R ₂	R ₃	R ₄	Reference
134g	R ₁ = R ₄ = OH				200	136g	R ₁ = R ₄ = OH				196
135g					196	137g	R ₁ = R ₂ = R ₃ = R ₄ =				196
											
Number	R ₁	R ₂	R ₃	R ₄	Reference						
138g	R ₁ = R ₂ = R ₃ = R ₄ =				196						
											
Number	R	Reference									
139g	R =	201									

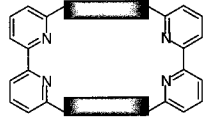
ridine with 6,6'-bis(acid chloride)-2,2'-bipyridine. Ligands **24h** and **25h** represent two in a family of several macrocyclic receptors containing bipyridine groups linked to two amino acids from the series comprising proline and valine. Only the valine-based macrocycles, which have the two pyridine rings

preorganized for binding, act to complex metals.²¹⁷ The macrocycles were also shown to bind phenolic hydroxyl groups via hydrogen bonding to the amide groups of the bridging chain.²¹⁷ Macrocycles **26h** and **27h**,²¹⁸ which have been characterized by X-ray crystallography, have been synthesized via four

Table 14



Number			Reference	Number			Reference
1h			202, 203	7h			206
2h			203	8h			206
3h			203	9h			207
4h			204	10h			206
5h			204	11h			206
6h			205	12h			208



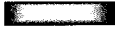


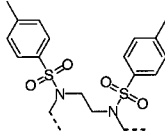
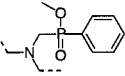
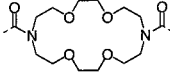


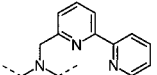
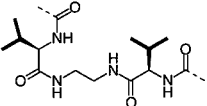
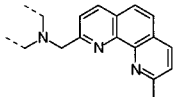
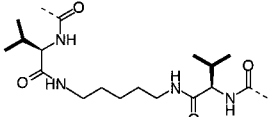
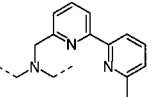
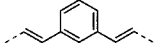
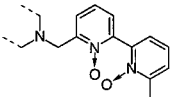
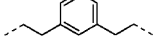
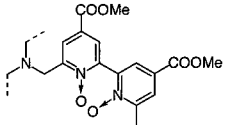
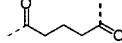
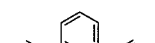
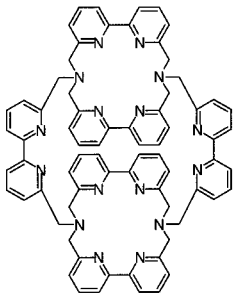
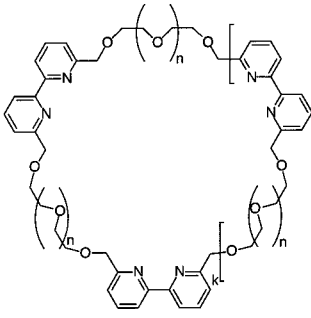




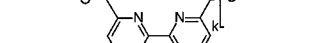
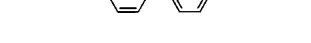

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14h		210	22h		215
15h		212	23h		216
16h		213	24h		217
17h		214	25h		217
18h		194	26h		218
19h		213	27h		218
20h		213	28h		219
			26h		218

Table 14 (Continued)

Number		Reference	Number		Reference	
27h		218	33h		222	
28h		219	34h		223	
29h		219	35h		n = 2	223
			36h		n = 3	223
			37h		n = 4	223
			38h		n = 5	223
30h		220	39h		208	
			40h		n = 2	208
			41h		n = 3	208
			42h		n = 4	208
31h		221	43h		219	
32h		222	44h		224	
			45h		224	
Number		Reference	Number		Reference	
46h	 R = H	225	54h		228	
47h	 R = H	227	55h	 R = H	228	
48h	 MeO ₂ C R = H CO ₂ Me	225	56h	 R = H and X = Br R = H and X = NO ₂ R = H and X = CO ₂ Et	228	
			57h		228	
			58h		228	
49h	 MeO ₂ C R = CO ₂ Me CO ₂ Me	225	59h	 R = H	225	
50h	 R = H	227	60h	 R = H	226	
51h	 R = H	225	61h	 R = H	226	
52h	 R = H	228	62h	 R = H	229	
53h	 EtO ₂ C S CO ₂ Et R = H	228			H ₃ COOC R = H COOCH ₃	

Table 14 (Continued)

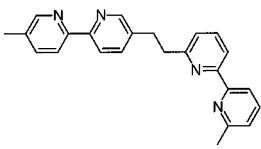
Number	Ligand	Reference	Number	Ligand	Reference
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			65h		208
			66h		208
			67h		208
			68h		208
			69h		208
			70h		208
			71h		208

concerted Wittig reactions between 6,6'-diformyl-2,2'-bipyridine and *m*-xylenebis(triphenylphosphonium) bromide. The hydrogenation of intermediate **26h** by H₂/Pd–C gives macrocycle **27h**. Macrocycles **28h** and **29h** are intermediates that were synthesized enroute to cyclohexipyridine.²¹⁹ In addition to the dimer compound **30h**, which has two bridging CH₂–S–CH₂ units, Newkome and co-workers have also isolated a trimer derivative, which is not represented in the tables.²²⁰ Ligand **31h** containing thiol groups at the two bridges has been synthesized by reacting the 1,3,4-thiadiazolium derivative with 3,6-dioxo-1,8-diaminodiyloctane in DMF and in the presence of NEt₃.²²¹ Using a [2 + 2] template condensation between 6,6'-bis(aminomethyl)-2,2'-bipyridine with 2,6-diformyl-*p*-cresol in the presence of a lanthanide acetate, Martell and co-workers synthesized ligand **32h**, whose reduction leads to macrocycle **33h**.²²²

The 2:2 macrocycle of crown ethers **34h**, **35h**, **36h**, **37h**, and **38h** have been isolated and separated from their 1:1 homologues, during the reaction of the corresponding disodium salt of poly(ethylene glycol) with 6,6'-dibromo-2,2'-bipyridine.²²³ Given that the presence of a linked heteroatom in positions 6 and 6' on the bipyridine hinders metal complexation due to steric considerations, Newkome and co-workers synthesized macrocycles containing a methylene group between the poly(ethylene glycol) chain and the bipyridine, by reacting 6,6'-bis(chloromethyl)-2,2'-bipyridine with the corresponding polyglycolates to produce ligands **39h**, **40h**, **41h**, and **42h**.²⁰⁸ Macrocycle **43h** has been synthesized starting from the macrocycle **28h** by reaction with hydroxylamine in acetic acid. Other cyclohexipyridines **44h** and **45h** that contain substituents have been synthesized by following Kröhnke cyclization procedures.²²⁴ High yields in the syntheses of these macrocycles are explained by a cation templating effect of Na⁺ or NH₄⁺.²²⁴

A large number of macrobicyclic-type cryptand ligands **46h**–**62h**, which are capable of complexing cations such as Li⁺, Na⁺, as well as lanthanides, have been synthesized by Lehn and co-workers. Here only those cycles containing at least two bipyridine units are included.^{225–229} All of these cryptands have been synthesized by starting from the macrocycle **5h** or a derivative thereof. The macrotricyclic cylindrical cryptand **63h**, which has six bipyridines connected

Table 15

Number	Ligand	Reference
1i		230

in positions 6 and 6', has been obtained as a secondary product during the synthesis of macrobicyclic **47h**, by reacting 6,6'-dibromo-2,2'-bipyridine with 6,6'-diamino-2,2'-bipyridine in a single step.²²⁵

Finally, Newkome et al. synthesized the bipyridine-containing crown-ether derivatives **64h**–**71h** by direct nucleophilic displacement, as in the case of **12h**, which is in the same ligand family.²⁰⁸ Complexes with Co(II), Cu(II), Zn(II), and Pd(II) have been reported using these ligands.²⁰⁸

VII. Ligands with 2,2'-Bipyridine Connected in Mixed Positions

Ligand **1i** (Table 15) was synthesized by condensing 6-bromomethyl-6'-methyl-2,2'-bipyridine with the monolithium salt of 5,5'-dimethyl-2,2'-bipyridine according to the same procedures as for ligand **9e**. Its Cu(I) and Cu(II) double-stranded helical complexes were characterized by X-ray crystallography and were shown to have a distorted tetrahedral and tetragonal pyramidal geometry, respectively, which are significantly different from results obtained using the related ligands **9e** and **1g**.²³⁰

VIII. Polymeric Ligands Containing 2,2'-Bipyridine Units

There have been fewer reported polymeric ligands with 2,2'-bipyridine than for the case of the oligobipyridine ligands that are described above. Initial attempts at preparing polymers with bipyridine repeat units relied more upon postsynthetic immobilization. That is to say, methods were found to graft bipyridine-containing functionality onto an existing polymer strand. Although this method can have practical advantages over the direct copolymerization of a bipyridine monomer with other monomers (such as overcoming the synthetic challenge of polymerizing charged metal complexes of bipyridine),

it often provides less control over the resulting spatial distribution of bipyridine sites along a single polymer strand.

One of the earliest reports of using a grafting approach to attach bipyridine to an existing polystyrene polymer strand is ligand **1j** (Table 16), which was synthesized by Card and Neckers. Ring bromination and lithiation were used to covalently attach bipyridine so that less than 25% of the phenyl residues in a polystyrene-2% divinylbenzene polymer were brominated. Conversion from brominated phenyl residues to bipyridylphenyl residues occurred in greater than 50% yield, resulting in polymers containing one bipyridyl group for each seven to eight polystyrene phenyl residues.²³¹ Various metal complexes of **1j** were synthesized, and the palladium acetate-bound **1j** produced an active catalyst for the hydrogenation of olefins at ambient temperature and pressure.²³¹ Polyurea **2j** was the first reported polar bipyridine polymer, which was prepared from the copolymerization of a Pd(II) complex of 4,4'-diamino-2,2'-bipyridine by reaction with toluenediisocyanate. Following polymer synthesis, the Pd(II) was reduced to Pd(0) with lithium aluminum hydride, and the catalytic activity of the metal-containing **2j** for olefin hydrogenation was investigated.²³² Another approach involved the attachment of the bipyridine via amide linkage in polymer **3j** to an already synthesized *p*-aminostyrene/*N*-vinyl-pyrrolidone copolymer that was prepared via free radical polymerization. The bipyridine was attached using a mixed anhydride method with ethyl chloroformate and 2,2'-bipyridine-3,3'-dicarboxylic acid to create approximately 10% molar substitution along the polymer backbone based on the amount of Ru(II) bound.²³³ The luminescence of the Ru(II)-bound **3j** and quenching of the excited state with Fe(II), Co(II), and Cu(II) was investigated.²³³ Meyer and co-workers have attached bipyridine moieties via amide links in synthesizing **4j** by reacting 4'-methyl-2,2'-bipyridine-4-carboxylic acid in the presence of Castro's reagent on styrene-*p*-(aminomethyl)styrene copolymers, which were obtained by first converting styrene-*p*-(chloromethyl)styrene copolymers into their phthalimide derivatives and subsequently treating with hydrazine. Polymer **4j** was synthesized as a mixed Ru(II) and Os(II) complex, and unreacted amino groups on the strand were capped with acetic anhydride.²³⁴ The metal-bound **4j** exhibits metal-to-ligand charge transfer absorptions and emissions.²³⁴ Meyer and co-workers also prepared polymer **5j** by derivatizing a polystyrene prepared by living anionic polymerization in a manner similar to that described above for **4j**.²³⁵ The incorporation of a Ru(II) complex of **5j** into a sol-gel/polymer composite material helped overcome stability issues of ion leaching to external solution for various technological applications.²³⁶ Yet another approach to amide formation in bipyridine-containing polymers was proposed in synthesizing polymers **6j**–**12j** by reacting 2,2'-bipyridine-5,5'-dicarboxylic acid with various aromatic diamines in hexamethylphosphoramide containing lithium chloride. The phase transition behaviors and Ru(II) complexes of the resulting polymers were investigated.²³⁷

Polymer **13j** was synthesized by reacting pyromellitic dianhydride with bipyridine in the presence of ZnCl₂, and its Fe(III), Cr(III), Ni(II), and Cu(II) complexes have been prepared.²³⁸ Polymer **14j** was synthesized by free radical polymerization of 4-vinyl-4'-methyl-2,2'-bipyridine in toluene using azobisisobutyronitrile as initiator.²³⁹ Polymers **15j** and **16j** were obtained by condensing 4-chloromethyl-4'-methyl-2,2'-bipyridine onto existing poly(vinyl alcohol) and polyethyleneimine, respectively.²³⁹ The attachment of the same bipyridine diacid as in the case of **2j** was accomplished via an ester linkage in polymer **17j** using nucleophilic displacement chemistry on an already synthesized polystyrene-polychloromethylstyrene copolymer, which was prepared by free-radical polymerization.^{240,241} The photophysics of the resulting Ru(II)-bound **17j** were investigated.²⁴⁰ Other investigators have started from the 4,4'-diacid and reacted it in a poly(phosphoric acid) medium with 4,6-diamino-1,3-benzenediol dihydrochloride, 2,5-diamino-1,4-benzenediol dihydrochloride, and 2,5-diamino-1,4-benzenedithiol dihydrochloride to produce polymers **18j**, **19j**, and **20j**, respectively.²⁴² The same set of reactions can be performed starting from the 5,5'-diacid to produce polymers **21j**, **22j**, and **23j**, respectively.²⁴² The Ru(II) complexes of these polymers have also been synthesized. In addition, investigation of the phase behavior indicated that the more rigid main chains in **18j**–**20j** gave rise to lyotropic liquid crystal phases, whereas the more flexible main chains of **21j**–**23j** produced polymers that did not show any anisotropy.²⁴² Polymer **24j** was prepared using nucleophilic displacement of Cl⁻ under basic conditions on a styrene-chloromethylstyrene copolymer. Mixed Ru(II) and Os(II) metal complexes were synthesized along **24j**, and energy transfer and quenching experiments were performed in which the anthryl groups acted as energy transfer relays in providing a spatial link between the metal-bound chromophores along the polymer backbone.^{241,243} Polymers **25j** through **28j** were synthesized by incorporating mesogenic bipyridinediyl units into a liquid-crystalline polyester using the PbO-promoted coupling between an ester and an alcohol to drive the polymerization. The introduction of Fe(II) and Cu(II) into the resulting copolymers was performed, and the effect of the metal incorporation on the liquid crystalline polymer characteristics was investigated. Polymers **25j** and **26j** containing up to a critical amount of metal remained smectic, whereas **27j** and **28j** showed the presence of a nematic mesophase.²⁴⁴ Polymer **29j**, like **17j** and **24j**, was synthesized using nucleophilic displacement of chloride under basic conditions by complexes containing 4-methyl-4'-(hydroxymethyl)-2,2'-bipyridine on an existing styrene-chloromethylstyrene copolymer. Polymer complexes with Ru(II) and Os(II) attached to the bipyridines of **29j** were prepared, and energy transfer processes in the resulting polymer system were investigated.²⁴⁵ The 2,2'-bipyridyl-branched **30j** was synthesized from the partially hydrolyzed poly(*N*-acetyleneimine) (prepared using aqueous NaOH) by reacting 3-[4-(4'-methyl-2,2'-bipyridyl)]propanoic acid in the presence of dicyclohexylcarbodiimide, for the purpose of syn-

Table 16

Number	Polymer Ligand	Reference	Number	Polymer Ligand	Reference
1j		231	14j		239
2j		232	15j		239
3j		233	16j		239
4j		234	17j		240
5j		235	18j		242
6j		237	19j		242
7j		237	20j		242
8j		237	21j		242
9j		237	22j		242
10j		237	23j		242
11j		237	24j		243
12j		237	25j		244
13j		238	26j		244
			27j		244
			28j		244
			29j		245

Table 16 (Continued)

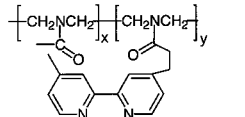
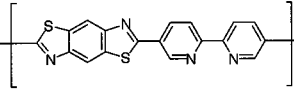
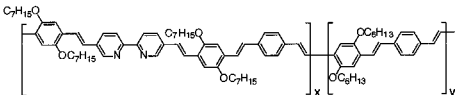
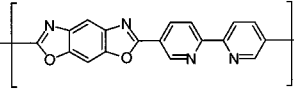
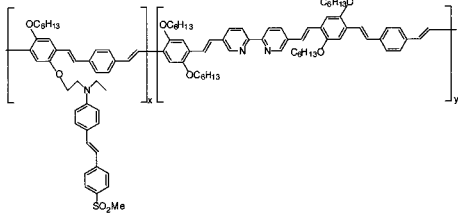
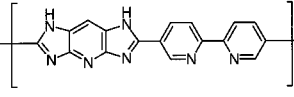
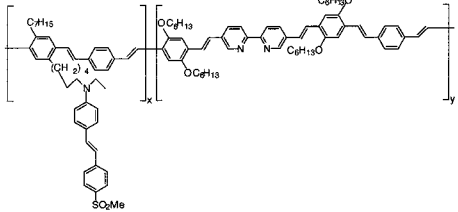
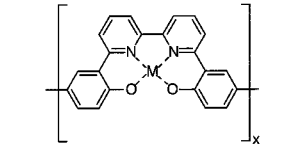
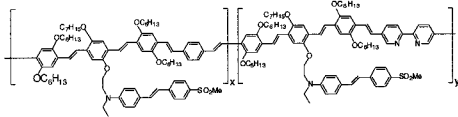
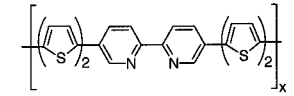
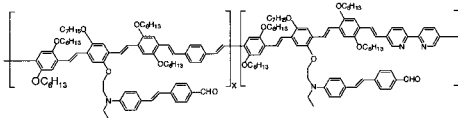
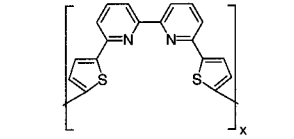
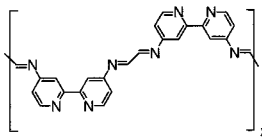
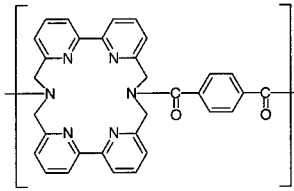
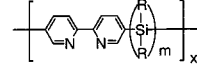
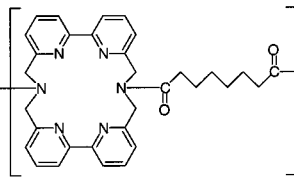
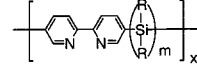
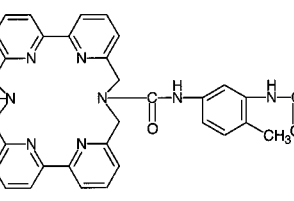
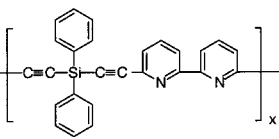
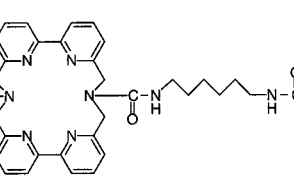
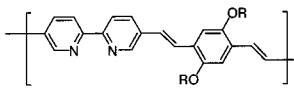
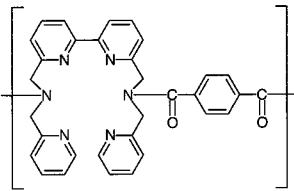
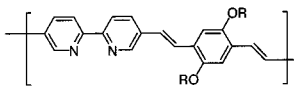
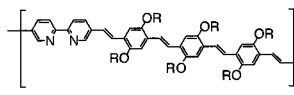
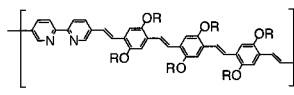
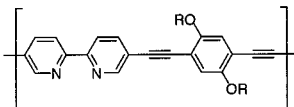
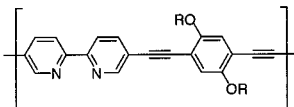
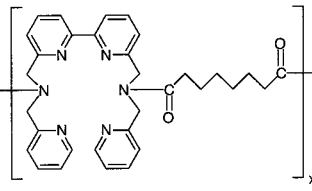
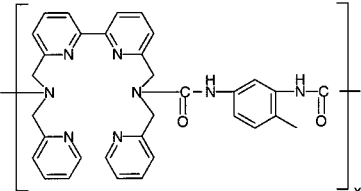
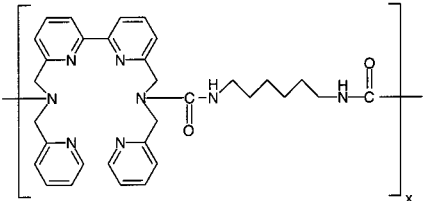
Number	Polymer Ligand	Reference	Number	Polymer Ligand	Reference
30j		x / y = 10 / 1 246	46j		252
31j		247	47j		252
32j		248	48j		252
33j		248	49j		253
34j		248	50j		254
35j		248	51j		255
36j		63	52j		256
37j		m = 2 R = Pr 249	53j		256
38j		m = 1 R = n-C6H13 249	54j		256
39j		250	55j		256
40j		R = 2-ethyl-hexyl 251	56j		256
41j		R = C10H21 117			
42j		R = 2-ethyl-hexyl 251			
43j		R = C10H21 117			
44j		R = (CH2)17CH3 118			
45j		R = (CH2)7CH3 118			

Table 16 (Continued)

Number	Polymer Ligand	Reference	Number	Polymer Ligand	Reference
57j		256	58j		256
			59j		256

thesizing polyoxazoline hydrogels prepared via metal coordination in water.²⁴⁶

One of the first examples of the direct copolymerization of charged Ru(II) bipyridine complexes using the Heck coupling reaction was provided by Peng and Yu in the synthesis of polymer **31j**.²⁴⁷ Other polymers such as **32j**–**35j** have also been reported using the Heck coupling reaction by the same authors.²⁴⁸ In the latter case, model reactions were investigated to elucidate the structural defects caused by side reactions of the Heck reaction. Eliminating the effect of these side reactions was reported to enhance the photorefractive response time of the polymer.²⁴⁸ Polymer **36j** was synthesized by the condensation of a diamine and dialdehyde using the same chemistry as for ligand **45b**, resulting in strands of approximately 20 repeat units. The Ru(II) complexes of **36j** were synthesized and compared with that obtained from model compound **45b**.⁶³ Polymers that contain a Si σ unit and a 2,2'-bipyridine π system in their backbone have also been synthesized. Thus, poly-(tetrapropylsilylanyl-2,2'-bipyridine-5,5'-diyl) **37j** and poly(dihexylsilylanyl-2,2'-bipyridine-5,5'-diyl) **38j** have been synthesized by dehalogenative coupling of 1,2-bis(2-bromo-5-pyridyl)tetrapropylsilane and bis-(2-bromo-5-pyridyl)dihexylsilane, respectively, using a Ni(0) catalyst to produce strands of 11 000 and 9 000 molecular weights, respectively, for the two polymers.²⁴⁹ The ruthenium complexes of **37j** and **38j** were also prepared and investigated for photoconductivity that was suggested to be the result of excitation in the bound Ru(II)-ligand moiety.²⁴⁹ A diphenylsilylene polymer **39j** containing main chain acetylene and bipyridyl groups has been synthesized by palladium-catalyzed cross-coupling of 6,6'-dibromo-2,2'-bipyridine and diethynyldiphenylsilane, and its Cu(I) complex has been synthesized by reaction with Cu(II) triflate followed by reduction with hydrazine monohydrate.²⁵⁰ Wasielewski and co-workers synthesized pseudo-conjugated polymers **40j** through **43j**, which contain chelating ligands that are based on precursors **32e**–**34e**. Upon complexing metals, these polymers supposedly undergo a conformational change, which permits the transformation of a partially conjugated polymer to a totally or quasi-totally conjugated one. These oligobipyridines in the non-

complexed state are reported to be not completely conjugated, because the dihedral angle given between pyridine planes is approximately 20°. However, upon metal ion chelation, the conformation of the bipyridine supposedly becomes planar, thus producing a totally conjugated polymer.^{117,251} Polymers **44j** and **45j** were synthesized by the Heck reaction of 5,5'-dibromo-2,2'-bipyridine and the corresponding 1,4-diethynyl-2,5-dialkoxybenzene, to give strands with a molecular weight of 23 350 for **44j** and 13 460 for **45j**. The polymers exhibited large fluorescence signatures and were compared with model ligand **35e**.¹¹⁸ The rigid-rod polymers **46j**, **47j**, and **48j** were synthesized by reacting 2,2'-bipyridine-5,5'-dicarbonyl dichloride with 2,5-diamino-1,4-benzenedithiol, 4,6-diamino-1,3-benzenediol, and 1,2,4,5-tetraaminopyridine, respectively. Polymer **48j** was reported to be the first benzobisimidazole polymer without any solubilizing pendants that exhibits lyotropic behavior.²⁵² Measurements of electrical conductivity gave values of 10⁻¹⁰ to 10⁻⁸ S/cm for the pristine polymers, 10⁻⁵ to 10⁻⁴ S/cm for polymers complexed with AgNO₃, and 25 to 42 S/cm after reduction of the Ag(I) to Ag(0) using NaBH₄.²⁵² Electrochemical polymerization was used to synthesize **49j**, **50j**, and **51j** from corresponding mono-bipyridine monomers.^{253–255} Cyclic voltammetry was used to investigate the electrochemistry of all polymers, and the metal in the center of ligand **49j** was exchanged with Mn(II), Cu(II), Co(II), Ni(II), and Zn(II).²⁵³

On the basis of model compounds **5h** and **13h**, polymers **52j**–**59j** were synthesized by treating the corresponding bipyridine monomer (**5h** for **52j**–**55j** and 6,6'-bis(2-picolyaminomethyl)-2,2'-bipyridine for **56j**–**59j**) with the corresponding diacid chloride (terephthaloyl chloride for **52j** and **56j** and suberoyl chloride for **53j** and **57j**) or diisocyanate (toluylene-2,4-diisocyanate for **54j** and **58j** and 1,6-diisocyanatohexane for **55j** and **59j**). The influence of the monomer composition on the degree of rigidity in the copolymer was investigated, and it was concluded that the polyureas possess a lower polymer degradation temperature than the corresponding polyamides.²⁵⁶ It is interesting to note that the polyamide **56j** forms stable 1:1 complexes with transition metals Co(II), Ni(II), and Cu(II), whereas the similar poly-

vide **52j** only forms a complex with Cu(II), even in the presence of excess amounts of Co(II) and Ni(II).²¹¹

IX. Conclusion

The exhaustive database of bipyridine-containing molecules presented above summarizes the major types of molecules comprising at least two 2,2'-bipyridine units. Application statements on the uses of these molecules have been provided, along with their chemical structural and synthetic information. It is our hope that this review will be useful to investigators by providing insight into the types of bipyridine-based systems that have already been synthesized in this area.

X. Acknowledgment

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