Construction of Preorganized Polytopic Ligands via Palladium-Promoted Cross-Coupling Reactions

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Rigid preorganized multitopic ligands have been designed and synthesized. The Pd(0)-catalyzed cross-coupling reactions between ethynylated derivatives of bipyridine or terpyridine and the corresponding bipyridine or terpyridine halides or triflates provide access to various homo-ditopic, hetero-ditopic, homo-tritopic, and hetero-tritopic ligands bearing acetylene or diphenylacetylene central units in fair to excellent yields. Optimal conditions were found with $[Pd(PPh_3)_2Cl_2]$, CuI in THF and diisopropylamine at rt, or with $[Pd(PPh_3)_4]$ in benzene and diisopropylamine at 80 °C. When a phenylethynyl group is present in the molecule, the relevant conditions involve $[Pd(PPh_3)_4]$ in *n*-propylamine at 60 °C. Oxidative dimerization of the ethynylated derivatives in the presence of cupric salts and oxygen gives the corresponding homo-ditopic ligands bearing diacetylene or diphenyldiacetylene as a spacer in good yields. These methods provide a practical approach to the rational design of multichelating ligands for coordination of redox and photoactive transition metals.

Introduction

Nanometer-sized molecules have emerged as one of the most exciting goals of molecular synthesis related to materials science. In particular, molecular architectures in which highly-efficient photoinduced energy- or electron-transfer processes can take place over long distances have attracted a lot of recent interest.[1,2] A variety of potential applications such as artificial photosynthesis,[3] photocatalysis,[4] molecular photovoltaic cells,[5] molecular informatics,[6] and optoelectronic devices,[7,8] are beginning to emerge from this new field of research. However, in order to favor vectorial transfer of information over long distances along the molecular axis, the use of extended and rigid linkages between two complexation sites is required.

Multidentate ligands, such as 2,3,5,6-tetrapyridinylpyrazine,[9] bis-[10] or tris-2,2′:6′,2″-terpyridine[11] or 3,3′,5,5′-tetrapyridyl-biphenyl[12] or polyphenyl back-to-back bis-2,2′:6′,2″-terpyridines[13] provide suitable molecular frameworks for the study of electronic coupling between two proximal redox centers. Surprisingly, to our knowledge only one example of the use of an acetylenic bridged bis-pyridine type ligand has been reported in electronically-coupled systems.[14]

We have recently demonstrated that efficient electron delocalization over extended π^* orbital occurs in ethynyl-bridged d^6 transition metal complexes.[15] These various experiments serve to indicate that polyynes are effective bridges for promotion of through-bond electron and hole-transfer processes. Since we showed that oligopyridines [bipyridine (bipy), phenanthroline (phen), naphthyridine, and terpyridine (terpy)] were easily functionalized with alkyne groups under mild conditions and in good yields,[16] we have refocused our interest in the synthesis of novel polytopic ligands using related methodology. Little is known about the substitution of N-heteroarenes with alkynes,[17−21] although recently, a ditopic bis-bipyridine ethynyl bicyclo[2.2.2]octane-bridged ligand, synthesized by bromine addition on the bis-alkene derivative followed by a basic dehydrobromination, has been reported.[22]

Previously, we described briefly the facile cross-coupling reaction of ethynyl-substituted bipy chelates with bromo- or triflate-functionalized bipy or terpy subunits in the presence of catalytic amounts of "Pd^0" and the self-coupling of ethynyl-substituted bipyridines in the presence of cupric salts to produce ditopic polypyridine ligands bridged by one and two acetylenic bonds,

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(1) Verhoeven, J. W.; Kroon, J.; Paddon-Row, M. N.; Warman, J. M. In *Supramolecular Chemistry*; Balzani, V., De Cola, L., Eds.; NATO ASI Ser. C, 1992; Vol. 371, p 181.
(2) Balzani, V.; Scandola, F. In *Supramolecular Photochemistry*; Harwood: Chichester, 1991.
(3) Gust, D.; Moore, T. A. *Science* **1989**, *244*, 35.
(4) Ziessel, R. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer Academic Publishers: Dordecht, 1993; p 217.
(5) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(6) Reynolds, J. R. *J. Mol. Electron.* **1986**, *2*, 1.
(7) Grubbs, R. H.; Gorman, C. B.; Ginsburg, E. J.; Perry, J. W.; Marder, S. R. In *Materials with Nonlinear Optics, Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stricky, G. D., Eds.; ACS Symposium Series, 1991; p 455.
(8) Barker, J. R. In *Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Edward Arnold: London, 1995; p 345.
(9) Thummel, R. P.; Chirayil, S. *Inorg. Chim. Acta* **1988**, *154*, 77.
(10) Constable, E. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1405.
(11) Constable, E. C.; Caryill-Thompson, A. M. W. *J. Chem. Soc., Chem. Commun.* **1992**, 617.
(12) Beley, M.; Collin, J.-P.; Louis, R.; Metz, B.; Sauvage, J. P. *J. Am. Chem. Soc.* **1992**, *113*, 8521. Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1993**, *32*, 4539.
(13) Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434. Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1775. Chodorowski-Kimmes, S.; Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **1996**, *37*, 2963.
(14) Taube, H.; Sutton, J. E. *Inorg. Chim. Acta* **1988**, *154*, 77.
(15) Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707.
(16) Suffert, J.; Ziessel, R. *Tetrahedron Letters* **1991**, *32*, 757. Ziessel, R.; Suffert, J.; Youinou, M.-T. *J. Org. Chem.* **1996**, *61*, 6535.
(17) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.
(18) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.
(19) Sakamoto, T.; Shiraiwa, M.; Kondo, Y.; Yamanaka, H. *Synthesis* **1983**, 312.
(20) Ciana, L. D.; Haim, A. *J. Heterocycl. Chem.* **1984**, *21*, 607.
(21) Tilley, J. W.; Zawoiski, S. *J. Org. Chem.* **1988**, *53*, 386.
(22) Vögtle, F.; Frank, M.; Nieger, M.; Belser, P.; Von Zelewsky, M.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1643.

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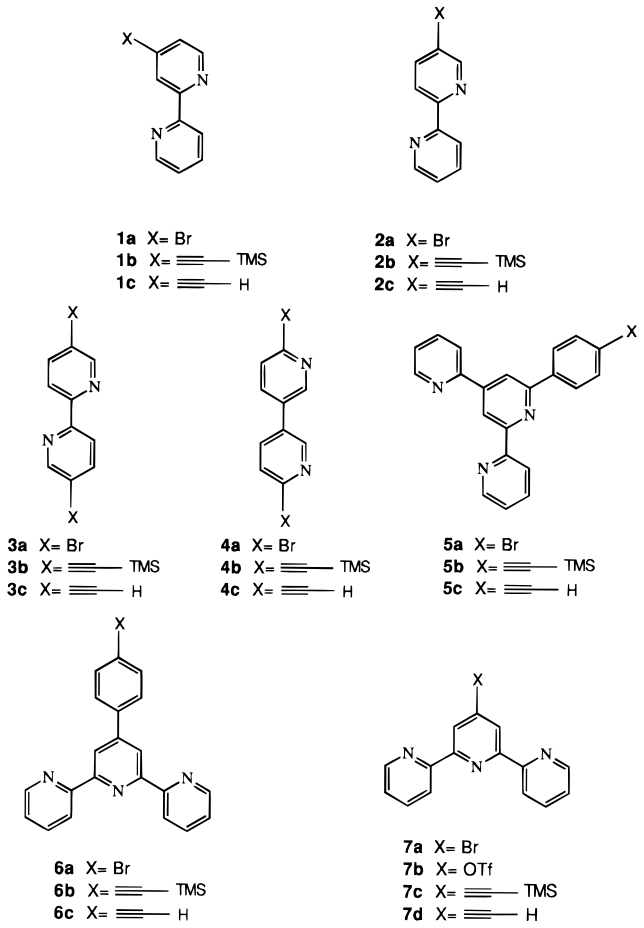
Chart 1



respectively.[23,24] We now present a detailed account of the synthesis of a variety of bipy and terpy preorganized rigid polytopic ligands suitable for the chelation of numerous metal centers.

These rationally designed polytopic ligands have been shown to self-assemble into well-defined supramolecular architectures in the presence of copper(I) and/or iron(II) salts.[25] They also form polyacetylene polymers bearing appended chromophoric and redox-active subunits upon electropolymerization of the ethynyl or diethynyl group in the corresponding transition metal complexes.[26]

Results and Discussion

Although alkynylation of pyridine halides catalyzed by palladium(0) has been pioneered by Sonogashira,[17] there were no reports describing palladium-catalyzed cross-coupling reactions with oligopyridines, when the present work started. We found that the palladium-catalyzed reaction of (trimethylsilyl)acetylene with bipys and terpys proceeded readily under mild conditions (Chart 1). Several ethynyl-substituted bipy and terpy compounds were prepared, in good yield, via treatment of the corresponding bromo- or triflate-substituted ligand with (trimethylsilyl)acetylene in the presence of catalytic amounts of palladium and a secondary or primary amine as base, as reported for aromatic compounds.[27,28] The palladium(0) catalyst could be either $[Pd(PPh_3)_4]$ in benzene and diisopropylamine at 80 °C (exp. conditions 1) or used as $[Pd(PPh_3)_4]$ in *n*-propylamine at 60 °C (exp. conditions 2). The active catalyst can also be generated in situ from $[Pd(PPh_3)_2Cl_2]$ and CuI in THF and diisopropylamine at rt (exp. conditions 3). When $[Pd(PPh_3)_4]$ is used, formation of the active catalytic species required a higher temperature (60 to 80 °C compared to the 20 °C used in exp. conditions 3) but in most cases gave a clean reaction and higher yields of the functionalized product (Scheme 1). The results are gathered in Table 1. For example, upon reaction of 4-bromo-2,2′-bipyridine **1a** with (trimethylsilyl)acetylene under exp. conditions 1, **1b** was isolated in 97% yield (entry 1 in Table 1). Surprisingly, upon reaction of **2a** with (trimethylsilyl)acetylene under exp. conditions 1 or exp. conditions 2 a very slow reaction occurs. However, under exp. conditions 3, in which CuI is present, the rate of the reaction was considerably enhanced, allowing isolation of **2b** in 88% yield. It has been reported that CuI facilitates alkynylation of the palladium(II) intermediate.[29] This effect has also been observed in other cases described here but has not been studied systematically. When the bromine atom is attached to a phenyl group (**5a** and **6a**), the coupling reaction was achieved in good yield with $[Pd(PPh_3)_4]$ and *n*-propylamine as solvent at 60 °C (exp. conditions 2). As shown by examination of Table 1, deprotection of the trimethylsilyl group with KF in methanol could be achieved in excellent yield (83 to 99%). K_2CO_3 could be used in the deprotection step, but in this case lower yields are obtained (60 to 70%).

The success achieved in the palladium-catalyzed coupling reactions of (trimethylsilyl)acetylene with bipy or terpy halides or triflates prompted us to investigate the cross-coupling reaction of ethynyl-substituted bipys or terpys with the parent bromo- or triflate-substituted bipy or terpy substrates (Scheme 2). This cross-coupling reaction provides access to a wide variety of rigid and preorganized di- and tritopic multichelating ligands (Charts 2−4) that display valuable complexation properties, thereby allowing synthesis of supramolecular polynuclear transition metal complexes.[25] As observed for the precursor synthesis (Chart 1 and Table 1), the highest isolated yields (80−90%) were obtained with exp. conditions 1. The results obtained under various experimental conditions are collected in Table 2. When exp. conditions 3 were used in the synthesis of the back-to-back ditopic terpyridines (Chart 2), insoluble polymeric deep-green copper complexes were formed. Under these conditions, the yield dramatically decreased (compare for instance entries 16 to 18 or entries 20 to 22 in Table 2). Copper decomplexation with KCN in methanol, prior to purification only slightly increases the overall reaction yield.

Again when phenyl substituents are present on the precursors (**5a**−**c** and **6a**−**c**), the palladium-catalyzed cross-coupling reaction was very sensitive to the nature of reaction conditions. The yields increase by a factor of 5 using *n*-propylamine instead of benzene/diisopropylamine as solvent (compare entries 21 and 22, or 30 and 31, in Table 2). This marked effect is not observed in the absence of phenyl groups (compare entries 18 and 19). Owing to the strong π-acidic character of a bipy or

(23) Grosshenny, V.; Ziessel, R. *Tetrahedron Lett.* **1992**, *33*, 8075.
(24) Romero, F. M.; Ziessel, R. *Tetrahedron Lett.* **1994**, *35*, 9203.
(25) Romero, F. M.; Ziessel, R.; Dupont-Gervais, A.; Van Dorsselaer *J. Chem. Soc., Chem. Commun.* **1996**, 551.
(26) Grosshenny, V.; Harriman, A.; Gisselbrecht, J.-P.; Ziessel, R. *J. Am. Chem. Soc.* **1996**, *118*, 10315.
(27) Heck, R. F. *Org. React.* **1981**, *27*, 345.
(28) Weijin, T.; Nesbitt, S.; Heck, R. F. *J. Org. Chem.* **1990**, *55*, 63.
(29) Cassar, J. *J. Organomet. Chem.* **1975**, *93*, 253. Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259.

Scheme 1

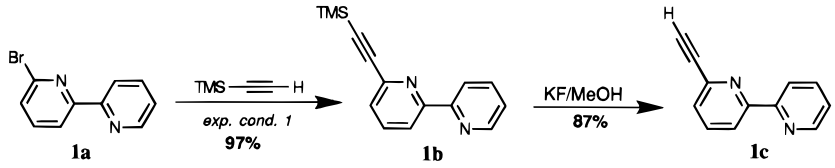
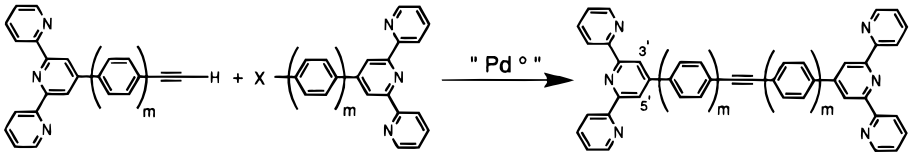


Table 1. Palladium-Catalyzed Ethynylation and Deprotection[a] of the Building Blocks

entry	product	catalysts + reaction conditions[b]	% yield[c] ethynylation/% yield deprotection
1	**1b**/**1c**	$[Pd(PPh_3)_4]/C_6H_6/^iPr_2NH$/80 °C (exp cond 1)	97/87
2	**2b**/**2c**	$[Pd(PPh_3)_4]/C_6H_6/^iPr_2NH$/80 °C (exp cond 1)	<5/83[d]
3	**2b**/**2c**	$[Pd(PPh_3)_4]/^nPrNH_2$/60 °C (exp cond 2)	<3/83[d]
4	**2b**/**2c**	$[Pd(PPh_3)_2Cl_2]$/CuI/$C_6H_6/^iPr_2NH$/20 °C (exp cond 3)	88/83
5	**3b**/**3c**	$[Pd(PPh_3)_4]/C_6H_6/^iPr_2NH$/80 °C (exp cond 1)	<5/99[d]
6	**3b**/**3c**	$[Pd(PPh_3)_2Cl_2]$/CuI/THF/$^iPr_2NH$/20 °C (exp cond 3)	76/99
7	**4b**/**4c**	$[Pd(PPh_3)_4]/^nPrNH_2$/60 °C (exp cond 2)	<7/92
8	**4b**/**4c**	$[Pd(PPh_3)_2Cl_2]$/CuI/THF/$^iPr_2NH$/20 °C (exp cond 3)	67/92
9	**4b**/**4c**	$[Pd(PPh_3)_4]/C_6H_6/^iPr_2NH$/80 °C (exp cond 1)	79/92
10	**5b**/**5c**	$[Pd(PPh_3)_4]/C_6H_6/^iPr_2NH$/80 °C (exp cond 1)	15/86
11	**5b**/**5c**	$[Pd(PPh_3)_4]/^nPrNH_2$/60 °C (exp cond 2)	96/86
12	**6b**/**6c**	$[Pd(PPh_3)_4]/^nPrNH_2$/60 °C (exp cond 2)	99/92
13[e]	**7c**/**7d**	$[Pd(PPh_3)_4]/^nPrNH_2$/60 °C (exp cond 2)	87/95
14[f]	**7c**/**7d**	$[Pd(PPh_3)_2Cl_2]$/CuI/THF/$^iPr_2NH$/20 °C (exp cond 3)	75/95
15[f]	**7c**/**7d**	$[Pd(PPh_3)_4]/C_6H_6/^iPr_2NH$/80 °C (exp cond 1)	67/95

[a] KF in methanol at room temperature. [b] 6 mol % in palladium and 20 mol % in copper when present. [c] All reported yields are isolated yields. [d] After 4 days heating at 80 °C. [e] Using 4′-bromo-2,2′:6′,2″-terpyridine as substrate. [f] Using 4′-[[(trifluoromethyl)sulfonyl]oxy]-2,2′:6′,2″-terpyridine as substrate.

Scheme 2



7d : m = 0
6c : m = 1

7a : X=Br, m=0
7b : X=OTf, m = 0
6b : X=Br, m = 1

8a : m = 0
9a : m = 1

terpy, the pyridinylacetylenic proton is more acidic than a phenylacetylenic proton. In (ethynylphenyl)bipyridine **5c** or in the (ethynylphenyl)terpyridine **6c**, a twisted conformation of the pyridine and the phenylethynyl fragment is expected in order to minimize steric interactions between the proton at the 5 position of the bipy or at the 3′ and 5′ positions of the terpy with the ortho protons of the phenyl subunits (see Scheme 2 and Chart 2 for labeling). This twisted conformation decreases the π-overlap and consequently attenuates the π-acceptor character of the bipy or terpy. The ethynylphenyl proton is consequently less acidic. The use of a primary amine instead of a secondary amine as base might facilitate proton abstraction, allowing subsequent coordination of the ethynyl anion to the palladium catalytic center (see Scheme 3).

Finally, the same methodology has been used for the synthesis of mixed bipy-terpy, phen-terpy, and bipy-bipy′ ligands (Chart 3 and 4). Insolubility of the resultant ligands drives the reaction to completion within a couple of hours. Good isolated yields were obtained (see Table 2). It is noteworthy that ligand **17** could be prepared independently by reaction of 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine with the 6,6′-dibromo-2,2′-bipyridine (entry 36) or by reaction of 6-bromo-5,5′-dimethyl-2,2′-bipyridine with the 6,6′-diethynyl-2,2′-bipyridine (entry 37). A higher yield is obtained in the latter case due to a better thermal stability of the 6,6′-diethynyl-2,2′-bipyridine compared to the 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine compound.

The mechanism of these palladium-catalyzed nucleophilic substitutions appears to involve a bis(triphenylphosphine)palladium(0) complex as catalytic species.[17,29] Formation of the active palladium(0) complex has been recently reinvestigated in light of the specific role played by halide ions.[30] The active species is generated from $[Pd(PPh_3)_2Cl_2]$ by reaction of the copper-activated acetylide anion to form the bis(triphenylphosphine)dialkynylpalladium complex, followed by reductive elimination of 1,4-bis(trimethylsilyl)butadiyne which, in the presence of the X anion, leads to the formation of $[Pd(PPh_3)_2X]^-$ (**A** in Scheme 3). In fact, a small amount of 1,4-bis(trimethylsilyl)butadiyne was observed in most of the reactions presented in Table 1. Oxidative addition of the bromo- or triflate-substituted substrate to the zero-valent anion **A** gives the five-coordinated intermediate **B**. Nucleophilic substitution of one of the halide ligands by (trimethylsilyl)acetylene affords intermediate **C**. Reductive elimination gives the (trimethylsilyl)ethynyl-substituted product and regenerates the starting Pd(0) anion **A**, which then perpetuates the catalytic cycle (Scheme 3).

The halide or pseudohalide ions originate from the divalent palladium precursor or from the organic halide or pseudohalide. Halide exchange reactions may take place between the steps considered in Scheme 3. In the cross-coupling reactions using $[Pd(PPh_3)_4]$ the mechanism

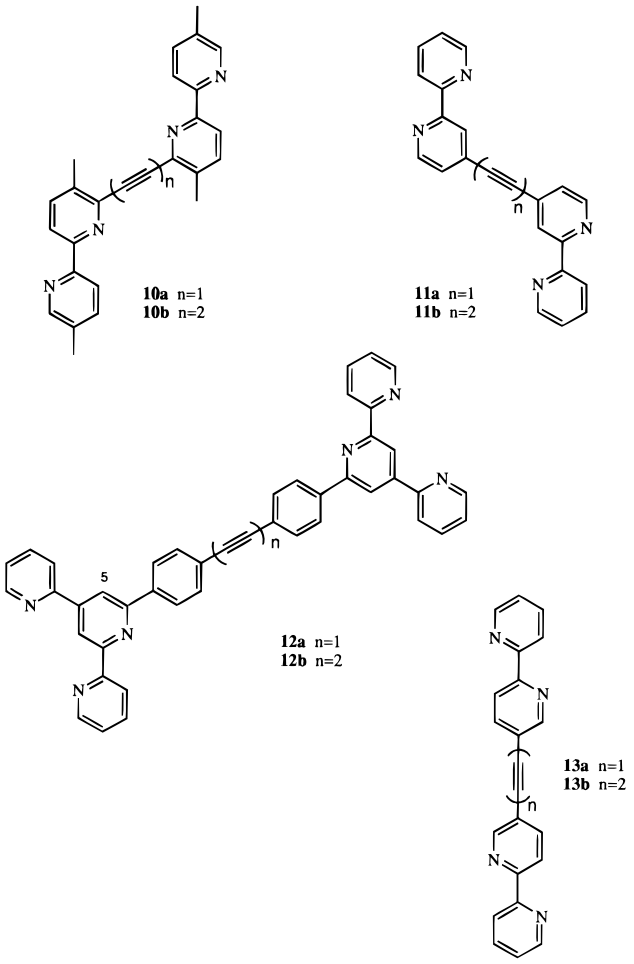
(30) Amatore, C.; Jutand, A.; Khalil, F.; M'Barki, M. A.; Mottier, L. *Organometallics* **1993**, *12*, 3168.

Table 2. Palladium-Catalyzed Synthesis of the Monoethynyl Di- and Tritopic Ligands

entry	product	catalysts[a]	solvent	base	*T* (°C)	isolated yield (%)
16	**8a**	$[Pd(PPh_3)_2Cl_2]$/CuI	THF	$^iPr_2NH$	40	23
17	**8a**	$[Pd(PPh_3)_2Cl_2]$/CuI	C_6H_6	$^iPr_2NH$	60	21
18	**8a**	$[Pd(PPh_3)_4]$	THF	$^iPr_2NH$	80	82
19	**8a**	$[Pd(PPh_3)_4]$	−	$^nPrNH_2$	60	85
20	**9a**	$[Pd(PPh_3)_2Cl_2]$/CuI	THF	$^iPr_2NH$	60	<5
21	**9a**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	15
22	**9a**	$[Pd(PPh_3)_4]$	−	$^nPrNH_2$	60	79
23	**10a**	$[Pd(PPh_3)_2Cl_2]$/CuI	THF	$^iPr_2NH$	40	25
24	**10a**	$[Pd(PPh_3)_2Cl_2]$/CuI	THF	Et_3N	40	29
25	**10a**	$[Pd(PPh_3)_2Cl_2]$/CuI	THF	$^nPrNH_2$	40	23
26	**10a**	$[Pd(PPh_3)_2Cl_2]$/CuI	CH_2Cl_2	$^iPr_2NH$	40	45
27	**10a**	$[Pd(PPh_3)_2Cl_2]$/CuI	C_6H_6	$^iPr_2NH$	40	52
28	**10a**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	99
29	**11a**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	80
30	**12a**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	23
31	**12a**	$[Pd(PPh_3)_4]$	−	$^nPrNH_2$	60	88
32	**13a**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	73
33	**14**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	75
34	**15**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	67
35	**16**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	87
36	**17**[b]	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	77
37	**17**[c]	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	93
38	**18**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	74
39	**19**[d]	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	<5
40	**19**[e]	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	67
41	**20**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	65
42	**21**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	75
43	**22**	$[Pd(PPh_3)_4]$	C_6H_6	$^iPr_2NH$	80	72

[a] 6 mol % in palladium and 20 % mol in copper when present. [b] Prepared from 6,6′-dibromo-2,2′-bipyridine and compound **1c**. [c] Prepared from 6,6′-diethynyl-2,2′-bipyridine and compound **1a**. [d] Prepared from compounds **4c** and **8b**. [e] Prepared from compounds **4a** and **8d**.

Chart 2



of the catalysis is similar. The nature of intermediate **A** is uncertain, but X could either be the pseudohalide or a solvent molecule.[31] The free pseudohalide could be generated by oxidative addition of the organic halide to "$Pd(PPh_3)_2$" which could be formed by a dissociative mechanism from $[Pd(PPh_3)_4]$.[32] Nucleophilic attack of ethynyl-substituted terpy substrate liberates the triflate anion, which could then form the $[Pd(PPh_3)_2OTf]^-$ active catalyst. In fact triphenylphosphine was observed by TLC in all cross-coupling reactions described in this manuscript. The formation of a stable *trans*-terpy/alkynyl palladium(II) species, as the key intermediate and as suggested in the initially reported mechanism,[17] represents a side reaction of the more efficient mechanism present in Scheme 3. As noticed in related reactions[33,34] the presence of copper(I) is not necessary for activation of the ethynyl substrate when $[Pd(PPh_3)_4]$ is used as catalyst precursor. In some cases described here, addition of CuI (20 mol %) significantly increases the yield (ca. 25%) of the functionalized product. This has been observed for related compounds,[35] but has not been found systematically here. Although Pd(II) forms very stable complexes with 2,2′-bipyridine,[36] or 2,2′:6′,2″-terpyridine,[37] the presence of such chelating ligands in the reaction mixture seems not to interfere with catalysis.

As emphasized above, one of the exciting goals in the field of molecular electronics is the study of electronic communication in metal complexes as a function of the length of the spacer.[1] At least for synthetic reasons, alkyne bonds are particularly suitable for assembling metal-containing building blocks into extended and rigid

(31) Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc.* **1993**, *115*, 9531.
(32) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.
(33) Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.
(34) Genet, J.-P.; Bluart, E.; Savignac, M. *Synlett* **1992**, 715.
(35) Ratovelomanana, V.; Linstrumelle, G. *Tetrahedron Lett.* **1981**, *22*, 315.
(36) Carty, A. J.; Chieh, P. C. *J. Chem. Soc., Chem. Commun.* **1972**, 158.
(37) Livingston, S. E.; Wheelahan, B. *Aust. J. Chem.* **1964**, *17*, 219.

Scheme 3

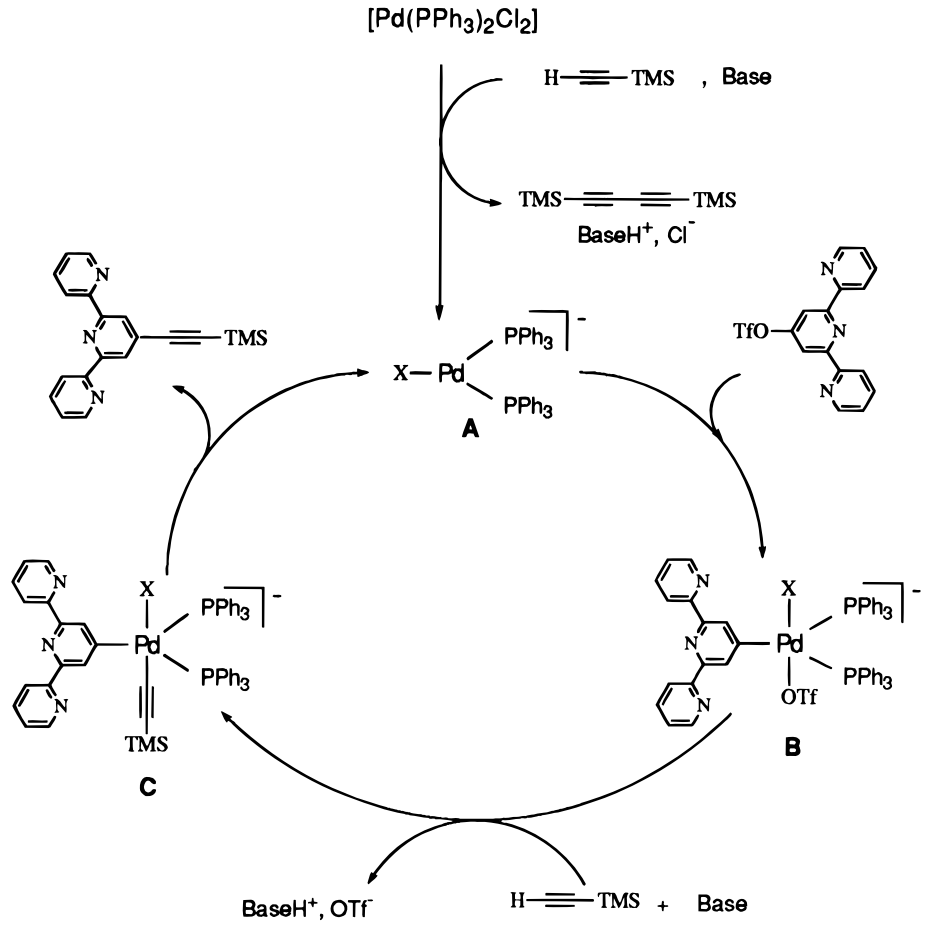


Chart 3

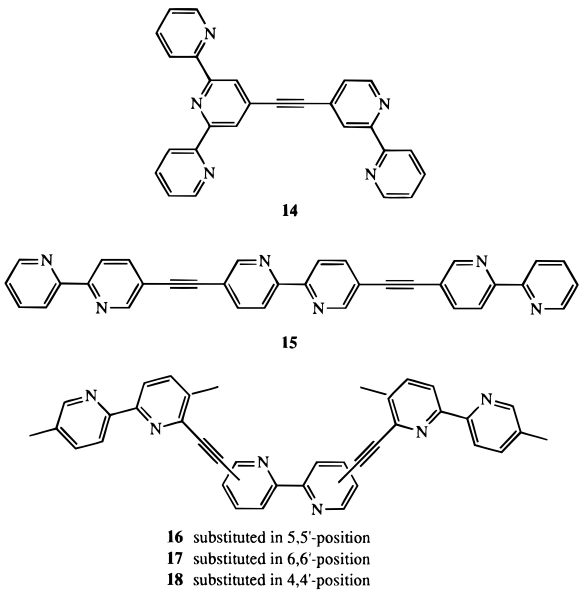
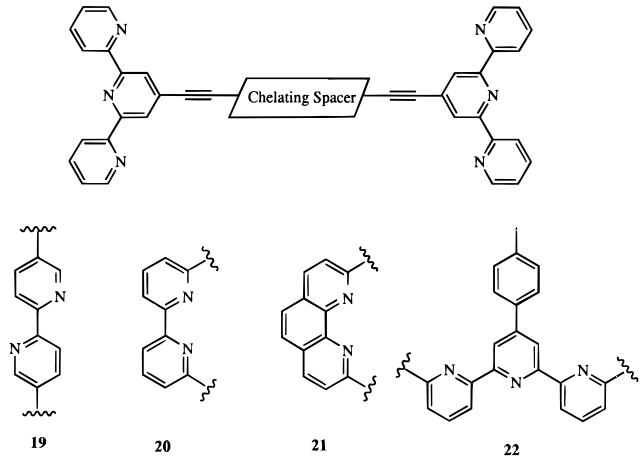


Chart 4



supramolecular structures.[38] Oxidative dimerization of bipy- or terpy-substituted terminal alkynes in the presence of cupric salts as reagent (Scheme 4) allows the efficient preparation of ditopic ligands bearing butadiyne or diphenylbutadiyne spacer units.

Oxidative coupling of monosubstituted ethynyl derivatives (**1c**, **2c**, **5c**, **6c**, and **7d**) with cupric salts proceeds very efficiently in solution (Chart 2 and Scheme 4). The results obtained under various experimental conditions are gathered in Table 3. In the case of bipy (entries 53−55) oxidative dimerization was successfully carried out in excellent yield with CuCl in the presence of a bidentate ligand such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and oxygen, at rt. In the case of terpyridine (entries 50, 51) the method of Hay[39] affords the desired ditopic ligand **9b** and **10b** but in much lower yield. Since terpyridine ligands are known to form stable complexes with copper(II),[40,41] we consider that formation of insoluble, deep-green, polymeric copper(II) complexes strongly disfavors

(38) Grosshenny, V.; Harriman, A.; Hissler, M.; Ziessel, R. *Platinum Met. Rev.* **1996**, *40*, 26 and *Platinum Met. Rev.* **1996**, *40*, 72.

(39) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275 and **1962**, *27*, 3320.
(40) Hogg, R.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 341.

Scheme 4

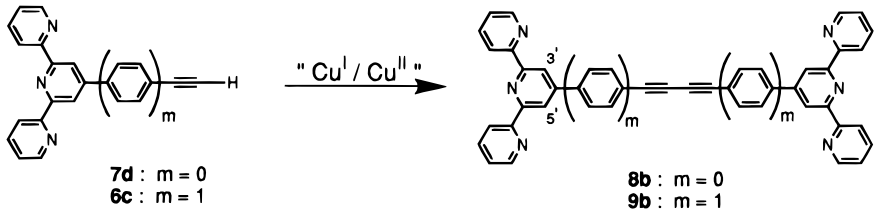


Table 3. Synthesis of the Diethynyl Ditopic Ligands

entry	product	reagents	solvent	t (°C)	isolated yields (%)
44	**8b**	$CuCl/CuCl_2$	pyridine	20	<1[a]
45	**8b**	$CuCl/CuCl_2/O_2$	pyridine	20	49[b]
46	**8b**	$CuCl/CuCl_2/O_2$	pyridine	80	22[b]
47	**8b**	$CuCl/CuCl_2$	DMF	20	16[b]
48	**8b**	$CuCl/CuCl_2/O_2$	DMF	80	12[b]
49	**8b**	$CuCl/CuCl_2/O_2$	DMF	20	67[b]
50	**8b**	$CuCl/TMEDA/O_2$	CH_3CN	20	10[b]
51	**9b**	$CuCl/TMEDA/O_2$	CH_3CN	80	14[b]
52	**9b**	$CuCl/CuCl_2/O_2$	DMF	20	46[b]
53	**10b**	$CuCl/TMEDA/O_2$	CH_3CN	20	78
54	**11b**	$CuCl/TMEDA/O_2$	CH_3CN	20	98
55	**12b**	$CuCl/TMEDA/O_2$	CH_3CN	20	97
56	**13b**	$CuCl/O_2$	pyridine	20	72

[a] Not isolated. [b] Obtained after copper decomplexation with potassium cyanide.

oxidative coupling. The dimerization of **6c** or **7d** following the method of Breslow[42] using $CuCl/CuCl_2$ under anaerobic conditions in anhydrous pyridine (entry 44) does not take place. However, aerobic conditions allow synthesis of the butadiyne compounds (entries 49 and 52). The use of a more polar solvent markedly increases the yield of the ditopic ligand **9b** (entry 49). Due to poor thermal stability of the ethynyl-substituted compound **7d**, in the presence of oxygen, oxidative coupling becomes less effective at higher temperature (compare entries 48/49). Copper decomplexation with KCN is needed prior to purify the terpy ligands **8b** and **9b**. Such treatment is not necessary in the bipy cases. A marked effect of oxygen using Breslow's conditions has also been observed during synthesis of multiring copper(I) catenates based on phenanthroline subunits.[43]

In conclusion, we have presented a general method for the preparation of rationally designed preorganized polytopic ligands. The alkyne-functionalized bipy and terpy building blocks have been used for the preparation of homo-polytopic ligands bearing acetylene and diphenylacetylene as spacers via palladium(0)-catalyzed cross-coupling reactions between bipy or terpy halides or triflate and the corresponding terminal alkynes. Hetero-polytopic ligands have also been synthesized by cross-coupling reactions of terpyridine-triflate and bipyridine-substituted terminal alkynes. Dimerization of terminal alkynes using an oxidative homo-coupling reaction afforded homo-ditopic ligands bearing butadiyne and diphenylbutadiyne spacer units. All these reactions markedly depend on the nature of the catalytic species, base, solvent, and temperature. The ready availability of the reagents, the simplicity of the procedures, the mildness of the reaction conditions, and the high yields obtained suggest that this method is highly useful for the preparation of multichelating ligands.

Experimental Section

General Methods. The 200.1 (^1H) and 50.3 MHz ($^{13}C\{^1H\}$) NMR spectra were recorded at rt, unless otherwise specified, using perdeuterated solvents as internal standard: δ (H) in ppm relative to residual protiated solvent in $CDCl_3$ (7.26), CD_2Cl_2 (5.32), DMF-d_7 (8.00, 3.07, and 2.90); δ (C) in ppm relative to the solvent $CDCl_3$ (77.0), CD_2Cl_2 (53.8). All carbon signals were detected as singlets. Fast-atom bombardement (FAB, positive mode) ZAB-HF-VB-analytical apparatus in a *m*-nitrobenzyl alcohol (*m*-NBA) as matrix. MS: electronic impact (EI) or chemical ionization (CI) on LKB-9000S apparatus. FT-IR spectra measured in KBr pellets or in solution with KBr cells. Melting points were obtained with a capillary melting point apparatus in open-ended capillaries and are uncorrected. Evidence for the molecular formulation is based on ^1H and $^{13}C\{^1H\}$ NMR for both structure and purity.

Materials. 6,6′-Diethynyl-2,2′-bipyridine,[16] 6-bromo-5,5′-dimethyl-2,2′-bipyridine,[44] 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine,[16] 4-bromo-2,2′-bipyridine (**1a**),[45] 5-bromo-2,2′-bipyridine (**2a**),[46,47] 5,5′-dibromo-2,2′-bipyridine (**3a**),[46,47] 6,6′-dibromo-3,3′-bipyridine (**4a**),[48] 4′-[{(trifluoromethyl)sulfonyl}oxy]-2,2′:6′,2″-terpyridine (**7b**),[49] 2,6-bis(2′-pyridyl)-4-pyridone,[49] 6,6″-dibromo-4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine,[50] 2,9-dichloro-1,10-phenanthroline,[51] 4,4′-dibromo-2,2′-bipyridine,[45] 6,6′-dibromo-2,2′-bipyridine,[52] $[Pd(PPh_3)_2Cl_2]$,[53] and $[Pd(PPh_3)_4]$[54] were prepared and purified according to the literature procedures. All reactions were carried out under dry argon by using Schlenk-tube techniques. Solvents, including diisopropylamine, were dried over suitable reagents and freshly distilled under argon before use.

General Procedure for the Preparation of the (Trimethylsilyl)alkyne Compounds and Polytopic Ligands Bearing One Alkyne, Following Experimental Conditions 1. A Schlenk flask was charged with the bromo or triflate derivatives in argon-degassed benzene, (trimethylsilyl)-acetylene, $[Pd(PPh_3)_4]$ (6 mol %), and finally argon-degassed diisopropylamine. The yellow solution was heated at 80 °C. After complete consumption of starting material (overnight), the solvent was evaporated to give a crude product which was purified by flash chromatography on silica gel, eluting with CH_2Cl_2/MeOH. For the cross-coupling reaction leading to the polytopic ligands, the bromo or triflate derivatives were dissolved in benzene at 80 °C. When a clear solution was obtained, $[Pd(PPh_3)_4]$ (6 mol %) and diisopropylamine were added. After 16 h of heating at 80 °C, the solvent was removed

(41) Allmann, R.; Henke, W.; Reinen, D. *Inorg. Chem.* **1978**, *17*, 378 and references cited therein.
(42) O'Krongly, D.; Denmeade, S. R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5545.
(43) Dietrich-Bucheker, C. O.; Khemiss, A.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1986**, 1376.
(44) Lehn, J. M.; Sauvage, J. P.; Simon, J.; Ziessel, R.; Piccinni-Leopardi, C.; Germain, G.; Declercq, J. P.; VanMeerssche, M. *Nouv. J. Chim.* **1983**, *7*, 413.
(45) Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745.
(46) Morgan, G.; Burstall, F. H. *J. Chem. Soc.* **1937**, 1649.
(47) Romero, F. M.; Ziessel, R. *Tetrahedron Lett.* **1995**, *36*, 6471.
(48) Baxter, P.; Lehn, J.-M.; Decian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 69.
(49) Potts, K. T.; Konwar, D. *J. Org. Chem.* **1991**, *56*, 4815.
(50) Constable, E. C.; Lewis, J. *Polyhedron* **1982**, *1*, 303.
(51) Lewis, J.; O'Donoghue, T. D. *J. Chem. Soc., Dalton Trans.* **1980**, 736 and references cited therein.
(52) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organomet. Chem.* **1973**, *56*, 53.
(53) Dangles, O.; Guibe, F.; Balavoine, G. *J. Org. Chem.* **1987**, *52*, 4984.
(54) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

under vacuum, and the residue was chromatographed (alumina, MeOH/CH_2Cl_2). Recrystallization from CH_2Cl_2/hexane yielded the desired compounds as white crystalline products.

General Procedure Following Experimental Conditions 2. To a stirred solution of equimolar quantities of the bromo and the ethynyl derivatives in *n*-propylamine (18 mL) was added a solution of [$Pd(PPh_3)_4$] (6 mol %) in *n*-propylamine. After 6 h of heating at 60 °C, the white solid was filtered and washed with ether. Recrystallization from CH_2Cl_2/MeOH/hexane yielded the desired compounds as white products.

General Procedure Following Experimental Conditions 3. To a 100-mL, round-bottomed Schlenk flask equipped with a septum, a Teflon-coated magnetic stirring-bar and the bromo or triflate derivative in argon-degassed THF were successively added (trimethylsilyl)acetylene, [$PdCl_2(PPh_3)_2$] (3 mol %), CuI (10 mol %), and finally diisopropylamine. The solution was stirred at rt during 2 h. During that time the color of the solution turned black with the formation of an abundant precipitate of the salt. After complete consumption of the starting material (determined by TLC), the mixture was treated with activated carbon (ca. 200 mg) and filtered over Celite. The filtrate was concentrated by rotary evaporation to give a crude product which was purified through a flash chromatography column packed with silica gel and eluted with CH_2Cl_2.

General Procedure for the Removal of the TMS Group. To a stirred solution of trimethylsilyl-protected compound in CH_3OH/THF (v/v 1/1) was added KF (1.2 equiv) as a solid. After complete consumption of the starting material (ca. 7 h), the solution was concentrated by rotary evaporation to give a crude product which was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH.

4-[2-(Trimethylsilyl)-1-ethynyl]-2,2′-bipyridine (1b). Prepared following exp. conditions 1; from 0.200 g (0.85 mmol) of **1a**, 20 mL of benzene, 0.246 mL (1.70 mmol) of (trimethylsilyl)-acetylene, 0.060 g (0.05 mmol) of [$Pd(PPh_3)_4$], and 8 mL of diisopropylamine; flash chromatography on silica gel, eluting with CH_2Cl_2/MeOH 99/1; to give 0.21 g (97%); mp 60−1 °C; ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9H), 7.23 (m, 2H), 7.72 (td, J = 8.0 Hz, J = 1.7 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 8.42 (s, 1H), 8.55 (d, J = 4.8 Hz, 1H), 8.61 (d, J = 4.8 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −0.4, 99.6, 102.3, 121.0, 123.3, 123.8, 125.3, 132.1, 136.8, 149.0, 155.3, 156.0; IR (KBr, cm^{-1}) 2158 (w), 1582 (s), 1534 (m), 1438 (s), 1388 (m), 1294 (w), 1248 (s), 894 (s), 846 (s); GC-MS m/z 252 (M^+, 61), 237 (M − CH_3, 100), 222 (M − 2CH_3, 3), 207 (M − 3CH_3, 5). Anal. Calcd for $C_{15}H_{16}N_2Si$: C, 71.38; H, 6.39; N, 11.10. Found: C, 71.22; H, 6.44; N, 10.91.

4-Ethynyl-2,2′-bipyridine (1c). Prepared from **1b** (0.200 g, 0.792 mmol), in MeOH/THF (20 mL), and KF (0.046 g, 0.792 mmol), to give 0.124 g (87%); mp 75−6 °C; ^{1}H NMR ($CDCl_3$) δ 3.30 (s, 1H), 7.31 (m, 2H), 7.77 (t, J = 7.7 Hz, 1H), 8.36 (d, J = 7.7 Hz, 1H), 8.48 (s, 1H), 8.63 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 81.2, 81.7, 121.1, 123.6, 124.0, 125.8, 131.2, 136.9, 149.1, 155.2, 156.2; IR (KBr, cm^{-1}) 3224 (w), 2106 (w), 1582 (s), 1538 (m), 1452 (s), 1384 (m), 1142 (m), 1096 (m), 840 (m), 792 (s); GC-MS m/z 180 (M^+, 100). Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.54. Found: C, 80.23; H, 4.63; N, 15.50.

5-[2-((Trimethylsilyl)-1-ethynyl]-2,2′-bipyridine (2b). Prepared following exp. conditions 3, from 0.400 g (1.71 mmol) of **2a**, 0.400 g (4.07 mmol) of (trimethylsilyl)acetylene, 0.123 g (0.175 mmol) of [$PdCl_2(PPh_3)_2$], 0.052 g (0.273 mmol) of CuI, 30 mL of THF, and 6 mL of diisopropylamine at rt, during two days; to give 0.334 g (77%); mp 45−6 °C; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9H), 7.27 (m, 1H), 7.81 (m, 2H), 8.34 (m, 2H), 8.64 (d, J = 4.4 Hz, 1H), 8.71 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −0.3, 99.3, 101.8, 120.0, 121.0, 121.2, 122.1, 123.7, 136.7, 139.2, 139.6, 149.0, 151.8; IR (KBr, cm^{-1}) 2158 (m), 1586 (m), 1541 (m), 1456 (s), 1250 (m), 867 (s), 842 (s); FAB$^+$ m/z 253.2 [M + H]$^+$, 100%. Anal. Calcd for $C_{15}H_{16}N_2Si$: C, 71.38; H, 6.39; N, 11.10. Found: C, 71.32; H, 6.29; N, 11.06.

5-Ethynyl-2,2′-bipyridine (2c). Prepared from 0.334 g (1.32 mmol) of **2b**, 0.157 g (2.64 mmol) of KF, and 30 mL of MeOH, at rt, overnight, to give 0.198 g (83%); mp 87−9 °C; ^{1}H NMR ($CDCl_3$) δ 3.29 (s, 1H), 7.30 (m, 1H), 7.85 (m, 2H), 8.37 (dd, J = 8.2 Hz, J = 0.8 Hz, 2H), 8.67 (d, J = 4.7 Hz, 1H), 8.76 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 80.8, 81.7, 119.0, 120.2, 121.3, 124.0, 136.8, 139.9, 149.2, 152.1, 155.2, 155.3; IR (KBr, cm^{-1}) 3188 (s), 2096 (w), 1587 (m), 1545 (m), 1458 (s), 1434 (m), 1368 (m), 1094 (m), 1042 (m), 859 (m), 796 (s), 746 (s); FAB$^+$ m/z 181.1 [M + H]$^+$, 100%. Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.54. Found: C, 79.73; H, 4.30; N, 15.32.

5,5′-Bis[2-(trimethylsilyl)-1-ethynyl]-2,2′-bipyridine (3b). Prepared following exp. conditions 3, from 1.500 g (4.8 mmol) of **3a**, 1.600 g (16.3 mmol) of (trimethylsilyl)acetylene, 0.30 g (0.427 mmol) of [$PdCl_2(PPh_3)_2$], 0.150 g (0.788 mmol) of CuI, 90 mL of THF, and 12 mL of diisopropylamine, at rt during 20 h, to give 1.272 g (76%); mp 176−8 °C; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 18H), 7.85 (dd, J = 8.2 Hz, J = 2.0 Hz, 2H), 8.35 (d, J = 8.2 Hz, 2H), 8.71 (d, J = 2.0 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −0.2, 99.3, 101.8, 120.2, 120.4, 139.6, 151.9, 154.1; IR (KBr, cm^{-1}) 2958 (s), 2161 (w), 1588 (s), 1531 (s), 1457 (s), 1363 (s), 1250 (s), 1220 (s); FAB$^+$ m/z 349.2, 100%. Anal. Calcd for $C_{20}H_{24}N_2Si_2$: C, 68.91; H, 6.94; N, 8.04. Found: C, 68.87; H, 6.83; N, 8.01.

5,5′-Diethynyl-2,2′-bipyridine (3c). Prepared from 0.212 g (0.61 mmol) of **3b**, 0.076 g (1.28 mmol) of KF, and 20 mL of MeOH, at rt overnight to give 0.123 g (99%); mp 130 °C dec; ^{1}H NMR ($CDCl_3$) δ 3.30 (s, 2H), 7.89 (dd, J = 8.2 Hz, J = 2.0 Hz, 2H), 8.38 (d, J = 8.3 Hz, 2H), 8.76 (d, J = 2.0 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 119.5, 120.6, 140.0, 152.3, 154.5; IR (KBr, cm^{-1}) 3262 (s), 2103 (w), 1584 (m), 1530 (m), 1464 (s), 1364 (s), 1261 (m), 1050 (m), 1026 (s), 839 (s), 633 (s); FAB$^+$ m/z 205.1 [M + H]$^+$, 100%. Anal. Calcd for $C_{14}H_8N_2$: C, 82.34; H, 3.95; N, 13.0724. Found: C, 82.03; H, 3.60; N, 13.47.

6,6′-Bis[2-(trimethylsilyl)-1-ethynyl]-3,3′-bipyridine (4b). Prepared following exp. conditions 3, from 0.600 g (1.9 mmol) of **4a**, 0.690 mL (4.78 mmol) of (trimethylsilyl)acetylene, 0.045 g (0.064 mmol) of [$PdCl_2(PPh_3)_2$], 0.045 g (0.06 mmol) of CuI, 30 mL of THF, and 9 mL of diisopropylamine at rt to give 0.444 g (67%); mp 193 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 18H), 7.50 (d, J = 8.1 Hz, 2H), 7.80 (dd, J = 8.1 Hz, J = 1.6 Hz, 2H), 8.73 (d, J = 1.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −0.4, 96.5, 103.2, 127.3, 131.8, 134.1, 142.7, 148.0; IR (KBr, cm^{-1}) 2163 (w), 1586 (m), 1539 (m), 1462 (m), 1250 (s), 867 (s), 845 (s); GC-MS m/z 348 (M^+, 65), 333 (M − CH_3, 100). Anal. Calcd for $C_{20}H_{24}N_2Si_2$: C, 68.91; H, 6.94; N, 8.04. Found: C, 68.76; H, 6.84; N, 7.95.

6,6′-Diethynyl-3,3′-bipyridine (4c). Prepared from 0.400 g (1.1 mmol) of **4b**, 0.150 g (1.1 mmol) of K_2CO_3, 10 mL of THF, and 15 mL of MeOH to give 0.216 g (92%): mp 181 °C dec; ^{1}H NMR ($CDCl_3$) δ 3.25 (s, 2H), 7.59 (dd, J = 8.1 Hz, J = 0.6 Hz, 2H), 7.88 (dd, J = 8.1 Hz, J = 2.4 Hz, 2H), 8.82 (dd, J = 2.4 Hz, J = 0.6 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 78.6, 82.3, 127.6, 132.3, 134.4, 142.2, 146.2; IR (KBr, cm^{-1}) 3278 (s), 2927 (s), 2110 (w), 1728 (s), 1538 (m), 1467 (s), 1349 (s), 1274 (s), 1123 (m), 995 (s); GC-MS m/z 204 (M^+, 100). Anal. Calcd for $C_{14}H_8N_2$: C, 82.34; H, 3.95; N, 13.72. Found: C, 82.08; H, 3.77; N, 13.61.

4-(2-Pyridyl)-6(4-bromophenyl)-2,2′-bipyridine (5a). Obtained as a side product during the synthesis of the 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine. A similar isomer 4-pyridyl-6-(4-methylphenyl)-2,2′-bipyridine was obtained during the synthesis of the 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine:[55] mp 176−7 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 2H), 7.63 (m, 2H), 7.85 (ddd, J = 13.7 Hz, J = 6.2 Hz, J = 1.7 Hz, 2H), 8.03 (ABq, J_{AB} = 7.5 Hz, $\Delta\nu$ value 122.5 Hz, 4H), 8.14 (m, 2H), 8.51 (s, 1H), 8.73 (m, 2H), 8.92 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 143.8, 147.4, 147.6, 149.7, 150.0, 150.1, 154.8, 158.0, 163.0, 163.2, 164.3, 174.5, 175.2, 176.1, 181.0, 182.1, 182.6; IR (KBr, cm^{-1}) 2360 (m), 1582 (s), 1548 (s), 1470 (s), 1395 (m), 1076 (m), 1007 (m); GC-MS m/z 387/389 (M^+, 100), 309/311 (M − C_5H_4N). Anal. Calcd for $C_{21}H_{14}N_3Br$: C, 64.96; H, 3.63; N, 10.82. Found: C, 64.76; H, 3.48; N, 10.61.

4-(2-Pyridyl)-6[4-{2-(trimethylsilyl)-1-ethynyl}phenyl]-2,2′-bipyridine (5b). Prepared following exp. conditions 2, from 0.142 g (0.366 mmol) of **5a**, 0.106 mL (0.732 mmol) of (trimethylsilyl)acetylene, 0.025 g (0.02 mmol) of [$Pd(PPh_3)_4$], and 11 mL of *n*-propylamine, at 60 °C during 8 h to give 0.142

(55) Collin, J. P.; Guillerez, S.; Sauvage, J. P.; Barigelletti, F.; De Cola, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230.

g (96%); mp 207−8 °C; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H), 7.31 (m, 2H), 7.81 (m, 2H), 7.96 (ABq, J_{AB} = 8.3 Hz, $\Delta\nu$ value 120.9 Hz, 4H), 7.98 (d, J = 7.9 Hz, 1H), 8.51 (d, J = 1.1 Hz, 1H), 8.69 (m, 3H), 8.89 (d, J = 0.7 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −0.01, 95.5, 105.1, 116.9, 117.9, 121.2, 123.8, 126.8, 131.7, 132.3, 136.9, 136.9, 139.1, 148.2, 148.9, 149.9, 154.8, 156.0, 156.2, 156.3; IR (KBr, cm^{-1}) 2956 (m), 2154 (m), 1582 (s), 1548 (m), 1470 (m), 1440 (m), 1390 (m), 1250 (m); GC-MS *m*/*z* 405 (M^+, 82), 390 (M − CH_3, 100), 375 (M − 2CH_3, 5), 360 (M − 3CH_3, 5), 332 (M − Si(CH_3)$_3$, 2). Anal. Calcd for $C_{26}H_{23}N_3Si$: C, 77.00; H, 5.72; N, 10.36. Found: C, 76.81; H, 5.50; N, 10.18.

4-(2-Pyridyl)-6-(4-ethynylphenyl)-2,2′-bipyridine (5c). Prepared from 0.186 g (0.459 mmol) of **5b**, 0.053 g (0.912 mmol) of KF, 6 mL of THF, and 9 mL of MeOH to give 0.131 g (86%); mp 171−3 °C; ^{1}H NMR ($CDCl_3$) δ 3.20 (s, 1H), 7.31 (m, 2H), 7.80 (d, J = 7.7 Hz, 2H), 7.91 (ABq, J_{AB} = 8.3 Hz, $\Delta\nu$ value 118.9 Hz, 4H), 7.97 (d, J = 7.9 Hz, 1H), 8.50 (s, 1H), 8.68 (m, 3H), 8.88 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 78.3, 83.7, 117.0, 118.0, 121.1, 121.4, 122.7, 126.9, 128.7, 131.7, 132.4, 136.9, 139.6, 148.3, 149.0, 149.9, 154.9, 156.1, 156.2, 156.5; IR (KBr, cm^{-1}) 3294 (m), 2924 (m), 1728 (m), 1582 (s), 1548 (s), 1470 (s), 1438 (m), 1386 (s), 1292 (m), 1260 (m), 1122 (m), 786 (s); GC-MS *m*/*z* 333 (M^+, 100). Anal. Calcd for $C_{23}H_{15}N_3$: C, 82.86; H, 4.54; N, 12.60. Found: C, 82.79; H, 4.40; N, 12.44.

4′-[4-{2-(Trimethylsilyl)-1-ethynyl}phenyl]-2,2′:6′,2″-terpyridine (6b). Prepared following exp. conditions 2, from 0.200 g (0.515 mmol) of **6a**, 0.149 mL (1.03 mmol) of (trimethylsilyl)acetylene, 0.036 g (0.03 mmol) of [Pd(PPh_3)$_4$], and 15 mL of *n*-propylamine, at 60 °C during 8 h to give 0.207 g (99%); mp 163−4 °C; ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 9H), 7.35 (m, 2H), 7.81 (m, 2H), 7.75 (ABq, J_{AB} = 8.5 Hz, $\Delta\nu$ value 57.8 Hz, 4H), 7.88 (m, 2H), 8.70 (d, J = 8.1 Hz, 4H), 8.73 (s, 2H); ^{13}C-{^{1}H} NMR ($CDCl_3$) δ −0.04, 95.8, 104.7, 118.6, 121.4, 123.9, 127.1, 132.2, 136.9, 138.3, 149.0, 149.3, 155.9, 156.0; IR (KBr, cm^{-1}) 2972 (w), 2154 (m), 1582 (s), 1564 (s), 1508 (m), 1466 (m), 1386 (s), 1252 (s), 1110 (m), 838 (s); GC-MS *m*/*z* 405 (M^+, 78), 390 (M − CH_3, 100), 375 (M − 2CH_3, 5). Anal. Calcd for $C_{26}H_{23}N_3Si$: C, 77.00; H, 5.72; N, 10.36. Found: C, 76.83; H, 5.61; N, 10.13.

4′-(4-Ethynylphenyl)-2,2′:6′,2″-terpyridine (6c). Prepared from 0.192 g (0.472 mmol) of **6b**, 0.030 g (0.516 mmol) of KF, 8 mL of THF, and 5 mL of MeOH to give 0.145 g (92%); mp 187−8 °C; ^{1}H NMR ($CDCl_3$) δ 3.20 (s, 1H), 7.32 (m, 2H), 7.73 (ABq, J_{AB} = 7.3 Hz, $\Delta\nu$ value 47.4 Hz, 4H), 7.83 (m, 2H), 8.62 (d, J = 7.9 Hz, 2H), 8.69 (s, 2H), 8.70 (d, J = 4.2 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 78.6, 83.3, 118.6, 121.3, 122.8, 123.8, 127.2, 132.6, 136.79, 138.7, 149.1, 156.0; IR (KBr, cm^{-1}) 3206 (s), 3064 (m), 2926 (m), 2096 (w), 1584 (s), 1542 (m), 1466 (s), 1442 (m), 1388 (s), 1076 (m), 1038 (m); GC-MS *m*/*z* 333 (M^+, 100). Anal. Calcd for $C_{23}H_{15}N_3$: C, 82.86; H, 4.54; N, 12.60. Found: C, 82.79; H, 4.50; N, 12.40.

4′-[2-(Trimethylsilyl)-1-ethynyl]-2,2′:6′,2″-terpyridine (7c). This compound was either prepared, in good yield, from 4′-bromo-2,2′:6′,2″-terpyridine **7a** or from 4′-[{(trifluoromethyl)-sulfonyl}oxy]-2,2′:6′,2″-terpyridine **7b**. Prepared following exp. conditions 2, from 0.200 g (0.620 mmol) of **7a**, 0.186 mL (1.282 mmol) of (trimethylsilyl)acetylene, 0.044 g (0.04 mmol) [Pd-(PPh_3)$_4$], 16 mL of *n*-propylamine, at 60 °C, 6 h to give 0.177 g (87%); or prepared following exp. conditions 3, from 0.600 g (1.575 mmol) of **7b**, 0.45 mL (3.15 mmol) of (trimethylsilyl)-acetylene, 0.070 g (0.1 mmol) of [Pd(PPh_3)$_2$$Cl_2$], 0.070 g (2.72 mmol) of CuI, 18 mL of THF, and 7.5 mL of diisopropylamine to give 0.390 g (75%); mp 100−1 °C; ^{1}H NMR ($CDCl_3$) δ −0.27 (s, 9H), 7.26 (dd, J = 6.6 Hz, J = 5.1 Hz, 2H), 7.77 (td, J = 7.8 Hz, J = 1.6 Hz, 2H), 8.47 (s, 2H), 8.52 (d, J = 7.8 Hz, 2H), 8.64 (d, J = 5.1 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −0.3, 99.4, 102.7, 121.0, 123.0, 123.9, 133.0, 136.7, 149.0, 155.3, 155.4; IR (KBr, cm^{-1}) 2828 (m), 2164 (m), 1584 (s), 1564 (s), 1544 (m), 1468 (s), 1392 (s), 1246 (s), 1110 (m), 926 (s), 850 (s), 790 (s); GC-MS *m*/*z* 329 (M^+, 100), 314 (M − CH_3, 95), 299 (M − 2CH_3, 10), 284 (M − 3CH_3, 8). Anal. Calcd for $C_{20}H_{19}N_3Si$: C, 72.91; H, 5.81; N, 12.75. Found: C, 72.80; H, 5.74; N, 12.53.

4′-Ethynyl-2,2′:6′,2″-terpyridine (7d). Prepared from 1.450 g (4.40 mmol) of **7c**, 0.307 g (5.28 mmol) of KF, 80 mL of THF, and 50 mL of MeOH to give 1.076 g (95%); mp 173−5 °C; ^{1}H NMR (CD_2Cl_2) δ 3.43 (s, 1H), 7.36 (ddd, J = 5.0 Hz, J = 4.8 Hz, J = 1.1 Hz, 2H), 7.88 (td, J = 7.9 Hz, J = 1.8 Hz, 2H), 8.53 (s, 2H), 8.60 (d, J = 7.9 Hz, 2H), 8.68 (ld, J = 4.8 Hz, 2H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 81.7, 81.9, 121.4, 123.6, 124.6, 132.5, 137.3, 149.7, 155.7, 156.1; IR (KBr, cm^{-1}) 3218 (s), 2924 (m), 2108 (m), 1584 (s), 1564 (s), 1566 (s), 1490 (s), 1046 (m), 987 (m); GC-MS *m*/*z* 257 (M^+, 100). Anal. Calcd for $C_{17}H_{11}N_3$: C, 79.36; H, 4.31; N, 16.33. Found: C, 79.18; H, 4.17; N, 16.12.

Bis(2,2′:6′,2″-terpyridin-4′-yl)ethyne (8a). Prepared using exp. conditions 1 from 4′-[{(trifluoromethyl)sulfonyl}oxy]-2,2′:6′,2″-terpyridine **7b** (0.150 g, 0.393 mmol), benzene (18 mL), 4′-ethynyl-2,2′:6′,2″-terpyridine **7d** (0.100 g, 0.393 mmol), [Pd(PPh_3)$_4$] (0.027 g, 0.023 mmol), and 3.5 mL of diisopropylamine at 80 °C, 16 h, chromatography (alumina 5% CH_3OH/CH_2Cl_2), recrystallized from CH_2Cl_2/hexane to give 0.157 g, 82%; mp >270 °C; ^{1}H NMR ($CDCl_3$) δ 8.75 (d, J = 4.1 Hz, 4H), 8.64 (s, 4H), 8.63 (d, J = 7.8 Hz, 4H), 7.89 (td, J = 7.8 Hz, J = 1.6 Hz, 4H), 7.38 (m, 4H); Raman (neat, cm^{-1}) 2224; EI MS *m*/*e* (rel intens) 488 (100), 256 (58). Anal. Calcd for $C_{32}H_{20}N_6$: C, 78.67; H, 4.13; N, 17.20. Found: C, 78.44; H, 3.97; N, 16.93.

Bis[(2,2′:6′,2″-terpyridin-4′-yl)phenyl]ethyne (9a). Prepared following exp. conditions 2, from 4′-(4-ethynylphenyl)-2,2′:6′,2″-terpyridine **6c** (0.100 g, 0.300 mmol) and 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine **6a** (0.117 g, 0.300 mmol), *n*-propylamine (18 mL), [Pd(PPh_3)$_4$] (0.021 g, 0.018 mmol), and *n*-propylamine (2 mL), 6 h, 60 °C, and recrystallized from CH_2-Cl_2/MeOH/hexane to give 0.151 g, 79%; mp >270 °C; ^{1}H NMR (DMF-d_7, 100 °C) δ 8.84 (d, J = 4.8 Hz, 4H), 8.83 (s, 4H), 8.80 (d, J = 7.8 Hz, 4H), 8.13 (td, J = 7.8 Hz, J = 1.8 Hz, 4H), 7.94 (ABq, J_{AB} = 8.6 Hz, $\Delta\nu$ = 21.8 Hz, 8H), 7.60 (ddd, J = 7.8 Hz, J = 4.8 Hz, J = 1.1 Hz, 4H); IR (KBr, cm^{-1}) 3489 (w), 3411 (w), 2989 (w), 1583 (s), 1561 (s), 1522 (m), 1467 (s), 1383 (s), 833 (m), 794 (s); FAB$^+$ MS *m*/*z* 641.1 [M^+ + H], 408.1 [M^+ − terpy]. Anal. Calcd for $C_{44}H_{28}N_6$: C, 82.48; H, 4.41; N, 13.12. Found: C, 82.13; H, 4.26; N, 12.80.

General Procedure for the Preparation of the Butadiyne Ligands. Method 1. To a stirred solution of the ethynyl derivative in DMF were added CuCl and $CuCl_2$ as a solid. The solution was saturated with oxygen and stirred, at rt for 5 days. After the disappearance of the starting ethynyl compound (TLC after copper decomplexation), addition of KCN in water (5 mL) led to copper decomplexation. After extraction of the free ligand with CH_2Cl_2, the crude product was chromatographed (alumina CH_2Cl_2/MeOH) and recrystallized from CH_2Cl_2/hexane.

Method 2. To a deep-green oxygen-degassed solution of CuCl and *N*,*N*′,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in MeCN was added the ethynyl derivative as a solid. Immediately after addition, the color of the solution turned brown. During the course of the reaction (at rt), an abundant precipitate formed. After 5 h, the crude product was filtered, washed with ether (3 × 25 mL), and purified through a flash chromatography column packed with silica gel and eluted with CH_2Cl_2/MeOH.

Method 3. To a solution of CuCl in pyridine was added the ethynyl derivative as a solid, and the solution was degassed under oxygen during 3 h. Immediately after addition, the color of the solution turned brown. During the course of the reaction (at rt), an abundant precipitate formed. After 5 h, the suspension was centrifuged, washed with ether (3 × 25 mL) and purified by chromatography on neutral alumina, eluting with CH_2Cl_2/MeOH (99/1 v/v).

Bis(2,2′:6′,2″-terpyridin-4′-yl)butadiyne (8b). Prepared following the general procedure (method 1) from 4′-ethynyl-2,2′:6′,2″-terpyridine **7d** (0.160 g, 0.622 mmol), DMF (15 mL), CuCl (1.846 g, 18.65 mmol), and $CuCl_2$ (0.836 g, 6.22 mmol), under oxygen at rt during 5 days, chromatography (alumina 3% MeOH/CH_2Cl_2), and recrystallization from CH_2Cl_2/hexane to give 0.107 g, 67%; mp >270 °C; ^{1}H NMR ($CDCl_3$) δ 8.74 (d, J = 4.8 Hz, 4H), 8.62 (d, J = 7.8 Hz, 4H), 8.60 (s, 4H), 7.87 (td, J = 7.8 Hz, J = 1.7 Hz, 4H), 7.38 (ddd, J = 7.5 Hz, J = 4.8 Hz, J = 1.1 Hz, 4H); Raman (neat product, cm^{-1}) 2224; EI MS *m*/*e* (rel intens) 512 (82), 256 (100). Anal. Calcd for $C_{34}H_{20}N_6$: C, 79.67; H, 3.93; N, 16.40. Found: C, 79.48; H, 3.72; N, 16.14.

Bis[(2,2′:6′,2″-terpyridin-4′-yl)phenyl]butadiyne (9b). Prepared following the general procedure (method 1), from 4′-(4-ethynylphenyl)-2,2′:6′,2″-terpyridine **6c** (0.200 g, 0.600 mmol), DMF (14 mL), CuCl (1.780 g, 17.980 mmol), $CuCl_2$ (0.806 g, 6.00 mmol), oxygen, rt, during 1 week, and recrystallized in CH_2Cl_2 to give 0.092 g, 46%; mp >270 °C; ^{1}H NMR (DMF-d_7, 120 °C) δ 8.92 (m, 12H), 8.22 (td, J = 7.7 Hz, J = 1.7 Hz, 4H), 8.03 (AB q, J_{AB} = 8.6 Hz, $\Delta\nu$ = 21.8 Hz, 8H), 7.69 (ddd, J = 7.4 Hz, J = 4.8 Hz, J = 1.0 Hz, 4H); IR (KBr, cm^{-1}) 2147 (w), 1605 (m), 1586 (s), 1583 (s), 1566 (m), 1467 (m), 1390 (m), 1264 (m), 790 (s); FAB$^+$ *m/z* 665.2 (M$^+$ + H), 432.2 (M$^+$ − terpy). Anal. Calcd for $C_{46}H_{28}N_6$: C, 83.11; H, 4.25; N, 12.64. Found: C, 82.89; H, 4.13; N, 12.56.

Bis(5,5′-dimethyl-2,2′-bipyridin-6-yl)ethyne (10a). Prepared following exp. conditions 1 from 6-bromo-5,5′-dimethyl-2,2′-bipyridine (0.126 g, 0.480 mmol), 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine (0.100 g, 0.480 mmol), 0.033 g (0.028 mmol) of [Pd(PPh$_3$)$_4$], 30 mL of benzene, and 6 mL of diisopropylamine to give 0.093 g (99%); mp 214−5 °C; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 6H), 2.62 (s, 6H), 7.61 (dd, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 8.29 (d, J = 8.1 Hz, 2H), 8.41 (d, J = 8.1 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 18.3, 19.5, 90.5, 120.3, 120.8, 133.3, 136.1, 137.4, 138.0, 141.8, 149.4, 153.0, 154.4; Raman (neat, cm^{-1}) 2204/2218; GC-MS *m/z* 390 (M$^+$, 100). Anal. Calcd for $C_{26}H_{22}N_4$: C, 79.97; H, 5.68; N, 14.35. Found: C, 79.69; H, 5.32; N, 14.17.

Bis(5,5′-dimethyl-2,2′-bipyridin-6-yl)butadiyne (10b). Prepared following the general procedure (method 2), from CuCl (0.024 g, 0.24 mmol) and TMEDA (0.036 mL, 0.24 mmol) in CH_3CN (10 mL) and 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine (0.209 g, 1.003 mmol). Purification by flash chromatography on silica gel, eluting with CH_2Cl_2/MeOH (97/3) to give 0.162 g (78%); mp 244−6 °C; ^{1}H NMR (2/3 CD_2Cl_2 + 1/3 CD_3OD) δ 2.34 (s, 6H), 2.50 (s, 6H), 7.66 (dd, J = 8.1 Hz, J = 1.9 Hz, 2H), 7.72 (dd, J = 8.1 Hz, J = 0.6 Hz, 2H) 1H), 8.12 (d, J = 8.2 Hz, 2H), 8.18 (d, J = 8.2 Hz, 2H), 8.39 (d, J = 0.6 Hz, 2H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 18.5, 19.4, 76.2, 81.3, 120.7, 121.3, 134.3, 137.9, 138.2, 138.6, 141.0, 150.0, 153.2, 155.1; Raman (neat, cm^{-1}) 2217; GC-MS *m/z* 414 (M$^+$, 100). Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; H, 13.52. Found: C, 80.87; H, 5.21; N, 13.29.

Bis(2,2′-bipyridin-4-yl)ethyne (11a). Prepared following exp. conditions 1 from 0.129 g (0.549 mmol) of **1a**, 0.099 g (0.549 mmol) of **1c**, 0.039 g (0.034 mmol) of [Pd(PPh$_3$)$_4$], 27 mL of benzene, and 6 mL of diisopropylamine to give 0.147 g (80%); mp >270 °C; ^{1}H NMR ($CDCl_3$) δ 7.38 (t, J = 7.1 Hz, 2H), 7.45 (d, J = 4.8 Hz, 2H), 7.87 (td, J = 7.1 Hz, J = 1.0 Hz, 2H), 8.44 (d, J = 8.0 Hz, 2H), 8.60 (s, 2H), 8.72 (d, J = 4.8 Hz, 4H); GC-MS *m/z* 334 (M$^+$, 100). Anal. Calcd for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.76. Found: C, 78.78; H, 4.02; N, 16.53.

Bis(2,2′-bipyridin-4-yl)butadiyne (11b). Prepared following the general procedure (method 2), from 0.147 g (0.816 mmol) of **1c**, 0.297 g (0.408 mmol) of CuCl, 0.060 mL (0.408 mmol) of TMEDA, and 15 mL of MeCN to give 0.072 g (98%); mp >270 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (t, J = 7.2 Hz, 2H), 7.41 (d, J = 4.9 Hz, 2H), 7.85 (d, J = 7.2 Hz, 2H), 8.41 (d, J = 7.9 Hz, 2H), 8.57 (s, 2H), 8.69 (d, J = 4.9 Hz, 4H); Raman (neat, cm^{-1}) 2223; GC-MS *m/z* 358 (M$^+$, 100). Anal. Calcd for $C_{24}H_{14}N_4$: C, 80.43; H, 3.94; N, 15.63. Found: C, 80.36; H, 3.83; N, 15.52.

Bis[4-(2,2′:4′,2″-terpyridin-6′-yl)phenyl]ethyne (12a). Prepared following exp. conditions 2 from 0.080 g (0.240 mmol) of **5c**, 0.093 g (0.240 mmol) of **5a**, 0.017 g (0.015 mmol) of [Pd(PPh$_3$)$_4$], and 16 mL of *n*-propylamine to give 0.136 g (88%); mp >270 °C; ^{1}H NMR ($CDCl_3$) δ 7.39 (t, J = 6.4 Hz, 4H), 7.89 (m, 4H), 8.03 (AB q, J_{AB} = 8.3 Hz, $\Delta\nu$ = 116.2 Hz, 8 H), 8.11 (d, J = 8.0 Hz, 2H), 8.62 (s, 2H), 8.77 (m, 6H), 8.99 (s, 2H); IR (KBr, cm^{-1}) 2926 (s), 2858 (m), 1656 (s), 1582 (s), 1548 (s), 1468 (s), 1440 (m), 1396 (s), 1264 (s), 1122 (m), 1074 (m), 842 (m), 778 (s); FAB$^+$ *m/z* 641 [M$^+$ + H], 332 [M − phenyl/bipy/py], 308 [M − C≡Cphenyl/bipy/py]. Anal. Calcd for $C_{44}H_{28}N_6$: C, 82.48; H, 4.40; N, 13.12. Found: C, 82.19; H, 4.19; N, 12.88.

Bis[4-(2,2′:4′,2″-terpyridin-6′-yl)phenyl]butadiyne(12b). Prepared following the general procedure (method 2), from 0.080 g (0.240 mmol) of **5c**, 0.012 g (0.120 mmol) of CuCl, 0.018 mL (0.120 mmol) of TMEDA, and 18 mL of CH_3CN to give 0.077 g (97%); mp >270 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (t, J = 6.5 Hz, 4H), 7.86 (m, 4H), 8.00 (ABq, J_{AB} = 8.2 Hz, $\Delta\nu$ = 114.9 Hz, 8H), 8.07 (d, J = 7.9 Hz, 2H), 8.59 (s, 2H), 8.69 (m, 6H), 8.95 (s, 2H); IR (KBr, cm^{-1}) 2922 (w), 1656 (w), 1582 (s), 1548 (s), 1470 (s), 1438 (m), 1392 (s), 1122 (s), 1046 (m), 774 (s); FAB$^+$ *m/z* 665 [M$^+$ + H], 332 [M/2 + C]. Anal. Calcd for $C_{46}H_{28}N_6$: C, 83.11; H, 4.25; N, 12.64. Found: C, 82.89; H, 4.13; N, 12.41.

Bis(2,2′-bipyridin-5-yl)ethyne (13a). Prepared following exp. conditions 1 from 0.083 g (0.35 mmol) of **2a**, 0.063 g (0.35 mmol) of **2c**, 0.038 g (0.03 mmol) of [Pd(PPh$_3$)$_4$], 5 mL of benzene, and 2 mL of diisopropylamine to give 0.086 g (73%); mp 230−2 °C; ^{1}H NMR ($CDCl_3$) δ 8.85 (d, J = 1.8 Hz, 2H), 8.70 (d, J = 4.5 Hz, 2H), 8.44 (d, J = 8.4 Hz, 4H), 7.97 (dd, J = 8.3 Hz, J = 2.1 Hz, 2H), 7.83 (pseudo td, J = 7.7 Hz, J = 1.7 Hz, 2H), 7.32 (dd, J = 6.5 Hz, J = 4.9 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 90.55, 119.73, 120.50, 121.53, 124.14, 137.08, 139.58, 149.43, 151.78, 155.38, 155.46; IR (KBr, cm^{-1}) 3049 (w), 2976 (m), 1588 (w), 1570 (s), 1543 (s), 1496 (s), 1435 (m), 1370 (s), 1243 (s), 1091 (m), 798 (s); FAB$^+$ MS *m/z* 335.2 [M + H]$^+$. Anal. Calcd for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.76. Found: C, 78.94; H, 4.15; N, 16.71.

Bis(2,2′-bipyridin-5-yl)butadiyne (13b). Prepared following the general procedure (method 3), from 0.090 g (0.50 mmol) of **2c**, 0.050 g (0.50 mmol) of CuCl, and 20 mL of pyridine to give 0.064 g (72%); mp 260 °C dec; ^{1}H NMR (D_2O + 20%DCl + 1% ^{t}BuOH) δ 8.94 (d, J = 6.8 Hz, 2H), 8.93 (s, 2H), 8.72 (m, 4H), 8.33 (m, 4H), 8.12 (m, 2H); IR (KBr, cm^{-1}) 2922 (w), 1640 (w), 1582 (s), 1542 (s), 1458 (s), 1435 (m), 1370 (m), 1042 (m), 852 (s), 791 (s), 733 (s); FAB$^+$ MS *m/z* 359.3 [M + H]$^+$, 100%. Anal. Calcd for $C_{24}H_{14}N_4$: C, 80.43; H, 3.94; N, 15.63. Found: C, 80.12; H, 3.69; N, 15.35.

4′-(2,2′-Bipyridin-4-ylethynyl)-2,2′:6′,2″-terpyridine (14). Prepared following exp. conditions 1 from 4′-ethynyl-2,2′:6′,2″-terpyridine **7d** (0.120 g, 0.466 mmol) and 4-bromo-2,2′-bipyridine **1a** (0.110 g, 0.466 mmol), benzene (20 mL), diisopropylamine (5 mL), and 0.032 g (0.025 mmol) of [Pd(PPh$_3$)$_4$], 22 h at 80 °C. Purified by chromatography (flash silica 2% MeOH/CH_2Cl_2) and recrystallized from CH_2Cl_2/hexane to give 0.144 g, 75%; mp 198−9 °C; ^{1}H NMR ($CDCl_3$) δ 7.39 (m, 4H), 7.63 (dd, J = 7.7 Hz, J = 1.8 Hz, 1H), 7.86 (m, 3H), 8.40 (d, J = 7.9 Hz, 1H), 8.60 (m, 4H), 8.70 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 90.8, 91.4, 121.1, 121.2, 123.0, 123.4, 124.1, 125.3, 128.3, 128.6, 131.5, 131.9, 132.0, 132.2, 136.9, 149.3, 155.2, 155.4, 155.7, 156.4; IR (KBr, cm^{-1}) 3050 (m), 2926 (m), 2858 (m), 1582 (s), 1566 (m), 1460 (s), 1114 (s), 786 (s), 730 (s); FAB$^+$ *m/z* 411 [M + H]$^+$. Anal. Calcd for $C_{27}H_{17}N_5$: C, 78.82; H, 4.16; N, 17.02. Found: C, 78.75; H, 4.12; N, 16.97.

5,5′-Bis(2,2′-bipyridin-5-ylethynyl)-2,2′-bipyridine (15). Prepared following exp. conditions 1, from 0.115 g (0.64 mmol) of **2c**, 0.100 g (0.32 mmol) of **3a**, 0.076 g (0.066 mmol) of [Pd(PPh$_3$)$_4$], benzene (10 mL), and diisopropylamine (4 mL) to give 0.110 g (67%); mp >300 °C; FAB$^+$ *m/z* 513 [M + H]$^+$; FT-IR (KBr, cm^{-1}) 3048 (m), 2976 (m), 1588 (m), 1569 (m), 1542 (m), 1463 (s), 1434 (m), 1368 (m), 1092 (m), 1050 (m), 1020 (m), 856 (m), 840 (s), 796 (s), 738 (s). Anal. Calcd for $C_{34}H_{20}N_6$: C, 79.51; H, 3.93; N, 16.40. Found: c, 79.51; H, 3.71; N, 16.27.

5,5′-Bis[(5,5′-dimethyl-2,2′-bipyridin-6-yl)ethynyl]-2,2′-bipyridine (16). Prepared following exp. conditions 1, from 0.100 g (0.32 mmol) of **3a**, 0.133 g (0.64 mmol) of 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine, 0.076 g (0.066 mmol) of [Pd(PPh$_3$)$_4$], benzene (10 mL), and diisopropylamine (4 mL) to give 0.158 g (87%); mp 264−5 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 6H), 2.60 (s, 6H), 7.63 (dd, J = 8.2 Hz, J = 2.0 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 8.06 (dd, J = 7.6 Hz, J = 2.0 Hz, 2H), 8.29 (d, J = 8.0 Hz, 2H), 8.37 (d, J = 8.0 Hz, 2H), 8.48 (s, 2H), 8.51 (d, J = 5.5 Hz, 2H), 8.94 (s, 2H); ^{13}C{^{1}H} NMR (D_2O + 20%DCl + 1% ^{t}BuOH) δ 18.3, 19.2, 87.8, 83.7, 121.92−148.68 (aromatics); FAB$^+$ *m/z* 569 [M + H]$^+$; FT-IR (KBr, cm^{-1}) 3012 (s), 2916 (s), 2220 (w), 1582 (s), 1550 (s), 1465 (s), 1252 (s), 1132 (s), 1069 (s), 1023 (s), 824 (s), 736 (m), 652 (m), 495 (m). Anal. Calcd for $C_{38}H_{28}N_6$: C, 80.26; N, 4.96; N, 14.78. Found: C, 79.83; H, 4.72; N, 14.69.

6,6′-Bis[(5,5′-dimethyl-2,2′-bipyridin-6-yl)ethynyl]-2,2′-bipyridine (17). Prepared following exp. conditions 1, from

0.100 g (0.32 mmol) of 6,6′-dibromo-2,2′-bipyridine, 0.133 g (0.64 mmol) of 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine, 0.072 g (0.062 mmol) of $[Pd(PPh_3)_4]$, benzene (10 mL), and diisopropylamine (3 mL) to give 0.140 g (77%); mp 277−8 °C; ^{1}H NMR (CD_2Cl_2) δ 2.07 (s, 6H), 2.31 (s, 6H), 7.38 (m, 6H), 7.60 (t, J = 7.9 Hz, 2H), 8.03 (t, J = 7.6 Hz, 4H), 8.17 (ls, 2H), 8.25 (d, J = 7.9 Hz, 2H); ^{13}C{^{1}H} NMR (D_2O + 20% DCl) δ 18.3, 19.5, 87.6, 92.8, 124.0, 124.3, 125.3, 132.1, 138.2, 139.8, 140.1, 141.4, 141.6, 142.0, 144.2, 144.6, 145.0, 147.6, 149.1; FAB$^+$ m/z 569 $[M + H]^+$; FT-IR (KBr, cm^{-1}) 2216 (w), 1556 (s), 1486 (m), 1434 (s), 1249 (m), 1131 (m), 1095 (m), 1068 (m), 1026 (m), 830 (s), 794 (s), 750 (m), 638 (m), 586 (m). Anal. Calcd for $C_{38}H_{28}N_6$: C, 80.26; H, 4.96; N, 14.78. Found: C, 80.07; H, 4.83; N, 14.62.

4,4′-Bis[(5,5′-dimethyl-2,2′-bipyridin-6-yl)ethynyl]-2,2′-bipyridine (18). Prepared following exp. conditions 1, from 0.100 g (0.32 mmol) of 4,4′-dibromo-2,2′-bipyridine, 0.133 g (0.64 mmol) of 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine, 0.072 g (0.062 mmol) of $[Pd(PPh_3)_4]$, benzene (10 mL), and diisopropylamine (3 mL) to give 0.134 g (74%); mp 241−2 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 12H), 2.60 (s, 12H), 7.54 (dd, J = 5.0 Hz, J = 1.5 Hz, 2H), 7.63 (dd, J = 8.2 Hz, J = 2.0 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 8.30 (d, J = 8.1 Hz, 2H), 8.37 (d, J = 8.1 Hz, 2H), 8.49 (s, 2H), 8.63 (s, 2H), 8.73 (d, J = 5.0 Hz, 2H); ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 18.4, 19.4, 89.7, 92.1, 120.8, 123.5, 126.0, 132.0, 133.6, 136.5, 137.5, 138.2, 141.4, 149.4, 149.6, 153.0, 154.6, 155.8; FAB$^+$ m/z 569 $[M + H]^+$; FT-IR (KBr, cm^{-1}) 2920 (m), 2208 (w), 1588 (s), 1553 (m), 1534 (m), 1487 (m), 1465 (m), 1444 (m), 1354 (m), 1099 (m), 1047 (m), 824 (s), 574 (m). Anal. Calcd for $C_{38}H_{28}N_6$: C, 80.26; H, 4.96; N, 14.78. Found: C, 80.11; H, 4.69; N, 14.57.

5,5′-Bis(2,2′:6′,2″-terpyridin-4′-ylethynyl)-2,2′-bipyridine (19). Prepared following exp. conditions 1, from 0.050 g (0.16 mmol) of **3a**, 0.083 g (0.32 mmol) of **7d**, 0.035 g (0.030 mmol) of $[Pd(PPh_3)_4]$, benzene (5 mL), and diisopropylamine (4 mL) to give 0.071 g (67%); mp >290 °C; FAB$^+$ m/z 667 $[M + H]^+$; IR (KBr, cm^{-1}) 3075 (m), 3037 (m), 3000 (m), 2920 (m), 2218 (w), 1581 (s), 1567 (s), 1384 (s), 1226 (m), 1022 (m), 997 (m). Anal. Calcd for $C_{44}H_{26}N_8$: C, 79.26; H, 3.93; N, 16.81. Found: C, 79.01; H, 3.73; N, 16.50.

6,6′-Bis(2,2′:6′,2″-terpyridin-4′-ylethynyl)-2,2′-bipyridine (20). Prepared following exp. conditions 1, from 0.066 g (0.32 mmol) of 6,6′-diethynyl-2,2′-bipyridine, 0.252 g (0.66 mmol) of **7d**, 0.025 g (0.022 mmol) of $[Pd(PPh_3)_4]$, benzene (18 mL), and diisopropylamine (3.5 mL), to give 0.139 g (65%): mp >300 °C. Due to the low solubility of this compound the NMR spectra could not be measured; FAB$^+$ m/z 667 $[M + H]^+$; IR (KBr, cm^{-1}) 3059 (m), 3010 (m), 2215 (w), 1565 (s), 1467 (s), 1390 (s), 1251 (s), 1152 (m), 988 (m), 887 (m). Anal. Calcd for $C_{44}H_{26}N_8$: C, 79.26; H, 3.93; N, 16.81. Found: C, 79.01; H, 3.89; N, 16.73.

2,9-Bis(2,2′:6′,2″-terpyridin-4′-ylethynyl)-1,10-phenanthroline (21). Prepared following exp. conditions 1, from 0.159 g (0.64 mmol) of 2,9-dichloro-1,10-phenanthroline, 0.325 g (1.28 mmol) of **7d**, 0.152 g (0.131 mmol) of $[Pd(PPh_3)_4]$, benzene (20 mL), and diisopropylamine (8 mL) to give 0.332 g (75%); mp >300 °C; ^{1}H NMR (CD_2Cl_2) δ 7.38 (ddd, J = 7.5 Hz, J = 4.8 Hz, J = 1.2 Hz, 2H), 7.91 (td, J = 7.2 Hz, J = 1.8 Hz, 6H), 7.96 (t, J = 8.4 Hz, 2H), 8.35 (d, J = 8.3 Hz, 2H), 8.66 (d, J = 8.0 Hz, 4H), 8.71 (dd, J = 4.8 Hz, J = 1.8 Hz, 4H), 8.79 (s, 4H); ^{13}C{^{1}H} NMR (CD_2Cl_2, 50.3 MHz) δ 156.3, 155.9, 149.8, 143.1, 137.3, 136.8, 128.9, 127.6, 127.3, 124.9, 124.5, 123.8, 123.6, 121.4, 93.3; FAB$^+$ m/z 691 $[M + H]^+$; IR (KBr, cm^{-1}) 3054 (w), 3000 (w), 1581 (s), 1565 (s), 1538 (m), 1490 (m), 1466 (m), 1389 (m), 862 (m), 793 (s), 743 (m), 620 (m). Anal. Calcd for $C_{46}H_{26}N_8$: C, 79.98; H, 3.79; N, 16.22. Found: C, 79.83; H, 3.70; N, 16.03.

6,6″-Bis(2,2′:6′,2″-Terpyridin-4′-ylethynyl)-4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine (22). Prepared following exp. conditions 1, from 0.120 g (0.25 mmol) of 6,6″-dibromo-4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine, 0.129 g (0.50 mmol) of **7d**, 0.036 g (0.031 mmol) of $[Pd(PPh_3)_4]$, benzene (14 mL), and diisopropylamine (2.4 mL) to give 0.150 g (72%); mp >300 °C; FAB$^+$ m/z 834.3 $[M + H]^+$; IR (KBr, cm^{-1}) 3417 (m), 1601 (m), 1564 (s), 1542 (m), 1460 (m), 1390 (s), 1262 (m), 1086 (m), 987 (m), 887 (m), 806 (m), 788 (s), 732 (m). Anal. Calcd for $C_{56}H_{35}N_9$: C, 80.65; H, 4.23; N, 15.12. Found: C, 80.20; H, 4.00; N, 14.69.

Supporting Information Available: Spectroscopic data for **2a**, **3a**, and **7a** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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