Synthesis of Quasi-Linear and Segmented Bis- to Penta-2,2′-bipyridine Polytopic Ligands Built via a Convergent Approach

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Reliable and practical routes for the preparation of segmented oligomeric 2,2′-bipyridine-based ligands possessing rigid and conjugated spacers are presented. The first series of ligands bears a single alkyne function as a bridge and has been built by Pd(0)-catalyzed cross-coupling reactions between ethynylated and bromo-substituted derivatives of 2,2′-bipyridine (bipy). These new ligands provide access to numerous hexameric, octameric, and decameric pyridine-based materials. Optimum conditions were found with $[Pd(PPh_3)_4]$ (6 mol %) in benzene containing diisopropylamine at 80 °C. The second series of soluble ligands was synthesized around a 1,4-diethynyl-2,5-didodecyloxybenzene bridging unit. The synthesis required a protection/deprotection methodology, as well as a chemioselective palladium-catalyzed Sonogashira−Hagihara cross-coupling protocol to obtain the target multitopic ligands. Within this strategy, the pivotal **15b**, **17**, and **19b** intermediates bearing one or two bipy and phenyl units are required and such entities have been isolated in excellent yield. The products are highly soluble and photostable. In each case, the final step involves a double cross-coupling reaction between the appropriate constituents, with the best preparative conditions involving $[Pd(PPh_3)_4]$ (6 mol %) in *n*-propylamine at 70 °C. The main advantage of this methodology lies in its synthetic versatility and adaptability for creating multitopic metal-binding scaffolds with a potentially large variety of bridging units and phenyl substituents. Spectroscopic data for the new oligomers show a steady decrease in optical energy with an increasing degree of oligomerization. The different results obtained with these ligands highlight the importance of the rigid 1,4-diethynylphenyl linker in directing the outcome of the nanosized molecules.

Introduction

The design and characterization of well-defined transition-metal complexes possessing interesting redox and/or photochemical properties is a research area that is attracting considerable interest.[1] Most of these complexes are constructed from aromatic polyimine ligands such as 2,2′-bipyridine (bipy) or 2,2′:6′,2″-terpyridine (terpy).[2,3] Because of their unique structural properties and synthetic versatility, these emergent luminescent molecules fulfill a pivotal role in the design of new optoelectronic devices,[4,5] as well as in the mimicry of natural photosynthetic processes.[6] In natural photosynthetic assemblies, regular arrays of pigments serve as light-harvesting units that direct incident photons toward a reaction center where electron-transfer reactions occur.[7] Recent structural determination of certain photosynthetic light-harvesting complexes from purple bacteria has suggested that these arrays effectively delocalize photons over a large number of spatially isolated but chemically identical pigment molecules.[8] This realization has stimulated us to design and prepare conjugated ligands bearing interconnected chelating centers. Furthermore, while a variety of luminescent scaffolds are available, probes based on electronically conjugated backbones offer some significant advantages for a number of applications where long-lived excited-state lifetimes and visible light activation are important considerations.[9] Within this family of substances, we and others have found that luminophoric centers connected via alkyne spacers are promising synthetic targets with respect to material

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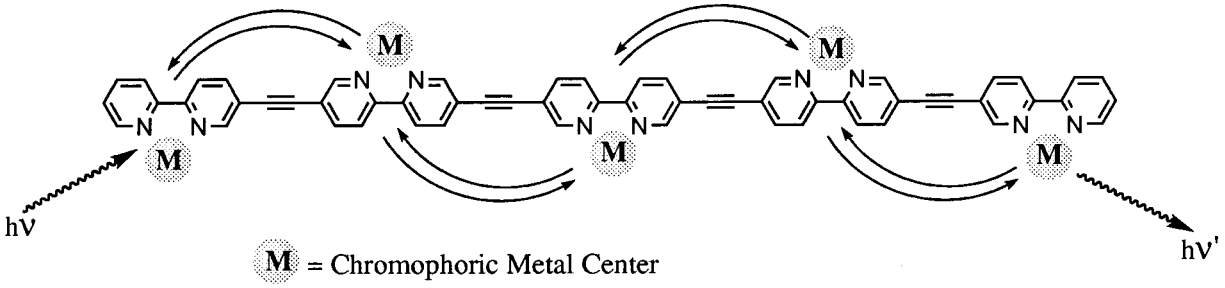

science applications.[10,11] Furthermore, alkyne-based modules have been used extensively in the field of crystal engineering,[12] liquid crystals,[13,14] and dendritic macromolecules.[15,16]

Several recent reports have described synthetic procedures for the step-by-step construction of rationally designed oligomeric structures bearing appropriate coordination sites. However, synthetic protocols for the preparation of ditopic ligands bearing an increasing number of spacer units are more commonplace, and some of the resultant d^8-block metal complexes display outstanding redox and photophysical properties.[17] We recently found a convergent synthetic pathway for the construction of back-to-back terpyridine ligands bearing an increasing number of phenylene/ethynylene modules. This strategy requires an iterative sequence of reactions that extend the central spacer framework outward from the 1,4-diethynylene-2,5-didocyloxybenzene core.[18]

2,2′-Bipyridine is well suited for the construction of polychelating molecules because it is rigid and quasi-planar when coordinated to a metallic center and forms stable complexes with a inordinately wide range of cations. It has also been shown that bipy itself can function as a tunable bridge.[19] Oligomeric pyridines have been known for a long time; however, there are few versatile synthetic routes, and poor solubility of the free ligands render their proper characterization a difficult task.[20] We might surmise that the synthesis of segmented ligands in which the chelating centers are bridged by one ethynylene or a 1,4-diethynylphenylene module might prove amenable to facile oligomerization. To test this idea, the preparation of a variety of rigid ligands bearing an increasing number of metal ion binding sites (1−5) separated by a single alkyne bond or by a 1,4-diethynylene-2,5-didocyloxybenzene moiety was attempted, and full synthetic details are provided here. Solubility problems associated with the increasing number of polyaromatic units can be circumvented by the use of solubilizing groups attached to the substituted phenylene unit. The combination of bipy templates with coupling reactions involving sp carbon centers illustrates the capacity of this approach.

Our motivation for this work arises, in part, from our desire to identify suitable luminophoric multimetallic complexes that are able to display intramolecular photon shuttling under visible light illumination. This concept, involving long-lived triplet excited states, is illustrated in insert I. This study complements an earlier preliminary report of the synthesis of these ligands.[21]

Results and Discussion

Preorganized ligands are usually constructed via a convergent strategy that consists of building suitably equipped modules before assembling these blocks into an appropriate array. When alkyne modules are used as spacers, the different part of the ligand can be interconnected by a palladium(0)-promoted cross-coupling reaction.[22,23] This stepwise synthetic approach, although tedious in operation, permits the engineering of multitopic ligands displaying disparate shapes, sizes, symmetry axes, and/or coordination sites.[24,25] As a first step toward the preparation of quasi-linear and photostable polypyridines based upon conjugated frameworks, we choose to use segmented hexameric, octameric, and decameric pyridine ligands (Scheme 1). The key to all of this chemistry is the availability of 5-bromo-2,2′-bipyridine and 5,5′-dibromo-2,2′-bipyridine which have previously been prepared by direct bromination of 2,2′-bipyridine hydrobromide salt at 180 °C.[23]

This method of preparation has many advantages in terms of brevity and adaptability. The pivotal intermediate **2** was readily synthesized by the cross-coupling of 5,5′-dibromo-2,2′-bipyridine with 5-ethynyl-2,2′-bipyridine in the presence of catalytic amounts of $[Pd^0(PPh_3)_4]$. It is notable that during this key step a side product, assigned as the tritopic ligand **1**, is formed in less than 10% isolated yield.[23] This compound could be removed easily from the reaction mixture, owing to its marked insolubility. Derivative **2** is converted to intermediate **3a**

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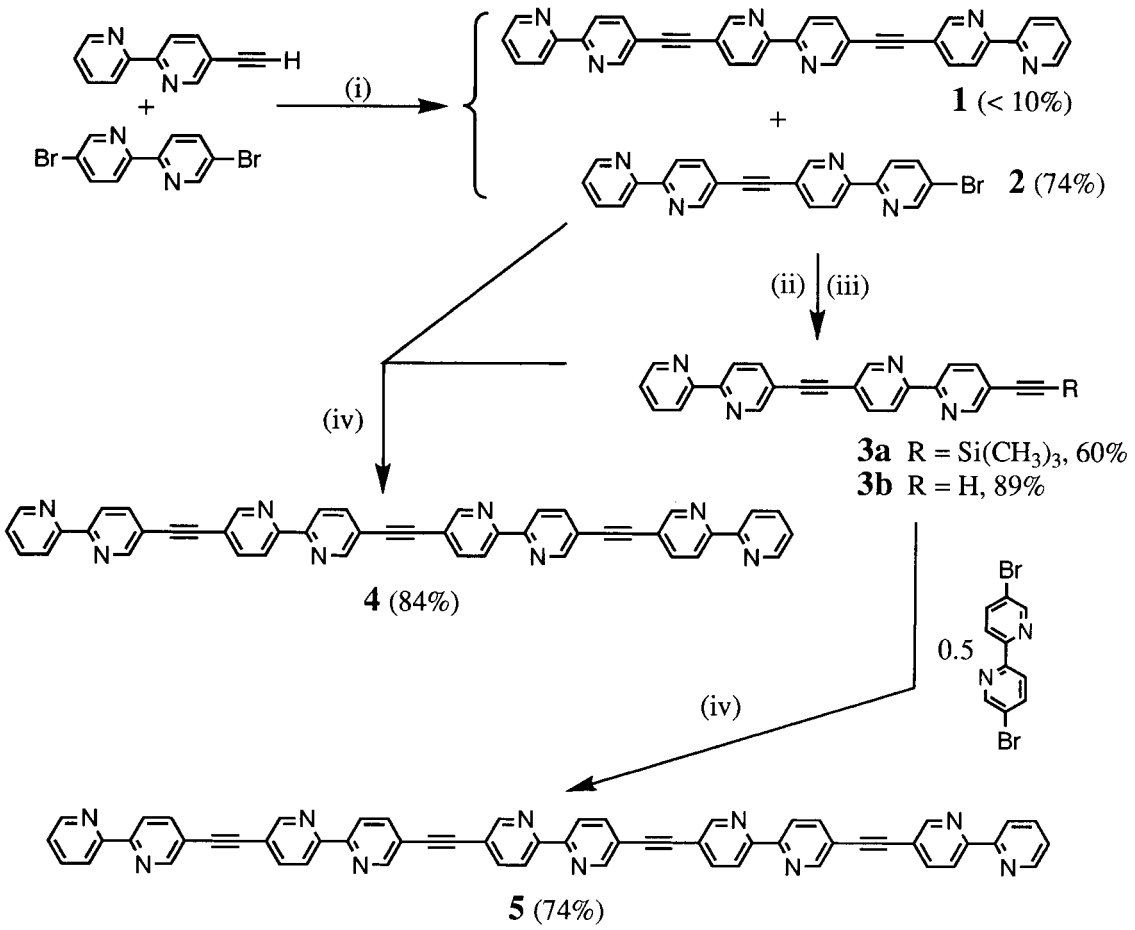
Scheme 1[a]



[a] Key: (i) $[Pd(PPh_3)_4]$ (6 mol %), benzene, $^iPr_2NH$, 80 °C; (ii) TMSC≡CH, $[Pd(PPh_3)_2Cl_2]$ (6 mol %), CuI (10 mol %), THF, $^iPr_2NH$, rt; (iii) K_2CO_3, CH_3OH, rt; (iv) $[Pd(PPh_3)_4]$ (6 mol %), benzene, $^iPr_2NH$, 80 °C.

by a Sonogashira−Hagihara coupling reaction[26,27] using (trimethylsilyl)acetylene and palladium(0) generated in situ from palladium(II) and cuprous salts, while deprotection, leading to compound **3b**, can be realized using K_2CO_3 in a protic solvent. Subsequent cross-coupling of stoichiometric amounts of **2** and **3b** afforded the tetratopic ligand **4** in good yield. Furthermore, double cross-coupling of an excess of **3b** with 5,5′-dibromo-2,2′-bipyridine gives rise to the corresponding pentatopic ligand **5** in fair yield. During this latter reaction, stepwise formation of the tritopic ligand bearing a bromo substituent in the 5′ position (a functionalized analogue of ligand **1**) is clearly observed by thin-layer chromatography but has not yet been isolated. As expected in light of the increasing number of aromatic and alkyne fragments, the target ligands are poorly soluble in most common organic solvents. This limits their structural characterization by classical spectroscopic tools, but FAB^+-MS, FT-IR, and elemental analysis are in keeping with the structural assignment. Despite their poor solubility, these ligands coordinate cationic "$Ru(bipy)_2$" metallofragments, leading to formation of soluble tri-, tetra-, and pentanuclear complexes which have been fully characterized. This, in turn, adds further confirmation for the assigned molecular structure of the multisite ligands.[28]

To access new ligands possessing improved solubility and to study their spectroscopic and luminescence properties, we have launched a new synthetic program aimed at producing extended ligands. The first step has involved exploring the chemistry of a monosubstituted 1,4-hydroquinone. O−Alkylation of bromohydroquinone with 1-bromododecane under basic conditions affords the trisubstituted derivative **6** (Scheme 2). A Sonogashira−Hagihara coupling reaction between **6** and propargylic alcohol, followed by deprotection under basic conditions, gives rise to the terminal alkyne derivative **8** in 66% overall yield, starting from commercially available materials. Coupling of **8** with either 5-bromo-2,2′-bipyridine or 5,5′-dibromo-2,2′-bipyridine is straightforward and yields respectively the mono- or disubstituted single bipy framework in acceptable yield (Scheme 2). Prior investigation into the synthesis of alkyne-grafted bipyridine has shown that conventional triphenylphosphine-ligated palladium catalysts are not poisoned by the presence of strongly chelating bipy fragments, and this finding has been confirmed here.[23] Furthermore, the mono- and disubstituted bipy ligands **9** and **10** are considered to be important control compounds for additional spectroscopic

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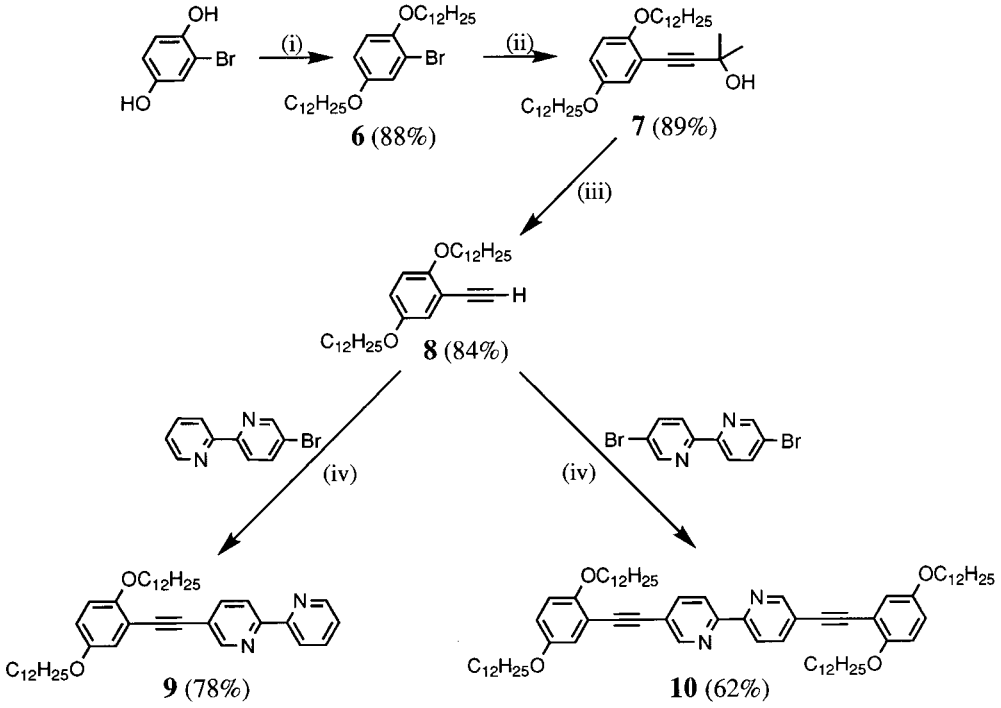
Scheme 2[a]

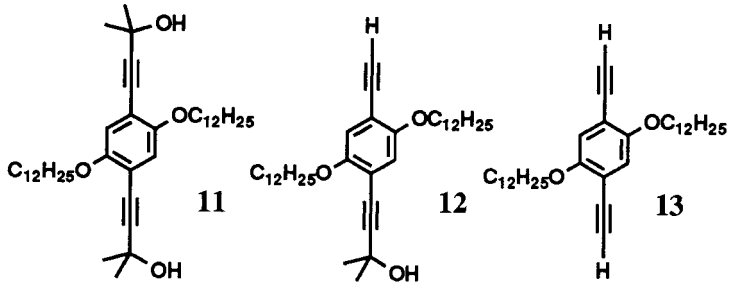


[a] Key: (i) 1-bromododecane, NaOH, DMF, 100 °C; (ii) $(CH_3)_2C(OH)C{\equiv}CH$, $^n PrNH_2$, $[Pd^0(PPh_3)_4]$ (6 mol %), 70 °C; (iii) NaOH (excess), benzene, 80 °C; (iv) $^n PrNH_2$, $[Pd^0(PPh_3)_4]$ (6 mol %), 70 °C.

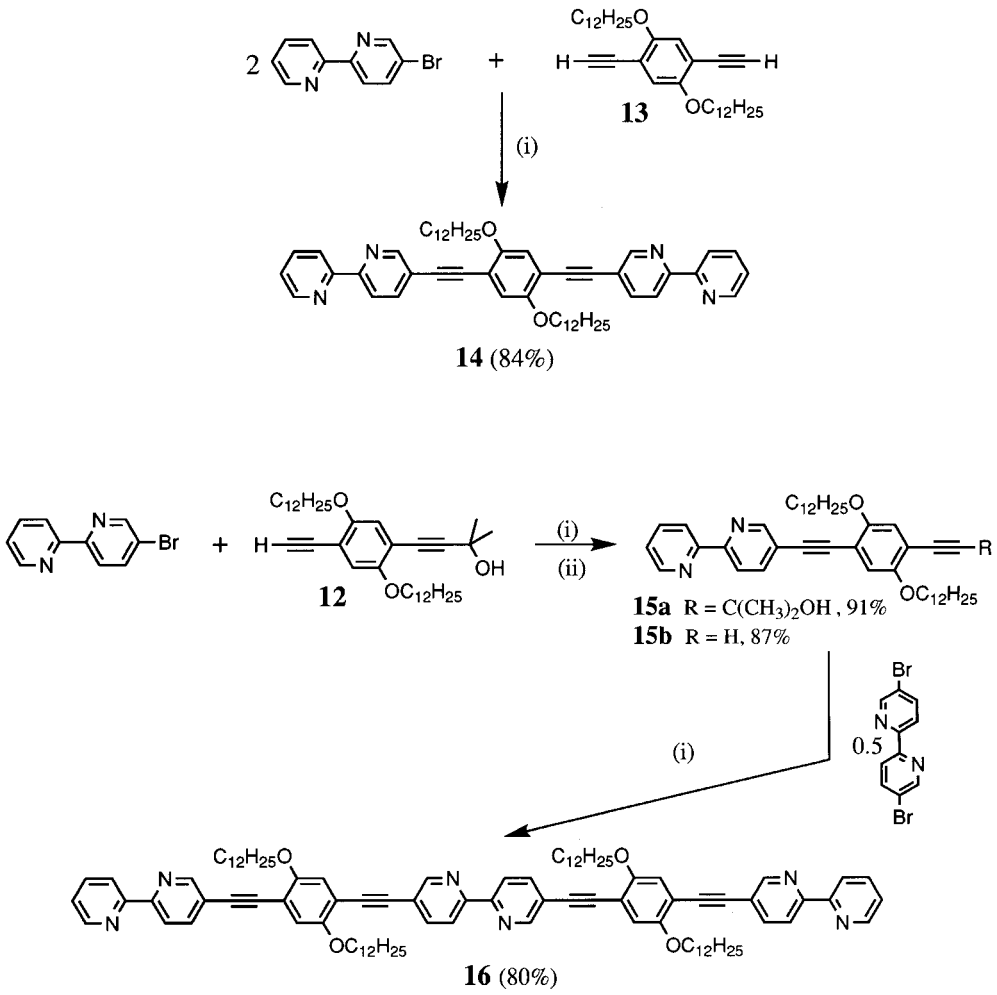
studies. An analogue of ligand **10** bearing methoxy groups in place of dodecyloxy substituents has recently been used as a model compound during the study of π-conjugated polymeric chromophores.[29]

With these convenient experimental conditions in hand, it was possible to construct the multitopic ligands as sketched in Scheme 3. Here, the molecules are synthesized outwardly from the dipropargylic/didodecyloxybenzene derivative **11** (insert II). The pivotal building blocks, bearing either a monoprotected alkyne function **12** or two terminal alkyne functions **13**, have been prepared previously and exploited for the synthesis of soluble bisterpyridine ligands displaying an increasing number of ethynylene/phenylene modules as spacers.[18] The ditopic ligand **14** was readily prepared in a one-step procedure from 5-bromo-2,2′-bipyridine, and derivative **13** was obtained from a double cross-coupling reaction catalyzed by a palladium(0) precursor in *n*-propylamine as the solvent. Synthesis of the analogous tritopic ligand **16** can be isolated from a similar process but requires three steps: (i) coupling of the bipy frame with the monoprotected alkyne derivative **12**; (ii) deprotection with excess NaOH; and (iii) double cross-coupling between derivative **15b** and 5,5′-dibromo-2,2′-bipyridine. During this last step, monografting of one bipy/phenyl/ethynyl module to the dibromo/bipy substrate is observed by thin-layer chromatography to be a minor pathway, and this is in keeping with a favorable reactivity of the second pyridine−Br bond. The grafting of the first module, which has a pronounced σ-inductive electron-withdrawing effect,[30] might be expected to induce polarization of the second C−Br bond such that subsequent oxidative addition to the low-valent palladium(0) metal center is facilitated during the catalytic process.[31] Double substitution of the dibromo/bipy species is likely promoted by any excess of the alkyne precursor. The good overall yield (63% for three steps) underlines the efficiency of this synthetic protocol.

Synthesis of the segmented hexapyridine ligand **16** relies upon the fact that no apparent side reaction is observed, and this is auspicious for the preparation of larger multisite ligands. Indeed, preparation of two additional precursors has been undertaken (Scheme 4). We selected a convergent synthesis that requires preparation of key intermediate **17**, bearing an additional bromo group with respect to the ditopic ligand **14**. This intermediate was prepared by monocoupling of intermediate **15b** with 5,5′-dibromo-2,2′-bipyridine. Compared to the earlier synthesis of **16**, the use of substoichiometric amounts of the alkyne reactant and the employment of



Scheme 3[a]



[a] Key: (i) $^{n}PrNH_2$, [$Pd^0(PPh_3)_4$] (6 mol %), 70 °C; (ii) NaOH (excess), benzene, 80 °C.

dilute solutions is clearly in favor of the monosubstituted derivative (76% isolated yield). The parasitic double-coupling reaction, leading to the formation of ligand **16**, appears to be inefficient under these conditions (less than 10% isolated yield). The importance of the careful choice of the experimental conditions for controlling the iterative synthesis of similar adducts possessing the potential to undergo further reactivity has been analyzed previously.[32] The first tetratopic ligand (**18**) was obtained in good yield by a double cross-coupling reaction of 2 equiv of **17** with the terminal dialkyne derivative **13** (Scheme 4).

Because the iterative synthetic scheme proceeds smoothly, we attempted the synthesis of a higher homologue of **15b** by grafting derivative **12** onto compound **17**. Deprotection under basic conditions leads to **19b**. It is of interest to note that an attempt to prepare compound **19b** in a single step by a selective monocoupling reaction between **17** and **13** failed for reasons inherent to the reactivity of the terminal alkyne function in derivative **19b**. This observation might be a general finding because **15b** could not be prepared from the reaction between intermediate **13** and 5-bromo-2,2′-bipyridine. Finally, the pentatopic ligand could be prepared in good yield by a double cross-coupling reaction between a slight excess of **19b** and 5,5′-dibromo-2,2′-bipyridine (Scheme 4). Again, a monosubstituted intermediate (a 5-bromo-substituted analogue of **16**) has been clearly identified. This is a clear indication for the construction of larger scaffolds.

With the exception of the first set of ligands shown in Scheme 1, all other ligands and intermediates are soluble in chlorinated solvents and are isolated as pale-yellow to deep-yellow powders. All ligands appeared to be thermally and photochemically stable in air. Characterization has been made by NMR, FAB^+-MS, UV−vis and steady-state fluorescence spectroscopy, FT-IR, and elemental analysis. All of the spectroscopic data are in accord with the proposed molecular structures. In particular, the ^1H and ^{13}C NMR spectra of the majority of the compounds presented here were free from overlapping resonances and exhibited the expected number of patterns. The ^{13}C NMR spectra are useful with respect to identification of the final structures. The resonances of the ethynylene sp carbon are readily identified as singlets in the range of 92.3−83.9 ppm and can be used

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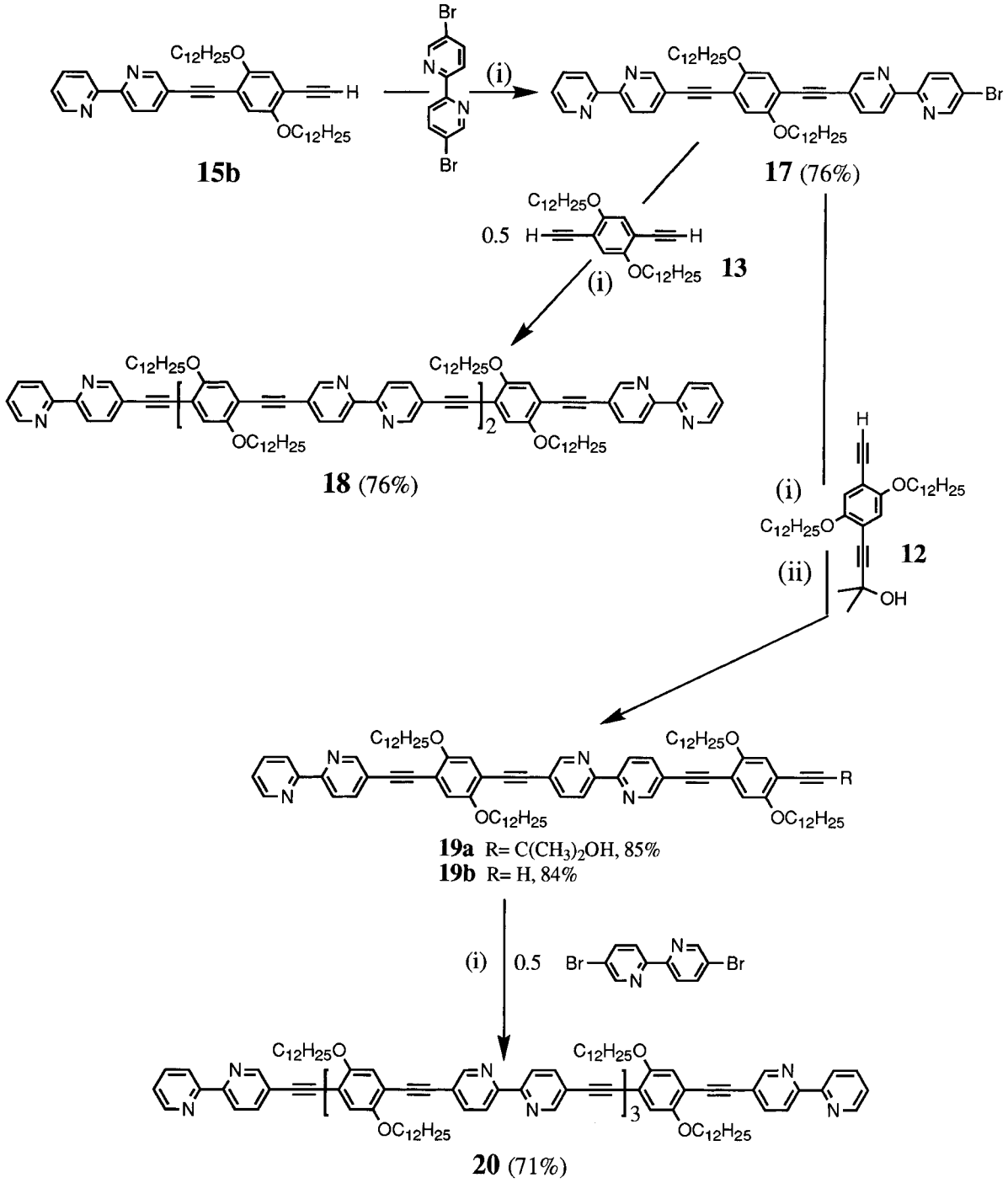
Scheme 4[a]



[a] Key: (i) $^{n}PrNH_2$, [$Pd^0(PPh_3)_4$] (6 mol %), 70 °C; (ii) NaOH (excess), benzene, 80 °C.

to monitor the number of triple bonds. These chemical shifts are in good agreement with those reported for other ethynylated compounds.[33] Increasing the number of bipy subunits resulted in the expected increase in the number of ethynylene carbon signals. There is significant shielding of these peaks with an increase in the size of the molecule. While the chemical shift of the sp carbon belonging to the monosubstituted bipy units (located at the terminal of the molecules) remains almost unchanged in ligands **16**, **18,** and **20** and resonates at ca. 92 ppm, the sp carbon belonging to the disubstituted bipy units (located at the center of the molecules) shifts progressively from ca. 88 ppm in ligand **16** to 84 ppm in **20**. This upfield shift is in keeping with the inductive electron-donating influence of the didodecyloxyphenyl moieties. For each ligand, the stretching vibrational mode of the ethynylene connecting unit could be resolved at about 2200 cm^{-1} in the solid-state IR spectrum and lies in the range expected for such compounds.[34]

The UV−vis absorption spectra of the mono- to penta-bipy ligands all display a pair of intense and well-resolved peaks, one lying at ca. 330 nm and the second in the

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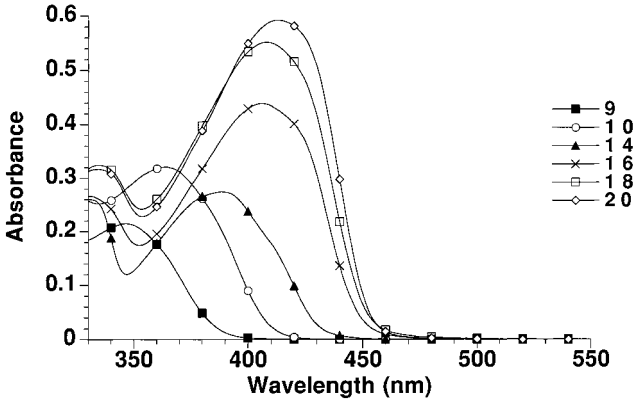

Figure 1. UV−vis absorption spectra measured in dichloromethane (2×10^{-5} M) at room temperature for various multitopic ligands.

range of 350−420 nm. Both transitions can be assigned to $\pi-\pi^*$ bands originating from the phenyl and pyridyl rings as well as from the ethynylene fragments (Figure 1). The lowest energy absorption transition is shifted progressively toward lower energy and appears more intense as the number of bipy/phenyl/ethynyl units increases. For instance, ligand **20** with a total of 100 conjugated π electrons exhibits the most red-shifted absorption maximum. The shift of λ drops from an initial step of $\Delta\lambda_{abs} = 12 \pm 2$ nm (for ligand **14** → **16**) to $\Delta\lambda_{abs} = 7 \pm 2$ nm (for ligand **16** → **18**) and finally to $\Delta\lambda_{abs} = 5 \pm 2$ nm (for ligand **18** → **20**). This attenuation is in keeping with limited electronic delocalization along the different parts of the molecule. Similar trends have recently been found in metal-capped wirelike polyynediyl chains.[35]

Furthermore, it is worth pointing out that grafting an additional ethynyldidocyloxyphenyl group to a single bipy generates a red shift of $\Delta\lambda_{abs} = 17 \pm 2$ nm for ligand **10** compared to ligand **9**, where the number of π electrons increases from 20 to 28. However, bridging two bipy's by a single diethynyldidocyloxyphenyl frame generates a bigger shift of the absorption band, with $\Delta\lambda_{abs} = 25 \pm 2$ nm for ligand **14** (bearing 34 π electrons) compared to ligand **9** (with 20 π electrons). The larger shift observed in the presence of two bipy units was assigned to the electron-withdrawing influence of the bipy moieties, which significantly decreases the energy level of the LUMO orbital of the spacing unit. The fact that neither the shape nor the position of these relatively narrow absorption bands changes significantly with increasing polarity of the solvent excludes the existence of charge-transfer absorption bands. Hence, this kind of transition is also present when nonsegmented ethynyldidocyloxyphenyl frameworks are used as spacers in back-to-back terpyridine ligands (Figure 2).[36]

Parallel behavior is seen by steady-state fluorescence spectrophotometry, where the intense peak of the fluorescence band is shifted progressively toward lower energy upon increasing the length of the molecule. Again, the relative shift in the emission maximum tends toward a plateau for the larger molecules with $\Delta\lambda_{em} = 11 \pm 2$ nm (for ligand **14** → **16**), $\Delta\lambda_{em} = 4 \pm 2$ nm (for ligand **16** → **18**), and $\Delta\lambda_{em} = 3 \pm 2$ nm (for ligand **18** → **20**). It is also noteworthy that the fluorescence quantum yields are

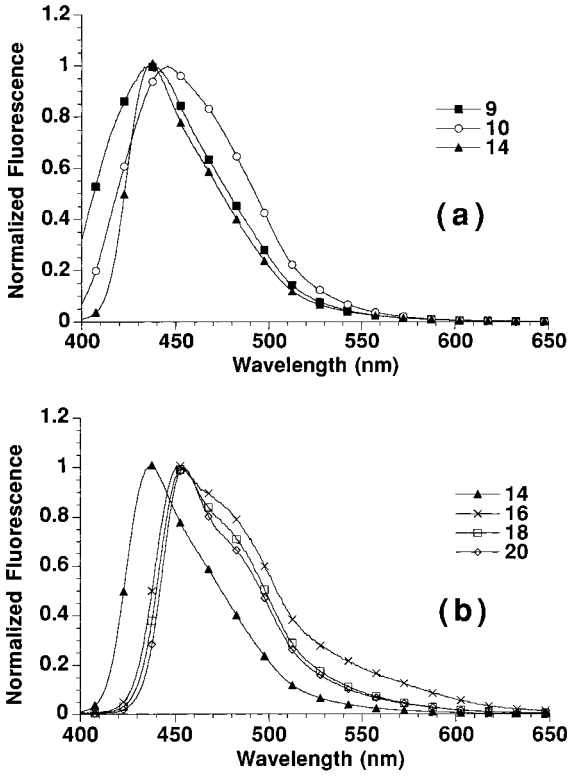

Figure 2. Normalized fluorescence emission spectra measured in degassed dichloromethane (ca. 1.2×10^{-6} M) at room temperature: (a) ligands **9**, **10,** and **14** with excitation wavelengths at 350, 360, and 392 nm, respectively; (b) ligands **14**, **16**, **18**, and **20** with excitation wavelength at 392 nm.

quite high and sensitive to the molecular size (Table 1). The highest value ($\phi \approx 31\%$) is found for ligand **20** which has also the highest oscillator strength for the corresponding absorption transition. More importantly, the fluorescence spectrum shows excellent mirror symmetry with the lowest energy absorption transition, and in fact, this is confirmed by an excitation spectra carried out under similar experimental conditions. On this basis, we assign the absorption and fluorescence peaks to allowed $\pi-\pi^*$ transitions. The apparent Stokes' shift, with values ranging from ca. 90 nm for the shorter molecules to 44 nm for the longest one, is rather large. The presence of a triplet excited state is excluded by the fact that no change in the steady-state emission was observed when the emission spectra of ligand **16** were carried out with an oxygen-degassed solution in dichloromethane at room temperature.[37] Consequently, the lowest energy singlet state $S_0 \rightarrow S_1$ is responsible for the intense fluorescence emission band.

Conclusion

The present work describes a logical and convenient synthetic protocol for the construction of quasi-linear polybipyridine ligands. Each chelating frame is connected by either a single ethynylene or diethynylenedidocyloxyphenyl bridge. Sequential deprotection−coupling steps have allowed the isolation of a series of soluble and rigid bipy-based ligands. The key intermediates carry a reac-

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Table 1. Spectroscopic Data for the Polytopic Ligands

ligands	^{13}C $\delta_{C\equiv C}$ (ppm)[a]	λ_{abs} (nm)[b]	λ_{em} (nm)[c]	ϕ (nm)[d]
9	90.2; 90.5	316 (13 600); 347 (10 700)	436	6.5
10	90.3; 90.7	324 (13 500); 364 (16 300)	446	10.1
14	92.2; 92.1	331 (13 000); 389 (13 700)	439	7.5
16	92.2; 90.5; 90.2; 88.2	331 (13 300); 401 (22 000)	450	19.4
18	92.3; 92.2; 92.1; 90.5; 90.2; 89.8	335 (19 800); 408 (36 900)	454	29.2
20	92.2; 92.1; 90.6; 90.5; 87.4; 87.3; 83.9	334 (23 900); 413 (39 900)	457	31.2

[a] Measured in $CDCl_3$. [b] Argon-degassed CH_2Cl_2 at room temperature; same results obtained in air. [c] In CH_2Cl_2, excitation wavelength at 350 nm for **9**, 360 nm for **10**, and 392 nm for **14**−**20**; concentration range $3.5-1.9 \times 10^{-6}$ M. [d] In CH_2Cl_2, at 350 nm for **9**, 360 nm for **10**, and 392 nm for **14**−**20**.

tive bromo function, while all of the phenyl intermediates are constructed with one or two terminal alkynes. This option is essential for the tailoring of the larger architectures. Inversion of these reactive functions on the building blocks does not provide the target compounds. The high yields obtained for the synthesis of these extended ligands underline the versatility of the synthetic protocol. It is anticipated that this procedure will be useful for synthesis of larger systems, because no major decrease of isolated yields has been detected among the various compounds obtained so far.

The ligands bearing one to five chelating centers are of nanometric dimensions and lie within the range of 21−72 Å, taking into account the edge-to-edge distance between the two external pyridine rings. Spectrophotometric studies have revealed that, by increasing the number of π electrons from 20 to 100, a significant bathochromic shift occurs for absorption and emission maxima. This effect is attenuated upon increasing the number of chelating sites. All ligands fluoresce strongly in solution at room temperature when excited in the less-energetic absorption band, with the fluorescence quantum yield increasing with increased molecular length. The chemical stability and photostability of these rigid-rod platforms makes them attractive for the engineering of luminophoric d^8-transition-metal centers, where each metallic dot might act as a relay station in photon-shuttling processes. The whole array might be expected to operate as an artificial photon-harvesting system.[38,39] The didodecyl fragments ability to markedly increase solubility is an additional tool for micromanipulation, such as supramolecular organization into mesophases, grafting of supplementary complexation sites in order to build 2D complexes, and modulation of the bridge energetics by incorporating donor/acceptor templates.

Experimental Section

General Methods. The 200.1 MHz ^1H and 50.3 MHz ^{13}C NMR spectra were recorded at room temperature, unless otherwise specified, using perdeuterated solvent as an internal standard: δ (H) in ppm relative to residual protiated solvent in $CDCl_3$ (7.26); δ (C) in ppm relative to the solvent in $CDCl_3$ (77.0); all carbon signals were detected as singlets. Melting points were obtained on a Büchi 535 capillary melting point apparatus in open-ended capillaries and are uncorrected. FT-IR spectra were measured in KBr pellets. UV−vis spectra were measured in CH_2Cl_2 at room temperature. Luminescence experiments were performed in dilute (ca. 2×10^{-6} M) degassed dichloromethane solutions at room temperature. Luminescence maxima reported are uncorrected for photomultiplier reponse. Luminescence quantum yields were measured following the opical dilution method, with $[Ru(bipy)_3]^{2+}$ in degassed acetonitrile as the standard with a quantum yield of $\Phi = 0.016$.[40,41] Fast atom bombardment (FAB, positive mode) mass spectra were obtained using *m*-nitrobenzyl alcohol (*m*-NBA) as the matrix; data are given as *m*/*z*, and the nature of the peak and relative intensity are given in parentheses. Elemental analyses were obtained from the microanalytical laboratory of the Institut Charles Sadron and the Institut Universitaire de Technologie in Strasbourg.

Materials. *n*-Propylamine, 1-bromododecane, and bromohydroquinone were purchased from ACROS; CuI from Fluka; and (trimethylsilyl)acetylene from Lancaster. 5-Bromo-2,2′-bipyridine,[42,43] 5-ethynyl-2,2′-bipyridine,[23] 5,5′-dibromo-2,2′-bipyridine,[42,43] 1,4-di(2-methyl-3-butyn-2-ol)-2,5-didodecyloxybenzene (**11**),[36] 1-(2-methyl-3-butyn-2-ol)-4-ethynyl-2,5-didodecyloxybenzene (**12**),[36] 1,4-diethynyl-2,5-didodecyloxybenzene (**13**),[36] and $[Pd^0(PPh_3)_4]$[44] were prepared and purified according to literature procedures. Diisopropylamine and tetrahydrofuran were dried over suitable reagents and freshly distilled under argon before use. All reactions were carried out under dry argon by using Schlenk tube techniques. Compound **1** obtained here as a side product has identical spectroscopic data as the sample previously prepared.[23]

General Procedures for the Preparation of the Arylacetylene, Bipyridine Derivatives, and Polytopic Ligands. Condition 1. A Schlenk flask equipped with a septum, a Teflon-coated magnetic stirring bar, and an argon inlet was charged with the ethynyl and bromo-2,2′-bipyridine derivatives in argon degassed benzene, and then $[Pd^0(PPh_3)_4]$ (6 mol %) was added as a solid, followed by argon-degassed diisopropylamine. The solution was heated at 80 °C. After complete consumption of the starting material (determined by TLC), the solvent was evaporated, and the crude product was washed successively by centrifugation with water, methanol, and finally dichloromethane.

Condition 2. A Schlenk flask was charged with bromo-2,2′-bipyridine derivatives in argon-degassed tetrahydrofuran, and (trimethylsilyl)acetylene, $[Pd(PPh_3)_2Cl_2]$ (6 mol %), CuI (10 mol %), and finally argon-degassed diisopropylamine were successively added. The solution was stirred at room temperature. After complete consumption of the starting material, the solvent was evaporated under vacuum, and the product was purified by chromatography on alumina using hexane with a gradient of dichloromethane.

Condition 3. A Schlenk flask was charged with the bromo-2,2′-bipyridine and ethynylbenzene derivatives in argon-degassed *n*-propylamine, and $[Pd^0(PPh_3)_4]$ (6 mol %) was added as a solid. After heating at 70 °C and complete consumption of the starting material, the solvent was removed under vacuum, and the residue was purified by chromatography on alumina, using dichloromethane with a gradient of methanol.

Condition 4a. To a stirred solution of the trimethylsilyl-protected compound in methanol was added as a solid K_2CO_3 (2 equiv). After complete consumption of the starting material, the reaction was quenched with water. The solution was concentrated by rotary evaporation, and the organic product was extracted with dichloromethane. The organic layers were evaporated to dryness under vacuum, and the residue was

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purified by chromatography on alumina, using dichloromethane with a gradient of methanol.

Condition 4b. To a stirred solution of the propargylic-protected compounds in benzene was added an excess of NaOH, and the mixture was heated at 80 °C. After consumption of the starting material, the reaction was quenched with an aqueous NH_4Cl-saturated solution. The organic products were extracted with dichloromethane, and the organic layers were dried with $MgSO_4$. The solvent was then removed under vacuum, and the compound was purified by chromatography on alumina, using dichloromethane with a gradient of methanol.

Synthesis of the Building Blocks. 5-(2,2′-Bipyridin-5-ylethynyl)-5′-bromo-2,2′-bipyridine (2). The compound was prepared according to experimental condition 1, from 0.107 g (0.59 mmol) of 5-ethynyl-2,2′-bipyridine, 10 mL of benzene, 0.280 g (0.89 mmol) of 5,5′-dibromo-2,2′-bipyridine, 0.041 g (0.035 mmol) of $[Pd^0(PPh_3)_4]$, and 3 mL of diisopropylamine. The reaction mixture was heated for 27 h at 80 °C. Purification was performed by chromatography on alumina with hexane/CH_2Cl_2 (0−50%) as eluant and afforded 0.180 g of **2** (74%): mp 237−8 °C; ^{1}H NMR ($CDCl_3$) δ 7.34 (dd, J = 4.8 Hz, J = 1.2 Hz, 1H), 7.84 (td, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.97 (m, 3H), 8.40 (m, 4H), 8.70 (dd, J = 4.7 Hz, J = 0.9 Hz, 1H), 8.74 (d, J = 2.4 Hz, 1H), 8.82 (dd, J = 4.0 Hz, J = 0.6 Hz, 1H), 8.85 (d, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 90.4 (C≡C), 90.8 (C≡C), 119.7, 120.1, 120.4, 120.5, 121.5, 121.6, 122.8, 124.2, 128.5, 128.7, 132.1, 132.3, 133.8, 137.1, 139.6, 149.4, 150.4, 151.8, 154.2, 155.4; FT-IR (KBr, cm^{-1}) 3421 (s), 2926 (s), 2191 (w, $\nu_{C\equiv C}$), 1654 (m), 1437 (m), 1388 (m), 1261 (s), 1091 (s), 1047 (s), 880 (m); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 273 (1600), 337 (7400), 356 (5800); FAB$^+$ 415 ([M + H]$^+$, 100), 413 ([M + H]$^+$, 90). Anal. Calcd for $C_{22}H_{13}N_4Br$: C, 63.94; H, 3.17; N, 13.56. Found: C, 63.89; H, 3.12; N, 13.54.

5-(2,2′-Bipyridin-5-ylethynyl)-5′-(trimethylsilylethynyl)-2,2′-bipyridine (3a). The compound was prepared according to experimental condition 2, from 0.280 g (0.68 mmol) of **2**, 20 mL of THF, 0.116 mL (0.81 mmol) of (trimethylsilyl)acetylene, 0.028 g (0.04 mmol) of $[Pd(PPh_3)_2Cl_2]$, 0.002 g (0.07 mmol) of CuI, and 5 mL of diisopropylamine. The reaction mixture was stirred at room temperature for 4 days. Purification was performed by chromatography on alumina with hexane/CH_2Cl_2 (50−100%) as the eluant and afforded 0.175 g of **3a** (60%): mp 212−3 °C; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, CH_3, 9H), 7.32 (dd, J = 4.8 Hz, J = 1.1 Hz, 1H), 7.84 (m, 2H), 7.94 (t, J = 1.9 Hz, 1H), 7.98 (t, J = 1.9 Hz, 1H), 8.41 (m, 4H), 8.70 (d, J = 4.8 Hz, 1H), 8.73 (d, J = 1.4 Hz, 1H), 8.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.1 (TMS), 90.5 (C≡C), 90.8 (C≡C), 99.7 (C≡C), 101.8 (C≡C), 119.7, 119.9, 120.5, 120.6, 120.8, 121.5, 124.1, 137.1, 139.6, 139.9, 149.4, 151.8, 152.2, 154.2, 154.6, 155.4; FT-IR (KBr, cm^{-1}) 3416 (s), 2962 (m), 2158 (m, $\nu_{C\equiv C}$), 1586 (m), 1456 (s), 1366 (m), 1250 (s), 1122 (s), 842 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 275 (2000), 345 (8500), 364 (8000); FAB$^+$ 431 ([M + H]$^+$, 100), 416 ([M − CH_3 + H]$^+$, 30), 415 ([M − CH_3]$^+$, 90). Anal. Calcd for $C_{27}H_{22}N_4Si$: C, 75.32; H, 5.15; N, 13.01. Found: C, 75.27; H, 5.08; N, 12.96.

5-(2,2′-Bipyridin-5-ylethynyl)-5′-ethynyl-2,2′-bipyridine (3b). The compound was prepared according to experimental condition 4a, from 0.108 g (0.25 mmol) of **3a**, 0.069 g (0.50 mmol) of K_2CO_3, and 20 mL of methanol. The solution was stirred at room temperature for 14 h. Purification was performed by chromatography on alumina with CH_2Cl_2/CH_3OH (0−2%) as the eluant and afforded 0.080 g of **3b** (89%): mp >250 °C; ^{1}H NMR ($CDCl_3$) δ 3.32 (s, C≡CH, 1H), 7.34 (dd, J = 4.8 Hz, J = 1.2 Hz, 1H), 7.90 (m, 4H), 8.44 (m, 5H), 8.71 (m, 1H), 8.78 (m, 1H), 8.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 80.7 (C≡C), 81.8 (C≡C), 90.4 (C≡C), 90.9 (C≡C), 119.5, 119.6, 120.1, 120.5, 120.7, 120.8, 121.5, 124.2, 137.1, 139.9, 140.1, 149.4, 151.7, 151.8, 152.4, 154.5, 154.6, 155.4; FT-IR (KBr, cm^{-1}) 3460 (s), 2923 (m), 2195 (w, $\nu_{C\equiv C}$), 1601 (m), 1460 (s), 1313 (m), 1243 (m), 1109 (s), 841 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 269 (1600), 341 (11 200), 361 (9200); FAB$^+$ 359 ([M + H]$^+$, 100). Anal. Calcd for $C_{24}H_{14}N_4$: C, 80.43; H, 3.94; N, 15.63. Found: C, 80.24; H, 3.81; N, 15.56.

1-Bromo-2,5-didodecyloxybenzene (6). In a 50 mL flask equipped with a reflux condenser and a magnetic stirring bar, 3.20 mL (13.22 mmol) of 1-bromododecane was added to a suspension of bromohydroquinone (1.250 g, 6.61 mmol) and NaOH (0.661 g, 16.53 mmol) in DMF (10 mL). After we heated the solution at 100 °C for 16 h, it was cooled to room temperature, and then 50 mL of water was added and the product was extracted with dichloromethane (3 × 50 mL). The solvent was evaporated under vacuum, and the residue was washed with ethanol, affording 3.050 g of **6** (88%): mp 43−4 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 6.1 Hz, CH_3, 6H), 1.28 (m, CH_2, 36H), 1.77 (m, CH_2, 4H), 3.88 (t, J = 6.6 Hz, OCH_2, 2H), 3.95 (t, J = 6.9 Hz, OCH_2, 2H), 6.76 (m, Ph, 2H), 7.11 (d, J = 2.2 Hz, Ph, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.2, 22.8, 26.1, 29.4, 29.5, 29.7, 32.1, 68.9, 70.3, 112.9, 114.4, 114.7, 119.6, 149.9, 153.7; FT-IR (KBr, cm^{-1}) 2922 (s), 2848 (s), 1500 (s), 1466 (s), 1396 (s), 1271 (s), 1219 (s), 1132 (w), 1046 (s), 1002 (m), 888 (m); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 296 (3400); FAB$^+$ 527 ([M + H]$^+$, 100), 525 ([M + H]$^+$, 96), 445 ([M − Br]$^+$, 15). Anal. Calcd for $C_{30}H_{53}O_2Br$: C, 68.55; H, 10.16. Found: C, 68.17; H, 9.89.

1-(2-Methyl-3-butyn-2-ol)-2,5-didodecyloxybenzene (7). The compound was prepared according to experimental condition 3, from 1.000 g (1.90 mmol) of **6**, 35 mL of *n*-propylamine, 0.184 mL (1.90 mmol) of 2-methyl-3-butyn-2-ol, and 0.132 g (0.15 mmol) of $[Pd(PPh_3)_4]$. The reaction mixture was heated for 22 h at 70 °C. Purification was performed by flash chromatography on silica gel with CH_2Cl_2/CH_3OH (0−2%) as the eluant and afforded 0.894 g of **7** (89%): mp 55−6 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.2 Hz, CH_3, 6H), 1.27 (m, CH_2, 36H), 1.62 (s, CH_3, 6H), 1.76 (m, CH_2, 4H), 2.50 (s, OH, 1H), 3.87 (t, J = 6.7 Hz, OCH_2, 2H), 3.94 (t, J = 6.6 Hz, OCH_2, 2H), 6.78 (m, Ph, 2H), 6.91 (d, J = 1.9 Hz, Ph, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.2, 22.8, 26.1, 29.4, 29.5, 29.6, 29.7, 31.6, 32.0, 65.7, 68.7, 69.7, 78.7 (C≡C), 97.8 (C≡C), 113.1, 114.0, 116.5, 118.5, 152.8, 154.1; FT-IR (KBr, cm^{-1}) 3516 (s), 3396 (s), 2919 (s), 2851 (s), 2015 (w, $\nu_{C\equiv C}$), 1602 (w), 1504 (s), 1469 (s), 1393 (m), 1274 (s), 1224 (s), 1159 (m), 1041 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 315 (6400); FAB$^+$ 529 ([M + H]$^+$, 100), 469 ([M − C(CH_3)$_2$OH]$^+$, 10). Anal. Calcd for $C_{35}H_{60}O_3$: C, 79.49; H, 11.44. Found: C, 79.22; H, 11.27.

1-Ethynyl-2,5-didodecyloxybenzene (8). The compound was prepared according to experimental condition 4b, from 0.600 g (1.13 mmol) of **7**, 1.000 g (25 mmol) of NaOH (excess), and 30 mL of benzene. The reaction mixture was heated for 20 h at 80 °C. Purification was performed by flash chromatography on silica gel with hexane/CH_2Cl_2 (60−100%) as the eluant and afforded 0.450 g of **8** (84%): mp 41−2 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.1 Hz, CH_3, 6H), 1.28 (m, CH_2, 36H), 1.80 (m, CH_2, 4H), 3.24 (s, C≡CH, 1H), 3.88 (t, J = 6.5 Hz, OCH_2, 2H), 3.97 (t, J = 6.6 Hz, OCH_2, 2H), 6.82 (m, Ph, 2H), 6.99 (d, J = 2.4 Hz, Ph, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.2, 22.8, 26.1, 29.3, 29.4, 29.5, 29.7, 29.8, 32.1, 68.7, 69.8, 80.3 (C≡C), 80.9 (C≡C), 112.5, 114.0, 117.0, 119.4, 152.8, 154.7; FT-IR (KBr, cm^{-1}) 3296 (m), 2921 (s), 2850 (s), 2064 (w, $\nu_{C\equiv C}$), 1502 (s), 1470 (s), 1396 (m), 1302 (m), 1272 (s), 1229 (s), 1163 (w), 1033 (s), 1004 (w), 801 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 316 (5200); FAB$^+$ 471 ([M + H]$^+$, 100), 289 ([M − $OC_{12}H_{25}$]$^+$, 10). Anal. Calcd for $C_{32}H_{54}O_2$: C, 81.64; H, 11.56. Found: C, 81.43; H, 11.21.

1-(2-Methyl-3-butyn-2-ol)-4-(2,2′-bipyridin-5-ylethynyl)-2,5-didodecyloxybenzene (15a). The compound was prepared according to experimental condition 3, from 0.026 g (0.09 mmol) of 5-bromo-2,2′-bipyridine, 16 mL of *n*-propylamine, 0.050 g (0.09 mmol) of **12**, and 0.006 g (0,005 mmol) of $[Pd(PPh_3)_4]$. The reaction mixture was heated for 2 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2/CH_3OH (0−1%) as the eluant and afforded 0.058 g of **15a** (91%): mp 81−2 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (m, CH_3, 6H), 1.25 (m, CH_2, 36H), 1.56 (s, CH_3, 6H), 1.80 (m, CH_2, 4H), 2.38 (s, OH, 1H), 3.98 (m, OCH_2, 4H), 6.91 (s, Ph, 1H), 6.97 (s, Ph, 1H), 7.32 (t, J = 6.2 Hz, 1H), 7.82 (td, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.89 (dd, J = 8.3 Hz, J = 1.9 Hz, 1H), 8.42 (d, J = 8.1 Hz, 2H), 8.68 (d, J = 4.6 Hz, 1H), 8.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.1, 29.4, 29.7, 31.5, 32.0, 65.8, 69.6, 69.7, 78.5 (C≡C), 90.2 (C≡C), 91.6 (C≡C), 99.7 (C≡C), 113.2, 114.1, 116.8, 117.1, 120.4, 120.6, 121.4, 124.0, 137.0, 139.3,

149.4, 151.7, 153.7, 153.8, 154.8, 155.6; FT-IR (KBr, cm^{-1}) 3437 (w), 2921 (s), 2851 (s), 2211 (w, $\nu_{C\equiv C}$), 1541 (w), 1503 (s), 1463 (s), 1413 (m), 1386 (m), 1276 (m), 1218 (s), 1156 (m), 1025 (w), 985 (w), 860 (m); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 261 (6300), 305 (12 500), 316 (13 300), 325 (15 100), 367 (14 700); FAB$^+$ 707 ([M + H]$^+$, 100), 521 ([M − $OC_{12}H_{25}$]$^+$, 10). Anal. Calcd for $C_{47}H_{66}N_2O_3$: C, 79.84; H, 9.41; N, 3.96. Found: C, 79.65; H, 9.19; N, 3.84.

1-(2,2′-Bipyridin-5-ylethynyl)-4-ethynyl-2,5-didodecyloxybenzene (15b). The compound was prepared according to experimental condition 4b, from 0.045 g (0.063 mmol) of **15a**, 0.100 g (2.50 mmol) of NaOH (excess), and 20 mL of benzene. The reaction mixture was heated for 14 h at 80 °C. Purification was performed by chromatography on alumina with hexane/CH_2Cl_2 (50−100%) as the eluant and afforded 0.036 g of **15b** (87%): mp 59−60 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (m, CH_3, 6H), 1.26 (m, CH_2, 36H), 1.83 (m, CH_2, 4H), 3.36 (s, C≡CH, 1H), 4.00 (m, OCH_2, 4H), 6.99 (s, Ph, 1H), 7.01 (s, Ph, 1H), 7.32 (t, J = 6.2 Hz, 1H), 7.82 (td, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.90 (dd, J = 8.3 Hz, J = 1.9 Hz, 1H), 8.42 (d, J = 8.1 Hz, 2H), 8.68 (d, J = 4.6 Hz, 1H), 8.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.0, 26.1, 29.2, 29.3, 29.4, 29.7, 32.0, 69.8, 80.0 (C≡C), 82.7 (C≡C), 90.0 (C≡C), 91.9 (C≡C), 113.4, 113.9, 117.0, 117.8, 120.4, 120.5, 121.4, 124.0, 137.0, 139.3, 149.4, 151.7, 153.7, 154.2, 154.9, 155.6; FT-IR (KBr, cm^{-1}) 3417 (m), 3289 (m), 2914 (s), 2850 (s), 2361 (w), 2336 (w), 2208 (w, $\nu_{C\equiv C}$), 1616 (w), 1503 (s), 1469 (s), 1411 (w), 1391 (s), 1277 (m), 1218 (s), 1029 (s), 860 (w); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 307 (16 700), 316 (18 100), 325 (20 000), 365 (17 700); FAB$^+$ 649 ([M + H]$^+$, 100), 463 ([M − $OC_{12}H_{25}$]$^+$, 10). Anal. Calcd for $C_{44}H_{60}N_2O_2$: C, 81.43; H, 9.32; N, 4.32. Found: C, 81.35; H, 9.22; N, 4.20.

1-(2,2′-Bipyridin-5-ylethynyl)-4-(2,2′-bipyridin-5-ylethynyl-5′-bromo)-2,5-didodecyloxybenzene (17). The compound was prepared according to experimental condition 3, from 0.050 g (0.077 mmol) of **15b**, 60 mL of *n*-propylamine, 0.048 g (0.154 mmol) of 5,5′-dibromo-2,2′-bipyridine, and 0.005 g (0.004 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 2 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2/CH_3OH (0−3%) as the eluant and afforded 0.052 g of **17** (76%): mp 124−5 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (m, CH_3, 6H), 1.23 (m, CH_2, 36H), 1.87 (m, CH_2, 4H), 4.06 (t, J = 6.3 Hz, OCH_2, 4H), 7.06 (s, Ph, 2H), 7.31 (td, J = 7.5 Hz, J = 5.9 Hz, J = 1.1 Hz, 1H), 7.82 (td, J = 7.8 Hz, J = 1.9 Hz, 1H), 7.89−7.96 (m, 3H), 8.31−8.44 (m, 4H), 8.70 (m, 2H), 8.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.2, 29.4, 29.5, 29.7, 29.9, 32.0, 69.7, 90.1 (C≡C), 90.5 (C≡C), 92.0 (C≡C), 92.2 (C≡C), 113.8, 114.0, 116.9, 120.3, 120.4, 120.5, 120.9, 121.4, 122.6, 124.0, 137.0, 139.3, 139.6, 149.4, 150.4, 151.7, 153.9, 154.1, 154.9, 155.6; FT-IR (KBr, cm^{-1}) 3441 (m), 2922 (s), 2853 (s), 2360 (m), 2209 (w, $\nu_{C\equiv C}$), 1501 (m), 1458 (s), 1413 (m), 1420 (m), 1379 (m), 1277 (m), 1217 (s), 1089 (w), 1034 (m), 844 (w); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 262 (5700), 333 (13 500), 391 (14 300); FAB$^+$ 881 ([M + H]$^+$, 85), 883 ([M + H]$^+$, 100), 801 ([M − Br]$^+$, 30). Anal. Calcd for $C_{54}H_{65}N_4O_2Br$: C, 73.53; H, 7.43; N, 6.35. Found: C, 73.29; H, 7.20; N, 6.17.

1-[1-(2,2′-Bipyridin-5-ylethynyl)-4-(2,2′-bipyridin-5,5′-yldiethynyl)-2,5-didodecyloxybenzene]-4-(2-methyl-3-butyn-2-ol)-2,5-didodecyloxybenzene (19a). The compound was prepared according to experimental condition 3, from 0.020 g (0.022 mmol) of **17**, 10 mL of *n*-propylamine, 0.013 g (0.022 mmol) of **12**, and 0.002 g (0,001 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 2 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2/CH_3OH (0−3%) as the eluant and afforded 0.026 g of **19a** (85%): mp 136−7 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (m, CH_3, 12H), 1.25 (m, CH_2, 72H), 1.64 (s, CH_3, 6H), 1.85 (m, CH_2, 8H), 2.33 (s, OH, 1H), 4.07 (m, OCH_2, 8H), 6.93 (s, Ph, 1H), 7.00 (s, Ph, 1H), 7.07 (s, Ph, 2H), 7.32 (td, J = 7.4 Hz, J = 5.8 Hz, J = 1.1 Hz, 1H), 7.78−7.96 (m, 4H), 8.42 (m, 4H), 8.69 (d, J = 4.8 Hz, 1H), 8.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.2, 29.4, 29.7, 31.5, 32.0, 65.8, 69.5, 69.7, 78.7 (C≡C), 90.2 (C≡C), 90.5 (C≡C), 91.2 (C≡C), 91.6 (C≡C), 92.6 (C≡C), 92.7 (C≡C), 99.7 (C≡C), 113.1, 116.9, 117.1, 120.1, 120.4, 120.6, 120.7, 120.8, 128.6, 128.7, 131.9, 132.0, 132.1, 132.3, 133.7, 139.3, 149.4, 151.6, 153.7, 153.9, 155.7; FT-IR (KBr, cm^{-1}) 3401 (w), 3284 (w), 3058 (w), 2922 (s), 2854 (s), 2211 (w, $\nu_{C\equiv C}$), 1502 (m), 1463 (s), 1420 (m), 1376 (m), 1276 (m), 1217 (s), 1158 (m), 1126 (s), 1060 (m), 1030 (m), 854 (m); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 261 (4400), 276 (6400), 295 (7700), 336 (12 200), 397 (20 600); FAB$^+$ 1353 ([M + H]$^+$, 100), 1167 ([M − $OC_{12}H_{25}$]$^+$, 30), 1108 ([M − $OC_{12}H_{25}$ − $C(CH_3)_2OH$]$^+$, 10). Anal. Calcd for $C_{91}H_{124}N_4O_5$: C, 80.72; H, 9.23; N, 4.14. Found: C, 80.59; H, 8.91; N, 3.99.

1-[1-(2,2′-Bipyridin-5-ylethynyl)-4-(2,2′-bipyridin-5,5′-yldiethynyl)-2,5-didodecyloxybenzene]-4-ethynyl-2,5-didodecyloxybenzene (19b). The compound was prepared according to experimental condition 4b, from 0.030 g (0.022 mmol) of **19a**, 0.080 g (2.00 mmol) of NaOH (excess), and 20 mL of benzene. The reaction mixture was heated for 2 days at 80 °C. Purification was performed by chromatography on alumina with CH_2Cl_2 as the eluant and afforded 0.024 g of **19b** (84%): mp 133−4 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (m, CH_3, 12H), 1.25 (m, CH_2, 72H), 1.85 (m, CH_2, 8H), 3.37 (s, C≡CH, 1H), 4.03 (m, OCH_2, 8H), 7.00 (s, Ph, 1H), 7.02 (s, Ph, 1H), 7.06 (s, Ph, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.96−7.80 (m, 4H), 8.44 (m, 4H), 8.70 (d, J = 5.4 Hz, 1H), 8.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 23.0, 26.0, 26.2, 29.5, 29.8, 32.0, 69.7, 80.0 (C≡C), 90.2 (C≡C), 90.3 (C≡C), 90.5 (C≡C), 90.6 (C≡C), 92.1 (C≡C), 92.2 (C≡C), 92.3 (C≡C), 113.4, 113.9, 116.9, 117.8, 120.7, 121.4, 124.1, 127.1, 128.8, 128.9, 131.0, 137.1, 139.3, 151.8, 153.7, 153.9, 154.2; FT-IR (KBr, cm^{-1}) 3418 (m), 3290 (m), 2916 (s), 2852 (s), 2363 (w), 2209 (m, $\nu_{C\equiv C}$), 1618 (m), 1505 (s), 1470 (s), 1393 (s), 1280 (m), 1220 (s), 1031 (s), 860 (m); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 274 (13 400), 306 (15 200), 335 (20 300), 396 (29 600); FAB$^+$ 1296 ([M + H]$^+$, 100), 1109 ([M − $OC_{12}H_{25}$]$^+$, 10). Anal. Calcd for $C_{88}H_{118}N_4O_4$: C, 81.56; H, 9.18; N, 4.32. Found: C, 81.38; H, 9.02; N, 4.19.

Synthesis of Polytopic Ligands. Ligand 4. This ligand was prepared according to experimental condition 1, from 0.058 g (0.14 mmol) of **2**, 25 mL of benzene, 0.050 g (0.14 mmol) of **3b**, 0.010 g (0.008 mmol) of [Pd^0(PPh_3)$_4$], and 3 mL of diisopropylamine. The reaction mixture was heated for 4 days at 80 °C. The crude precipitate was filtered and washed successively by centrifugation with H_2O (3 × 10 mL), CH_3OH (3 × 10 mL), and CH_2Cl_2 (3 × 10 mL) and afforded 0.082 g of **4** (84%): mp >250 °C; FT-IR (KBr, cm^{-1}) 3049 (m), 2977 (m), 2200 (w, $\nu_{C\equiv C}$), 1589 (m), 1569 (m), 1542 (m), 1465 (s), 1434 (m), 1368 (m), 1022 (m), 840 (s), 796 (s), 738 (s); FAB$^+$ 691 ([M + H]$^+$, 100). Anal. Calcd for $C_{46}H_{26}N_8$: C, 79.98; H, 3.79; N, 16.22. Found: C, 79.61; H, 3.72; N, 15.86.

Ligand 5. This ligand was prepared according to experimental condition 1, from 0.050 g (0.14 mmol) of **3b**, 20 mL of benzene, 0.022 g (0.07 mmol) of 5,5′-dibromo-2,2′-bipyridine, 0.010 g (0.008 mmol) of [Pd^0(PPh_3)$_4$], and 2.5 mL of diisopropylamine. The reaction mixture was heated for 4 days at 80 °C. The crude precipitate was filtered and washed successively by centrifugaion with H_2O (3 × 10 mL), CH_3OH (3 × 10 mL), and CH_2Cl_2 (3 × 10 mL) and afforded 0.045 g of **5** (74%): mp >250 °C; FT-IR (KBr, cm^{-1}) 3050 (m), 2979 (m), 2216 (w, $\nu_{C\equiv C}$), 1590 (m), 1467 (s), 1439 (m), 1375 (m), 1032 (m), 799 (s), 742 (s); FAB$^+$ 869 ([M + H]$^+$, 100). Anal. Calcd for $C_{58}H_{32}N_{10}$: C, 80.17; H, 3.71; N, 16.12. Found: C, 79.80; H, 3.49; N, 15.89.

Ligand 9. This ligand was prepared according to experimental condition 3, from 0.062 g (0.265 mmol) of 5-bromo-2,2′-bipyridine, 15 mL of *n*-propylamine, 0.125 g (0.265 mmol) of **8**, and 0.018 g (0.016 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 2 days at 70 °C. Purification was performed by flash chromatography on silica gel with CH_2Cl_2/CH_3OH (0−1%) as the eluant and afforded 0.130 g of **9** (78%): mp 45−6 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (m, CH_3, 6H), 1.26 (m, CH_2, 36H), 1.79 (m, CH_2, 4H), 3.91 (t, J = 6.3 Hz, OCH_2, 2H), 4.00 (t, J = 6.3 Hz, OCH_2, 2H), 6.84 (m, Ph, 2H), 7.05 (d, J = 2.4 Hz, Ph, 1H), 7.29 (m, 1H), 7.80 (td, J = 7.8 Hz, J = 1.9 Hz, 1H), 7.93 (dd, J = 8.1 Hz, J = 2.2 Hz, 1H), 8.40 (d, J = 8.3 Hz, 2H), 8.68 (m, 1H), 8.82 (d, J = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.1, 26.2, 29.5, 29.8, 32.0, 68.8, 69.8, 90.2 (C≡C), 90.5 (C≡C), 113.0, 114.0, 117.3, 118.4, 120.4, 120.9, 121.4, 123.9, 137.0, 139.2, 149.3, 151.7, 152.9, 153.9, 154.4, 154.7, 155.7; FT-IR (KBr, cm^{-1}) 3447 (m), 3050 (w), 2919

(s), 2849 (s), 2210 (w, $\nu_{C\equiv C}$), 1588 (m), 1542 (m), 1502 (s), 1468 (s), 1420 (m), 1394 (m), 1279 (s), 1222 (s), 1154 (m), 1032 (s), 854 (m), 792 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 316 (13 600), 347 (10 700); FAB$^+$ 625 ([M + H]$^+$, 100), 439 ([M − $OC_{12}H_{25}$]$^+$, 30). Anal. Calcd for $C_{42}H_{60}N_2O_2$: C, 80.72; H, 9.68; N, 4.48. Found: C, 80.53; H, 9.47; N, 4.38.

Ligand 10. This ligand was prepared according to experimental condition 3, from 0.042 g (0.133 mmol) of 5,5′-dibromo-2,2′-bipyridine, 15 mL of *n*-propylamine, 0.125 g (0.265 mmol) of **8**, and 0.018 g (0.016 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 2 days at 70 °C. Purification was performed by flash chromatography on silica gel with CH_2Cl_2 as the eluant and afforded 0.090 g of **10** (62%): mp 50−1 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (m, CH_3, 12H), 1.27 (m, CH_2, 72H), 1.81 (m, CH_2, 8H), 3.92 (t, J = 6.6 Hz, OCH_2, 4H), 4.01 (t, J = 6.3 Hz, OCH_2, 4H), 6.85 (m, Ph, 4H), 7.05 (d, J = 2.2 Hz, Ph, 2H), 7.92 (m, 2H), 8.35 (t, J = 8.2 Hz, 1H), 8.45 (d, J = 8.3 Hz, 1H), 8.79 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.1, 26.2, 29.4, 29.5, 29.8, 32.0, 68.8, 69.8, 90.3 (C≡C), 90.7 (C≡C), 112.9, 114.0, 117.4, 118.4, 120.3, 139.2, 150.4, 151.8, 152.9, 154.1, 155.4; FT-IR (KBr, cm^{-1}) 2919 (s), 2850 (s), 2360 (m), 2209 (w, $\nu_{C\equiv C}$), 1531 (w), 1500 (s), 1468 (s), 1423 (m), 1392 (m), 1279 (m), 1222 (s), 1154 (m), 1029 (s), 839 (m), 785 (m); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 324 (13 500), 364 (16 300); FAB$^+$ 1093 ([M + H]$^+$, 100), 907 ([M − $OC_{12}H_{25}$]$^+$, 10). Anal. Calcd for $C_{74}H_{112}N_2O_4$: C, 81.27; H, 10.32; N, 2.56. Found: C, 81.04; H, 10.18; N, 2.38.

Ligand 14. This ligand was prepared according to experimental condition 3, from 0.029 g (0.122 mmol) of 5-bromo-2,2′-bipyridine, 10 mL of *n*-propylamine, 0.030 g (0.061 mmol) of **13**, and 0.008 g (0.007 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 20 h at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2 as the eluant and afforded 0.041 g of **14** (84%): mp 105−6 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (m, CH_3, 6H), 1.25 (m, CH_2, 36H), 1.88 (m, CH_2, 4H), 4.06 (t, J = 6.3 Hz, OCH_2, 4H), 7.06 (s, Ph, 2H), 7.32 (t, J = 5.9 Hz, 2H), 7.83 (t, J = 7.8 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H), 8.42 (d, J = 8.1 Hz, 4H), 8.69 (d, J = 4.6 Hz, 2H), 8.83 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.2, 29.5, 29.8, 32.0, 69.7, 90.2 (C≡C), 92.1 (C≡C), 113.9, 116.9, 120.4, 120.6, 121.4, 124.0, 137.0, 139.3, 149.4, 151.7, 153.9, 154.9, 155.6; FT-IR (KBr, cm^{-1}) 3447 (m), 3055 (w), 2921 (s), 2851 (s), 2356 (w), 2208 (w, $\nu_{C\equiv C}$), 1730 (m), 1587 (m), 1544 (m), 1502 (s), 1461 (s), 1415 (s), 1388 (m), 1276 (m), 1216 (s), 1128 (w), 1071 (s), 1026 (m), 996 (m), 862 (m), 745 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 260 (5900), 331 (13 000), 389 (13 700); FAB$^+$ 803 ([M + H]$^+$, 100), 617 ([M − $OC_{12}H_{25}$]$^+$, 20). Anal. Calcd for $C_{54}H_{66}N_4O_2$: C, 80.76; H, 8.28; N, 6.98. Found: C, 80.63; H, 8.13; N, 6.85.

Ligand 16. This ligand was prepared according to experimental condition 3, from 0.028 g (0.043 mmol) of **15b**, 15 mL of *n*-propylamine, 0.007 g (0.021 mmol) of 5,5′-dibromo-2,2′-bipyridine, and 0.003 g (0,003 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 3 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2 as the eluant and afforded 0.025 g of **16** (80%): mp 139−140 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (m, CH_3, 12H), 1.23 (m, CH_2, 72H), 1.88 (m, CH_2, 8H), 4.07 (t, J = 5.9 Hz, OCH_2, 8H), 7.06 (s, Ph, 2H), 7.07 (s, Ph, 2H), 7.33 (m, 2H), 7.79−7.96 (m, 6H), 8.44 (m, 6H), 8.69 (d, J = 4.8 Hz, 2H), 8.83 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.2, 29.3, 29.4, 29.5, 29.7, 32.0, 69.8, 88.2 (C≡C), 90.2 (C≡C), 90.5 (C≡C), 92.2 (C≡C), 113.9, 114.0, 116.9, 120.4, 120.5, 120.6, 120.7, 121.4, 124.0, 124.1, 137.1, 137.9, 139.3, 149.4, 151.7, 152.4, 153.9, 154.2, 155.6; FT-IR (KBr, cm^{-1}) 3415 (s), 3054 (w), 2922 (s), 2852 (s), 2364 (w), 2202 (w, $\nu_{C\equiv C}$), 1640 (m), 1618 (m), 1507 (w), 1460 (m), 1437 (s), 1261 (w), 1222 (w), 1191 (s), 1118 (s), 1068 (m), 1026 (m), 799 (m), 721 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 261 (8400), 331 (13 300), 401 (22 000); FAB$^+$ 1450 ([M + H]$^+$, 100), 1264 ([M − $OC_{12}H_{25}$]$^+$, 15), 1094 ([M − $OC_{12}H_{25}$ − $C_{12}H_{25}$]$^+$, 5). Anal. Calcd for $C_{98}H_{124}N_6O_4$: C, 81.17; H, 8.62; N, 5.80. Found: C, 80.83; H, 8.45; N, 5.57.

Ligand 18. This ligand was prepared according to experimental condition 3, from 0.020 g (0.022 mmol) of **17**, 10 mL of *n*-propylamine, 0.006 g (0.011 mmol) of **13**, and 0.002 g (0,001 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 4 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2/CH_3OH (0−5%) as the eluant and afforded 0.018 g of **18** (76%): mp 162−3 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (m, CH_3, 18H), 1.24 (m, CH_2, 108H), 1.89 (m, CH_2, 12H), 4.07 (t, J = 6.2 Hz, OCH_2, 12H), 7.07 (s, Ph, 6H), 7.33 (td, J = 7.5 Hz, J = 1.9 Hz, 2H), 7.84 (td, J = 7.5 Hz, J = 1.6 Hz, 2H), 7.94 (dd, J = 8.4 Hz, J = 1.9 Hz, 6H), 8.44 (m, 8H), 8.69 (d, J = 4.8 Hz, 2H), 8.83 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.2, 29.4, 29.5, 29.8, 32.0, 69.7, 89.8 (C≡C), 90.2 (C≡C), 90.5 (C≡C), 92.1 (C≡C), 92.2 (C≡C), 92.3 (C≡C), 113.8, 113.9, 114.0, 116.7, 120.4, 120.5, 120.7, 121.4, 137.0, 139.3, 149.4, 151.8, 153.9, 154.2, 154.9, 155.6; FT-IR (KBr, cm^{-1}) 3056 (w), 2921 (s), 2852 (s), 2360 (m), 2342 (m), 2203 (w, $\nu_{C\equiv C}$), 1504 (m), 1458 (m), 1437 (s), 1384 (w), 1262 (m), 1217 (m), 1193 (s), 1120 (s), 1024 (m), 801 (m), 721 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 259 (12 900), 335 (19 800), 408 (36 900); FAB$^+$ 2096 ([M + H]$^+$, 100), 1910 ([M − $OC_{12}H_{25}$]$^+$, 30), 1741 ([M − $OC_{12}H_{25}$ − $C_{12}H_{25}$]$^+$, 20). Anal. Calcd for $C_{142}H_{182}N_8O_6$: C, 81.33; H, 8.75; N, 5.34. Found: C, 81.23; H, 8.71; N, 5.19.

Ligand 20. This ligand was prepared according to experimental condition 3, from 0.024 g (0.018 mmol) of **19b**, 10 mL of *n*-propylamine, 0.003 g (0.009 mmol) of 5,5′-dibromo-2,2′-bipyridine, and 0.002 g (0,001 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 4 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2/CH_3OH (0−10%) as the eluant and afforded 0.018 g of **20** (71%): mp 179−180 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (m, CH_3, 24H), 1.24 (m, CH_2, 144H), 1.89 (m, CH_2, 16H), 4.07 (t, J = 6.3 Hz, OCH_2, 16H), 7.07 (s, Ph, 8H), 7.34 (m, 2H), 7.78−7.97 (m, 10H), 8.32−8.47 (m, 10H), 8.70 (m, 3H), 8.84 (s, 7H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.2, 29.5, 29.7, 29.8, 32.0, 69.7, 83.9 (C≡C), 87.3 (C≡C), 87.4 (C≡C), 90.5 (C≡C), 90.6 (C≡C), 92.1 (C≡C), 92.2 (C≡C), 113.9, 116.8, 120.7, 130.2, 131.5, 133.6, 139.3, 151.8, 153.9; FT-IR (KBr, cm^{-1}) 3443 (w), 3303 (m), 3051 (m), 2923 (s), 2856 (s), 2361 (w), 2203 (w, $\nu_{C\equiv C}$), 1662 (m), 1593 (m), 1443 (s), 1379 (m), 1269 (m), 1184 (s), 1116 (s), 1030 (m), 886 (w), 714 (s); UV−vis (CH_2Cl_2) λ, nm (ϵ, M^{-1} cm^{-1}) 261 (14 400), 334 (23 900), 413 (39 900); FAB$^+$ 2743 ([M + H]$^+$, 100), 2371 ([M − 2$OC_{12}H_{25}$]$^+$, 30), 2244 ([M − 2$OC_{12}H_{25}$ − C_9H_{19}]$^+$, 10). Anal. Calcd for $C_{186}H_{240}N_{10}O_8$: C, 81.42; H, 8.82; N, 5.10. Found: C, 81.19; H, 8.69; N, 4.75.

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