Synthesis of Soluble Bis-terpyridine Ligands Bearing Ethynylene−Phenylene Spacers

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Soluble and rigid terpyridine-based ditopic ligands bearing one to five phenylene/ethynylene modules have been synthesized by way of a stepwise procedure. Each module is attached to the terpyridine unit via an ethynylene fragment and functionalized at the 4-position with an additional ethynylene connector and in the 2,5-positions with two flexible dodecyloxy chains. The synthetic protocol is based on sequential Pd(0)-catalyzed cross-coupling reactions between a terpyridine subunit grafted with the necessary diethynyl/phenyl or ethynylphenyl/bromide appendage. For ditopic ligands displaying an even number of phenyl/ethynylene modules, the final step involves a single cross-coupling reaction between 4′-ethynylene-2,2′:6′,6″-terpyridine and the appropriate bromo derivative. In the case of the ligands having an odd number of phenylene/ethynylene fragments, a double cross-coupling reaction between an extended dibromopolyphenylene intermediate and 4′-ethynylene-2,2′:6′,6″-terpyridine or 1-(4′-ethynylene-2,2′:6′,2″-terpyridine)-4-ethynylene-2,5-didodecyloxybenzene is required. For ligands **I**−**V**, optimal preparative conditions were found with $[Pd^0(PPh_3)_4]$ (6 mol %) in *n*-propylamine at 70 °C. Oxidative dimerization of the 1-(4′-ethynylene-2,2′:6′,2″-terpyridine)-4-ethynylene-2,5-didodecyloxybenzene derivative in the presence of cupric salts and oxygen gives the corresponding homoditopic ligand $\mathbf{II_2}$ bearing a central diphenyldiacetylene spacer. Spectroscopic data for the new oligomers are discussed in terms of the extent of π-electron conjugation. Upon increasing the number of phenylene/ethynylene modules, there is a progressive lowering in energy of absorption and fluorescence transitions.

Introduction

The design of multicomponent molecules of precise length and shape has attracted much interest due to their potential use as building blocks for construction of nanoarchitectures, such as molecular wires or molecular-scale electronic devices.[1,2] An important, but as yet unresolved, issue concerns how best to interlock the various components (chromophores, conductor, electronic relays...) into ordered arrays that allow controlled transfer of stored information along the molecular axis. Particularly attractive are molecular-based systems where photoinduced energy- or electron-transfer processes can be realized over large distances and in preferred directions.[3] Earlier work has shown that the nature of the spacer separating photoactive terminals plays a crucial role in the efficiency and mechanism of information transfer. Various types of connecting bridge have been explored, including cyanides,[4] DNA,[5,6] polypeptides,[7,8] aliphatic chains,[9−11] *p*-phenylenevinylene oligomers,[12] polyenes,[13,14] polyalkynes,[15−19] polyphenylenes,[20−22] polyphenyl/alkyne,[23,24] or polythiophenes[25,26] units.

In particular, we note that extremely fast electron exchange has been observed to take place along polyalkynylene bridges, with the rate of transfer being almost insensitive to the length of the connector.[27] Recent results have also shown that the electronic conductivity of polyalkynes can be modulated by inserting aromatic units into the carbon chain.[28] These various experiments infer that preorganized modules bearing central acetylene

(1) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707.
(2) Seminario, J. M.; Tour, J. M. In *Molecular Electronics-Science and Technology*; Aviran, A., Ratner, M., Eds.; New York Academy of Science, New York, 1998; p 69.
(3) Balzani, V.; Scandola, F. *Supramolecular Chemistry: Concepts and Perspectives*; Horwood: Chichester, UK, 1991.
(4) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, *112*, 7099 and references therein.
(5) Dandliker, P. J.; Holmlin, R. E.; Barton, J. K. *Science* **1997**, *275*, 1465. Kelley, S. O.; Jackson, N. M.; Hill, M. G.; Barton, J. K. *Angew. Chem., Int. Ed.* **1999**, *38*, 941 and references therein.
(6) Harriman, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 945.
(7) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369.
(8) McLendon, G.; Hake, R. *Chem. Rev.* **1992**, *92*, 481.
(9) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440;
(10) Paddon-Row: M. N. *Acc. Chem. Res.* **1994**, *27*, 18.
(11) Klan, P.; Wagner, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 2198.
(12) Davis, W. B.; Svec, W. A.; Ratner, M. A., Wasielewski, M. R. *Nature* **1998**, *396*, 60.
(13) Effenberger, F.; Wolf, H. C. *New J. Chem.* **1991**, *15*, 117.
(14) Pickaert, G. Ziessel, R. *Tetrahedron Lett.* **1998**, *39*, 3497.
(15) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996.
(16) Harriman, A.; Ziessel, R. *Platinum Met. Rev.* **1996**, *40*, 26; **1996**, *40*, 72.
(17) Tzalis, D.; Tor, Y. *Chem. Commun.* **1996**, 1043. Tzalis, D.; Tor, Y. *J. Am. Chem. Soc.* **1997**, *119*, 852. Connors, P. J., Jr.; Tzalis, D.; Dunnick, A. L.; Tor, Y. *Inorg. Chem.* **1998**, *37*, 1121.
(18) Schermann, G.; Grösser, T.; Hampel, F.; Hirsch A. *Chem. Eur. J.* **1997**, *3*, 1105.
(19) Siemeling, U.; Vorfeld, U.; Neumann, B.; Stammler, H.-G.; Zanello, P.; Fabrizi de Biani, F. *Eur. J. Inorg. Chem.* **1999**, 1.
(20) Kim, Y.; Lieber, C. M. *Inorg. Chem.* **1989**, *28*, 3990.
(21) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.
(22) Schlicke, B.; Belser, P.; De Cola, L.; Sabbioni, E.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 4207.
(23) Grubbs, R. H.; Kratz, D. *Chem. Ber.*, **1993**, *126*, 149.
(24) Jones, L., II; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388. Huang, S.; Tour, J. M. *Tetrahedron Lett.* **1999**, 40, 3347.
(25) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.
(26) Vollmer, M. S.; Würthner, F.; Effenberger, F.; Emele, P.; Meyer, D. U.; Stümpfig, T.; Port, H.; Wolf, H. C. *Chem. Eur. J.* **1998**, *4*, 260.
(27) Harriman, A.; Ziessel, R. *Coord. Chem. Rev.* **1998**, *171*, 331.

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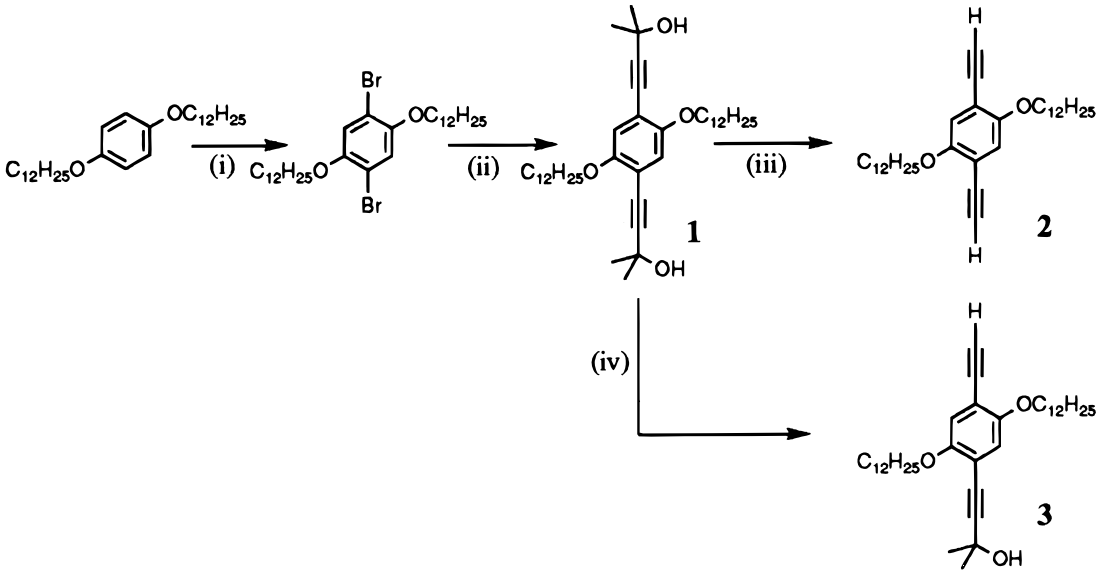
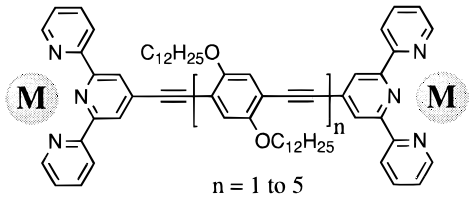
Scheme 1[a]



[a] Key: (i) CCl_4, Br_2 (4 equiv), 80 °C, 10 h, 97%; (ii) HC≡C$(CH_3)_2$OH (2 equiv), $^nPrNH_2$, [$Pd^0(PPh_3)_4$] (6 mol %), 60 °C, 20 h, 86%; (iii) NaOH (excess), toluene, 100 °C, 24 h; 81%; (iv) NaOH (excess), benzene, 70 °C, 22 h, 69%.

bonds might be suitable for building macroscopic electronic devices. The realization that pulsed illumination provides a rapid and easy way to trigger such devices has ensured study of many different chromophores, such as porphyrinic arrays,[29−31] polypyridine complexes,[32] and numerous organic molecules.[33] More recently, attention has focused on oligopyridines that are readily functionalized with alkyne groups under mild conditions and in good yield.[34] Despite the synthetic versatility and diversity of these ligands, there are important drawbacks associated with the use of alkynylated polycyclic aromatic hydrocarbons. In particular, the solubility of the resultant ligands decreases significantly as more acetylene groups are added, thereby hindering construction of molecules of nanometric dimension.[35]

A plausible way to extend the molecular length of such wires without introducing undue solubility problems is to make use of 1,4-disubstituted phenylene fragments bearing solubilizing groups in the 2,5-positions.[22,36,37] We now present a detailed description of the preparation of back-to-back terpyridine-based ligands of nanometric dimension which are suitable for the chelation of luminophoric metal centers. The synthesis of these rationally designed ditopic ligands requires an iterative strategy based on palladium-promoted cross-coupling reactions to extend the central spacer framework outward from the 1,4-diethynylene-2,5-didodecyloxybenzene core. This study complements an earlier preliminary report of the synthesis of these ligands.[37]

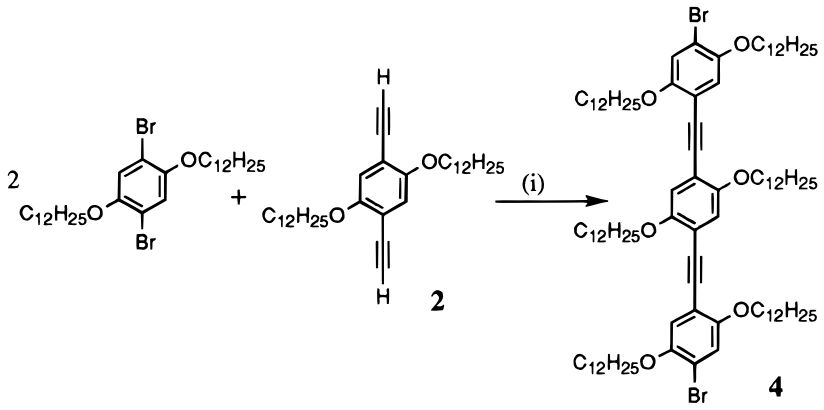


Results and Discussion

A synthetic strategy was developed for the synthesis of a set of linear terpyridine-based ditopic ligands retaining identical chelating functions but of varying molecular length. The adopted procedure utilizes key intermediates **1**−**8**, each of which is readily prepared by palladium-mediated coupling chemistry.[38,39] Precursor **1** is synthesized by reaction of the corresponding dibromo derivative with propargylic alcohol (Scheme 1). Complete deprotection, performed in refluxing toluene under basic conditions, affords the bis-terminal alkyne **2** in good yield. Selective monodeprotection, giving access to **3** in 81% yield, was achieved by refluxing in benzene under basic conditions for relatively short reaction times. Owing to the poor solubility of the mineral base in aromatic solvents, it is surmised that these deprotection reactions are essentially heterogeneous. Cross-coupling of **2** with 1,4-dibromo-2,5-(didodecyloxy)benzene forms the pivotal intermediate **4** (Scheme 2) in modest yield. The limited efficiency of this reaction is attributed to the presence of two reactive aryl bromide functions, which lead to competitive polymerization steps. In developing this procedure, a set of general conditions has been identified, and the main points are gathered in Table 1. The isolated yield of **4** increases significantly with (i) increasing

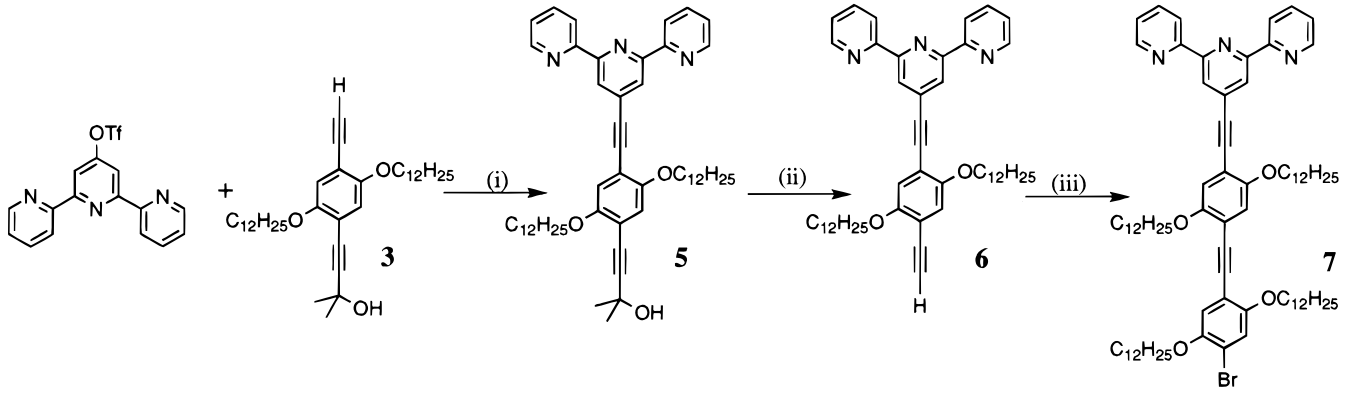
(28) Hissler, M.; El-ghayoury, A.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1717.
(29) Osuka, A.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Tamai, N. *J. Am. Chem. Soc.* **1990**, *112*, 4958.
(30) Li, F.; Yang, S. Ik.; Ciringh, Y.; Seth, J.; Martin, C. H.; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 10001.
(31) Harriman, A.; Hissler, M.; Trompette, O.; Ziessel, R. *J. Am. Chem. Soc.* **1999**, *121*, 2516.
(32) Ziessel, R. *J. Chem. Educ.* **1997**, *74*, 673 and references therein.
(33) Kumar, C. V.; Tolossa, L. M. *J. Phtochem. Photobiol. A: Chem.* **1994**, *78*, 63. Zeng, H.-H.; Wang, K.-M.; Li, D.; Yu, R.-Q. *Talanta* **1994**, *41*, 969. Mohr, G. J.; Lehmann, F.; Grummt, U.-W.; Spichiger-Keller, U. E. *Anal. Chem. Acta* **1997**, *344*, 215 and references therein.
(34) Ziessel, R.; Suffert, J.; Youinou, M.-T. *J. Org. Chem.* **1996**, *61*, 6535.
(35) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491.
(36) Huang, S.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 4908.
(37) Khatyr, A.; Ziessel, R. *Tetrahedron Lett.* **1999**, *40*, 5515.
(38) Heck, R. F. *Org. React.* **1981**, *27*, 345.
(39) Weijin, T.; Nesbitt, S.; Heck, R. F. *J. Org. Chem.* **1990**, *55*, 63.

Scheme 2[a]



[a] Key: (i) $^{n}PrNH_2$, [$Pd^0(PPh_3)_4$] (6 mol %), 70 °C, 48 h, 81%.

Scheme 3[a]



[a] Key: (i) $^{i}PrNH$, benzene, [$Pd^0(PPh_3)_4$] (6 mol %), 60 °C, 40 h, 70%; (ii) NaOH (excess), benzene, 80 °C, 36 h, 70%; (iii) 1,4-dibromo-2,5-(dodecyloxy)benzene, $^{n}PrNH_2$, [$Pd^0(PPh_3)_4$] (6 mol %), 70 °C, 4 days, 62%.

Table 1. Palladium-Catalyzed Synthesis of Dibromo Derivative 4[a]

ratio of equivalent dibromo cmpd/derivative **2**	volume of $^{n}PrNH_2$ (mL)	reaction time (days)	isolated yields (%)
2.4	30	3	14
2.4	20	3	31
2.5	15	3	50
3.0	15	2	81
3.0	15	3	73
3.0	10	3	68

[a] At 70 °C using 6 mol % in palladium.

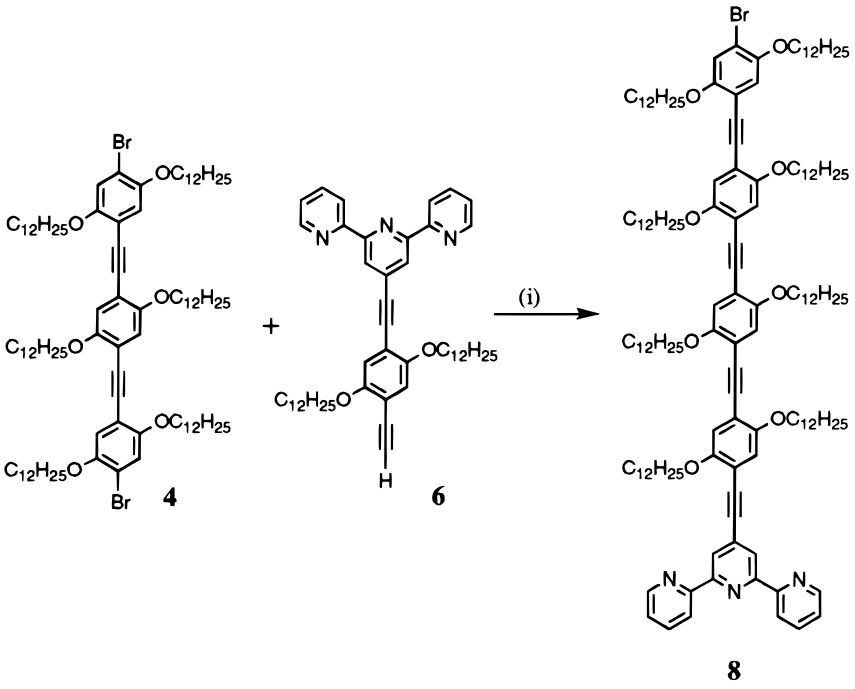
concentration of reactants and (ii) increasing ratio of dibromo versus diethynylene derivative. In this latter case, shorter reaction times are possible and the optimal yield reaches about 80%.

Access to the family of rigid ligands bearing an even number of phenylene/ethynylene modules requires the terpyridine-based precursors **6**, **7**, and **8**. The key species **6** was prepared in 49% overall yield by a cross-coupling reaction between **3** and 4′-[[(trifluoromethyl)sulfonyl]-oxy]-2,2′:6′,2″-terpyridine (terpy-OTf) in the presence of catalytic amounts of a palladium(0) complex, followed by deprotection under basic conditions. Further reaction of **6** with 1,4-dibromo-2,5-(dodecyloxy)benzene under similar conditions affords intermediate **7** in 62% yield (Scheme 3). Here, the side product assigned as ligand **III** (16%) results from parasitic cross-coupling between **7** and residual **6**. Despite varying the experimental conditions, this side reaction could not been prevented entirely. Similarly, reaction of **6** with the extended dibromo derivative **4** favors preparation of intermediate **8** in 47% yield (Scheme 4), while inescapable cross-coupling between **8** and **6** affords ligand **V** as a side-product (15%). The importance of a careful choice of the experimental conditions for controlling the iterative divergent/convergent synthetic approach of similar adducts, possessing dual potentiality to undergo further reactivity, has been observed previously.[40]

In fact, the rigid ditopic ligands were readily prepared by a Pd(0)-promoted reaction using the appropriate precursors by way of a single cross-coupling step for the ligands bearing an even number of phenylene/ethynylene modules and through a double cross-coupling step for ligand build with an odd number of modules. Thus, ligand **I** was obtained by reacting 2 equiv of terpy-OTf with the diethynylene-derivative **2**, whereas ligand $\mathbf{II_1}$ was prepared under stoichiometric conditions from intermediate **7** and 4′-ethynylene-2,2′:6′,6″-terpyridine (Scheme 5). Furthermore, ligand **III** was synthesized by the reaction of 2 equiv of 4′-ethynylene-2,2′:6′,6″-terpyridine with the extended dibromo derivative **4** while ligand **IV** was obtained under similar experimental conditions from intermediate **7** and 4′-ethynylene-2,2′:6′,6″-terpyridine (Scheme 6). Finally, **V** was obtained from 2 equiv of intermediate **6** and the dibromo derivative **4**. Application

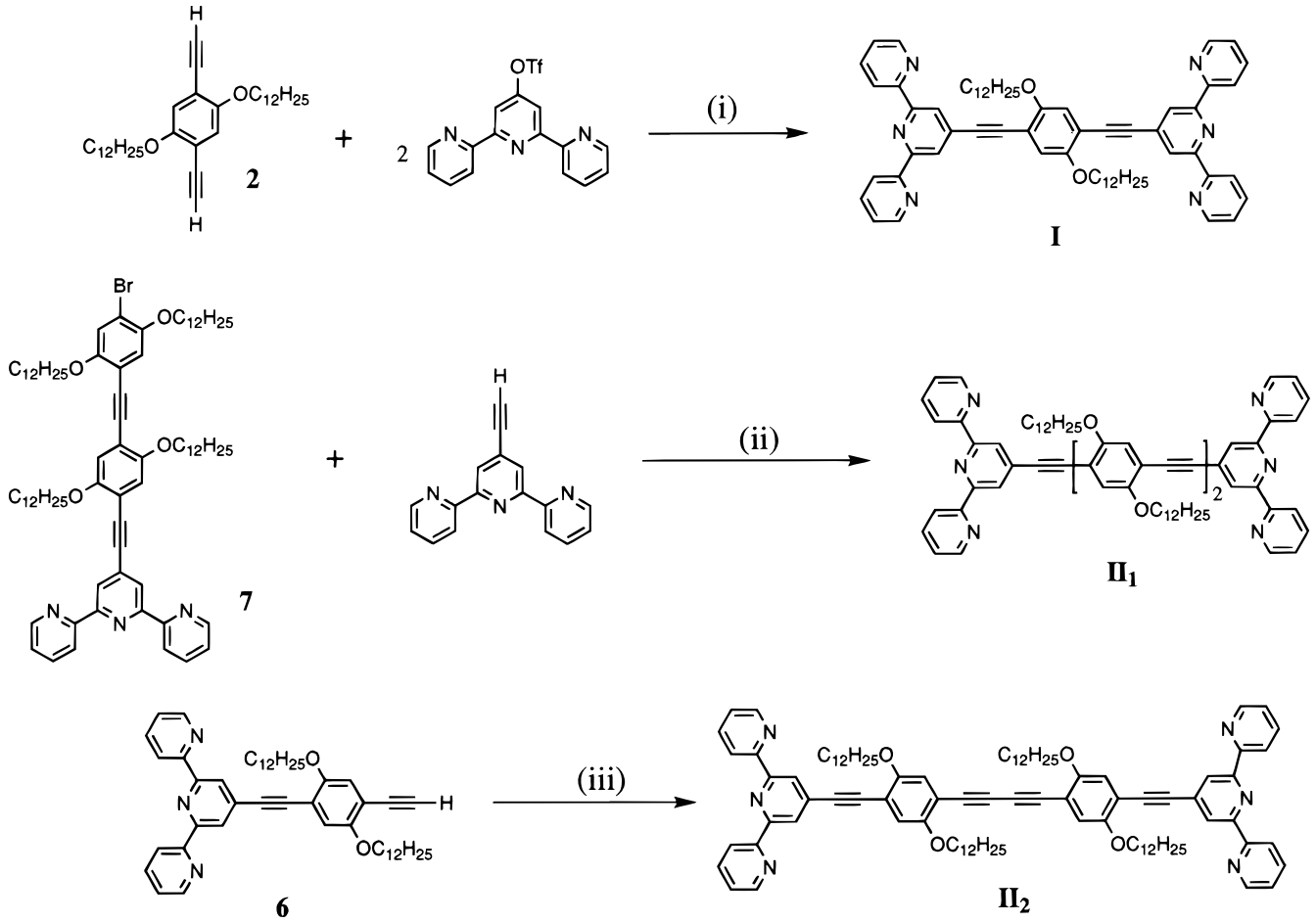
(40) Ley, K. D.; Li, Y.; Johnson, J. V.; Powell, D. H.; Schanze, K. S. *Chem. Commun.* **1999**, 1749.

Scheme 4[a]



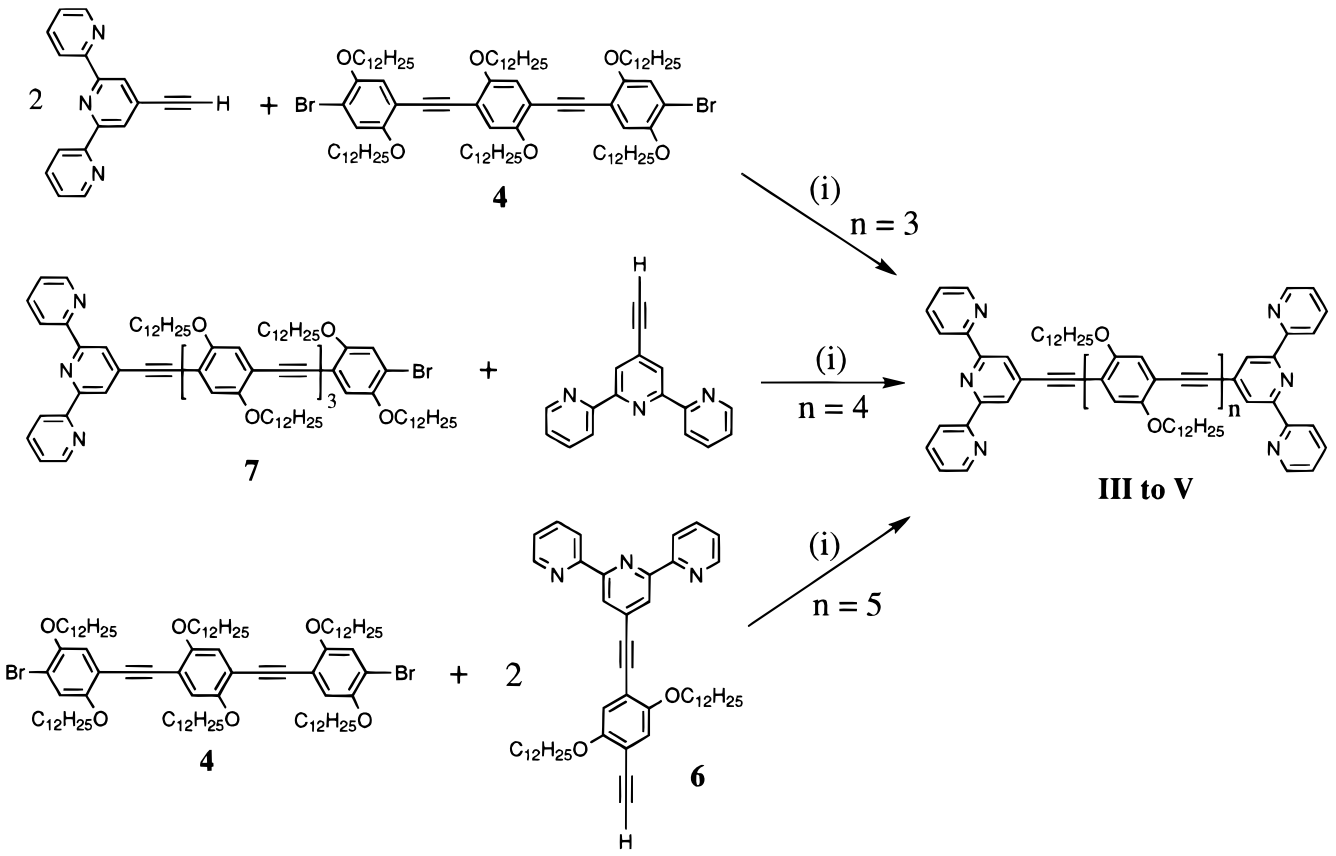
[a] Key: (i) $^{n}PrNH_2$, [$Pd^0(PPh_3)_4$] (6 mol %), 70 °C, 4 days, 47%.

Scheme 5[a]



[a] Key: (i) $^{i}Pr_2NH$, benzene, [$Pd^0(PPh_3)_4$] (6 mol %), 60 °C, 3 days, 80%; (ii) $^{n}PrNH_2$, [$Pd^0(PPh_3)_4$] (6 mol %), 60 °C, 3 days, 70%; (iii) CuCl (0.5 equiv), TMEDA (0.5 equiv), acetonitrile, O_2, rt, 5 days, 74%.

Scheme 6[a]



[a] Key: (i) $^{n}PrNH_2$, $[Pd^0(PPh_3)_4]$ (6 mol %), 70 °C, 2−5 days, 55% for **III**, 27% for **IV**, 57% for **V**.

of these coupling reactions is straightforward and gives the required ditopic ligand in acceptable yield (Scheme 6).

Oxidative homocoupling of monosubstituted ethynylene derivatives with cupric salts in oxygenated solutions is usually efficacious.[41] In the case of compound **6**, oxidative dimerization with CuCl proceeded smoothly to give the desired product in excellent yield. This reaction is best performed in the presence of a bidentate ligand, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and oxygen at room temperature.[42] The final product, ligand $\mathbf{II_2}$, carries a central butadiyne diphenyl spacer subunit (Scheme 5).

The pure ligands and intermediates are soluble in most chlorinated solvents and are isolated as pale-yellow to deep-yellow powders. Characterization has been made by NMR, mass spectrometry, UV−vis spectroscopy, and FT-IR and elemental analysis. All data are consistent with the assigned structures, and in particular, the observed carbon and proton chemical shifts and vibrational stretching frequencies are in good agreement with those reported for other ethynylated derivatives.[35,43,44] The ^1H NMR spectrum recorded for each ligand clearly indicates the absence of any overlap between those signals belonging to the terpyridine fragments and orther aromatic protons, thereby clarifying the nature of the molecular framework. Nonetheless, the ^{13}C NMR spectra are more useful with respect to identification of the final structures. The region between $\delta = 93$ and 90.5 ppm, being typical of acetylenic signals, clearly points to the number of triple bonds. Upon systematically increasing the number of ethynylene/phenylene modules there is the expected increase in the number of ethynylene carbon signals. There is no significant shielding [with the exception of ligand $\mathbf{II_2}$] of these peaks, as previously observed with diethynyleneated or triethynyleneated compounds.[34] As might be expected, the sp-hybridized C atoms tend to give signals lying at very similar chemical shifts as the chain grows longer but the expected number of signals is always reflected in the spectrum. The FT-IR spectra remain similar throughout the series, with the most pronounced bands occurring at $\nu \approx 3000$, 1650−1100, and between 850 and 620 cm^{-1}. The spectrum is dominated by vibrations associated with the aromatic rings, but the acetylene stretching vibration, although rather weak, can be resolved and at about 2200 cm^{-1} in each case.

An important question relating to these ditopic ligands concerns the extent of electronic communication along the molecular axis. In part, this point can be addressed using UV−visible absorption spectroscopy, and the main findings are collected in Figures 1 and 2. It is seen that the lowest energy absorption transition is shifted progressively toward lower energy as the number of repeat units increases. Thus, ligand **5** with a total of 78 conjugated π-electron units exhibits the most pronounced red-shift absorption maximum (Figure 1). The shift of λ drops from an initial step of $\Delta\lambda_{abs} = 25 \pm 2$ nm ($\mathbf{I} \rightarrow \mathbf{II_{1or2}}$)

(41) Eglinton, G.; McCrae, W. *Adv. Org. Chem*. **1963**, *4*, 225.
(42) Hay, A. S. *J. Org. Chem*. **1960**, *25*, 1275; **1962**, *27*, 3320.
(43) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.
(44) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem*. **1981**, *46*, 2280.

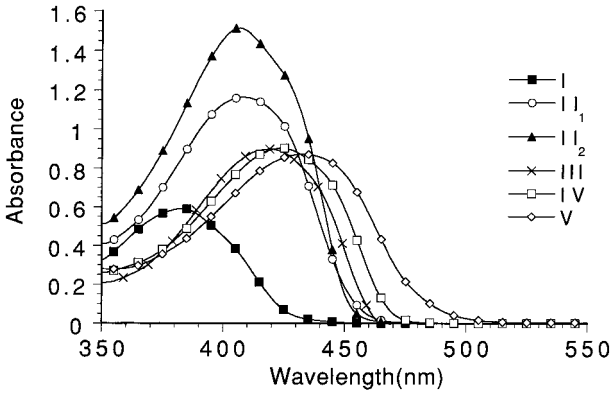


Figure 1. UV−vis absorption spectra measured in dichloromethane (2×10^{-5} M) at room temperature for various ligands **I**−**V**.

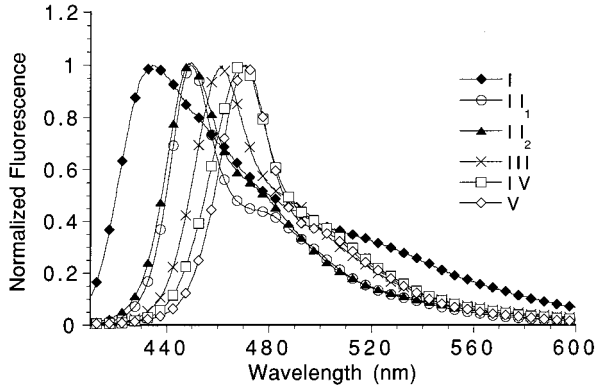


Figure 2. Normalized fluorescence emission spectra measured in degassed dichloromethane (ca. 1.2 10^{-6} M) at room temperature for various ligands **I**−**V** (excitation wavelength at 383 nm for **I** and 402 nm for the other ligands). Emission wavelengths are as follows: 434 nm for **I**; 451 nm for $\mathbf{II_1}$; 450 nm for $\mathbf{II_2}$; 461 nm for **III**; 469 nm for **IV**; 472 nm for **V**.

to $\Delta\lambda_{abs} = 13 \pm 2$ nm ($\mathbf{II_1} \rightarrow \mathbf{II_2}$) and to $\Delta\lambda_{abs} = 9 \pm 2$ nm (**IV** → **V**). Ligand **I** shows a pronounced long-wavelength absorption tail that is not obvious for the other compounds. This tail might be due to overlap of π-orbitals of the phenylene and acetylene units that is hidden by more intense absorption bands for the other compounds. 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 **I** were carried out with an oxygen-degassed solution in dichloromethane at room temperature.[45] The broad and structureless absorption bands exhibited by these linear ditopic ligands are reminescent of charge-transfer (CT) transitions, and it is noteworthy that the compounds contain an electron donor (i.e., the 2,5-dialkoxybenzene unit) and an electron acceptor (i.e., the terminal terpyridine unit). The apparent Stokes' shift (range of 51 to 39 nm) is too large for a π,π^* state but quite normal for a CT state.

The ditopic ligands fluoresce quite strongly in dichloromethane solution, with the peak of the fluorescence band shifting toward lower energy with increasing number of repeat units in the bridge. Again, the relative shift in emission maximum tends toward a plateau for the longer molecules (Figure 2). Thus, there is a weak decrease of λ_{em} from $\Delta\lambda_{em} = 16 \pm 2$ nm (**I** → $\mathbf{II_{1or2}}$) to $\Delta\lambda_{em} = 8 \pm 2$ nm (**III** → **IV**) and $\Delta\lambda_{em} = 3 \pm 2$ nm (**IV** → **V**). It is also noteworthy that the fluorescence quantum yields are relatively high and quite insensitive to the molecular length [$\phi = 25.3\%$ for **I**; $\phi = 30.1\%$ for $\mathbf{II_1}$; $\phi = 42.2\%$ for $\mathbf{II_2}$; $\phi = 38.5\%$ for **III**; $\phi = 30.1\%$ for **IV**; $\phi = 29.2\%$ for **V**, in argon-degassed dichloromethane solutions with an excitation wavelength at 383 nm for **I** and at 402 nm for the orther ligands]. The highest value is found for ligand $\mathbf{II_2}$, which has the highest oscillator strength for the corresponding absorption transition. In fact, the ratio of molar extinction coefficients measured for ligand $\mathbf{II_2}$ and $\mathbf{II_1}$ (75 800 versus 58 300 $M^{-1}cm^{-1}$) reflects the relative fluorescence yields. More importantly, the fluorescence spectrum shows poor mirror symmetry with the lowest energy absorption transition, and in fact, the absorption and fluorescence spectra look quite different. This is also partially confirmed by excitation spectra carried out under similar experimental conditions. Whereas the fluorescence band can safely be attribute to a π,π^* state, it follows that the absorption transition is not due to the same state. Either the absorption transition is belonging to a higher lying π,π^* state or to a state of different character, e.g., a CT state. Either way, the lowest energy singlet state $S_0 \rightarrow S_1$ (the one seen in fluorescence) must be hidden beneath the more intense $S_0 \rightarrow S_2$ band.[46]

The limiting effect observed on the decrease in λ shifts for the increasing number of phenyl/ethynyl modules may be inferred to the fact that the number of conjugated units might be limited to the first phenylene/acetylene moieties, whereas vibration of the molecular framework and rotation about the $sp-sp^2$ linkage drastically reduce delocalization. Alternatively, it is to be expected that charge is mainly localized at each adjoining unit, and the small but significant effects observed with increasing number of n are a result of minor disturbances which perturb the localized system. It is anticipated that complexation of each terpyridine to a transition metal will be a possible way of increasing electronic delocalization by indirect lowering of the LUMO-orbital in these oligomeric frameworks.[28,47]

In summary, we have presented a logical synthetic protocol for the synthesis of soluble back-to-back terpyridine-based ditopic ligands. At each stage of the procedure, key intermediates were prepared by either a selective or a complete deprotection reaction. One set of reaction conditions based on Pd(O)-catalyzed Sonogashira cross-coupling reactions[48] is suitable for the entire iterative synthetic sequence. For each phenylene/ethynylene increment a small bathochromic shift in absorption and emission maxima is observed. This effect is attenuated by increasing the length of the spacer. All ligands exhibit a high fluorescence quantum yield when excited in the less energetic absorption band. The ready availability of the reagents, the overall simplicity of the procedure, the use of mild reaction conditions, and the resonable yields obtained suggest that this methodology will be useful for

(45) Kaiwar, S. P.; Vodacek, A.; Blough, N. V.; Pilato, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 3311. Pilato, R. S.; Van Houten, K. A. In *Multimetalliv and Macromolecular Inorganic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1999; Vol. 4, pp 185−214.

(46) Birks, J. B. In *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.

(47) Ziessel, R. *J. Incl. Phenom. Macro. Chem.* **1999**, *35*, 369.

(48) Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, L., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1990; Vol. 3, pp 545−547.

the preparation of other polytopic ligands. The chemical and photostability of these rigid-rod conjugated oligomers make them very attractive for the construction of luminophoric d-block metal complexes where they could act as molecular wires.

Experimental Section

General Methods. The 200.1 (^{1}H) and 50.3 MHz (^{13}C) NMR spectra were recorded at room temperature, unless otherwise specified, using perdeuterated solvent as 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 measured in KBr pellets. UV−vis spectra were measured in CH_2Cl_2 at room temperature. Luminescence experiments were performed in dilute (ca. 1.2 10^{-6} M) dichloromethane solutions at room temperature. Luminescence maxima reported are uncorrected for photomultiplier response. Luminescence quantum yields were measured following the optical dilution method,[49] with $[Ru(bpy)_3]^{2+}$ in degassed acetonitrile with as the standard with a quantum yield of $\phi = 0.016$.[50] Fast-atom bombardement (FAB, positive mode) mass spectra were obtained using *m*-nitrobenzyl alcohol (*m*-NBA) as matrix.

Materials. *n*-Propylamine and 2-methyl-3-butyn-2-ol were purchased from ACROS; CuCl was purchased from Aldrich Chemical Co.; *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was purchased from Fluka; 1,4-dibromo-2,5-(dodecyloxy)-benzene,[51] 4′-[[(trifuoromethyl)sulfonyl]oxy]-2,2′:6′,6″-terpyridine,[52] and 4′-ethynyl-2,2′:6′,6″-terpyridine,[53] $[Pd^0(PPh_3)_4]$[54] were prepared and purified according to literature procedures. Diisopropylamine and acetonitrile 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.

General Procedure for the Preparation of the Arylacetylenes 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 bromo and ethynyl derivatives in argon-degassed *n*-propylamine, and finally $[Pd^0(PPh_3)_4]$ (6 mol %) was added as a solid. After heating at 60−70 °C and complete consumption of the starting material (determined by TLC), the solvent was evaporated, and the residue was purified by chromatography on alumina for terpyridine derivatives or silica gel for the benzene derivatives, using dichloromethane with a gradient of methanol or ethyl acetate as the mobile phase.

Condition 2. A Schlenk flask was charged with the triflate and ethynyl derivatives in argon-degassed benzene, then $[Pd^0(PPh_3)_4]$ (6 mol %) was added as a solid and followed by argon-degassed diisopropylamine. The yellow solution was heated at 70 °C. After complete consumption of the starting material, the solvent was evaporated and the product was purified by chromatography on alumina eluting with dichloromethane.

Condition 3. To a deep-green oxygen-degassed solution of CuCl and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in acetonitrile, the ethynyl derivative was added and the solution stirred at room temperature. During the course of the reaction, periodic oxygenation of the solution, with a gentle flow of pure molecular oxygen, was carried out, and a white precipitate was formed. After 5 days, an aqueous solution (5 mL) of KCN (0.1 mmol) was added and the solvent was evaporated. The residue was extracted with dichloromethane (3 × 50 mL), and the product was purified by chromatography on alumina with dichloromethane as the mobile phase.

Condition 4a. To a stirred solution of the protected ethynyl derivative in benzene was added excess NaOH, and the mixture was heated at 70 °C. When the monodeprotected derivative was the major product (determined by TLC), the reaction was quenched with water and a saturated solution of NH_4Cl. The product was extracted with dichloromethane, and the organic layers were dried over $MgSO_4$. The solvent was then evaporated and the compound purified by flash chromatography on silica gel, eluting with dichloromethane with a gradient of methanol.

Condition 4b. Similar to 4a but using refluxing toluene.

Synthesis of Ligand Precursors. 1,4-(2-Methyl-3-butyn-2-ol)-2,5-didodecyloxybenzene (1). The compound was prepared according to experimental conditions 1, from 0.250 g (0.41 mmol) of 1,4-dibromo-2,5-(dodecyloxy)benzene, 20 mL of *n*-propylamine, 0.080 mL (0.83 mmol) of 2-methyl-3-butyn-2-ol, and 0.029 g (0,02 mmol) of $[Pd(PPh_3)_4]$. The reaction mixture was heated during 20 h at 60 °C. Purification was performed by flash chromatography on silica gel with CH_2Cl_2/CH_3OH (0 to 10%) as eluant and afforded 0.218 g of **1** (86%): mp 93−4 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.4$ Hz, CH_3, 6H), 1.27 (m, CH_2, 36H), 1.62 (s, CH_3, 12H), 1.78 (m, CH_2, 4H), 2.10 (s, OH, 2H), 3.93 (t, $J = 6.4$ Hz, OCH_2, 4H), 6.85 (s, Ph, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 26.0, 29.3, 29.4, 29.6, 31.4, 31.9, 65.6, 69.4, (78.4, 99.1, C≡C), 113.3, 116.9, 153.5; FT-IR (KBr, cm^{-1}) 2921 (s), 2853 (s), (2227 (w, C≡C), 1400 (s), 1220 (s); UV−vis (CH_2Cl_2): λ nm (ϵ, M^{-1} cm^{-1}) 246 (1600), 281 (10 600), 335 (11 000); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 611 ($[M + H]^+$, 100), 551 ($[M - C(CH_3)_2OH]^+$, 20). Anal. Calcd for $C_{40}H_{66}O_4$: C, 78.64; H, 10.89. Found: C, 78.52; H, 10.69.

1,4-Diethynyl-2,5-didodecyloxybenzene (2). The compound was prepared according to experimental conditions 4b, from **1** 0.100 g (0.16 mmol), 1 g of NaOH (excess), and 20 mL of toluene. The reaction mixture was heated during 24 h at 100 °C. Purification was performed by flash chromatography on silica gel with CH_2Cl_2 as eluant and afforded 0.066 g of **2** (81%): mp 81−2 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.4$ Hz, CH_3, 6H), 1.27 (m, CH_2, 36H), 1.80 (m, CH_2, 4H), 3.33 (s, C≡CH, 2H), 3.97 (t, $J = 6.6$ Hz, OCH_2, 4H), 6.95 (s, Ph, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.9, 29.1, 29.4, 29.6, 31.4, 31.9, 69.6, (79.8, 82.4, C≡C), 113.2, 117.7, 153.9; FT-IR (KBr, cm^{-1}) 3282 (s), 2921 (s), 2847 (s), (2107 (w, C≡C), 1957 (w), 1501 (s), 1465 (s), 1384 (s), 1211 (s), 1112 (m), 1030 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 233 (20 900), 262 (14 800), 271 (23 500), 337 (6800); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 495 ($[M + H]^+$, 100), 309 ($[M - OC_{12}H_{25}]^+$, 15). Anal. Calcd for $C_{34}H_{52}O_2$: C, 82.53; H, 11.00. Found: C, 82.53; H, 10.67.

1-(2-Methyl-3-butyn-2-ol)-4-ethynyl-2,5-didodecyloxybenzene (3). The compound was prepared according to experimental conditions 4a, from **1** 0.100 g (0.16 mmol), 1 g of NaOH (excess), and 20 mL of benzene. The mixture was heated during 22 h at 70 °C. Purification was preformed by flash chromatography on silica gel with CH_2Cl_2/MeOH (95/5) as eluant and afforded 0.017 g of **3** (69%): mp 71−2 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.2$ Hz, CH_3, 6H), 1.26 (m, CH_2, 36H), 1.63 (s, CH_3, 6H), 1.79 (m, CH_2, 4H), 2.31 (s, OH, 1H), 3.31 (s, C≡CH, 1H), 3.95 (td, $J = 6.2$, 12.1 Hz, OCH_2, 4H), 6.87 (s, Ph, 1H), 6.92 (s, Ph, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.1, 22.7, 25.9, 26.0, 29.1, 29.3, 29.6, 31.4, 31.9, 46.4, 57.8, 65.7, 69.5, 69.6, (78.3, 79.9, 82.1, 99.3, C≡C), 112.6, 114.1, 117.1, 117.7, 153.4, 154.1; FT-IR (KBr, cm^{-1}) 3425 (w), 3270 (s), 2923 (s), 2852 (s), 1502 (s), 1467 (m), 1391 (s), 1274 (m), 1220 (s), 1160 (m), 1020 (m), 960 (w); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 242 (8500), 266 (19 600), 275 (28 100), 337 (12 600); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 553 ($[M + H]^+$, 100), 493 ($[M - C(CH_3)_2OH]^+$, 15). Anal. Calcd for $C_{37}H_{60}O_3$: C, 80.38; H, 10.94. Found: C, 80.53; H, 10.52.

1,4-[1-Bromo-2,5-(dodecyloxy)benzene)-4-ylethynyl]-2,5-didodecyloxybenzene (4). The compound was prepared according to experimental conditions 1, from 0.034 g (0.068 mmol) of 1,4-diethynyl-2,5-(dodecyloxy)benzene **2**, 15 mL of *n*-propylamine, 0.100 g (0.165 mmol) of 1,4-dibromo-2,5-(dodecyloxy)benzene, and 0.012 g (0.01 mmol) of $[Pd(PPh_3)_4]$. The reaction mixture was heated during 3 days at 70 °C. Purification was performed by flash chromatography on silica

(49) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
(50) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.
(51) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.
(52) Potts, K. T.; Konwar, D. *J. Org. Chem.* **1991**, *56*, 4815.
(53) Grosshenny, V.; Ziessel, R. *J. Organomet. Chem.* **1993**, *453*, 19.
(54) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

gel with hexane/CH_2Cl_2 (70/30) as eluant and afforded **7** 0.052 g (50%): mp 82−3 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (m, CH_3, 18H), 1.28 (m, CH_2, 108H), 1.87 (m, CH_2, 12H), 3.98 (m, OCH_2, 12H), 6.98 (s, Ph, 2H), 7.00 (s, Ph, 2H), 7.10 (s, Ph, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 26.0, 29.4, 31.9, 69.7, 70.0, (90.6, 90.9, C≡C), 113.3, 114.3, 117.3, 117.7, 118.3, 153.5, 154.1; FT-IR (KBr, cm^{-1}) 2923 (s), 2851 (s), 1465 (s), 1217 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 252 (5800), 304 (25 400), 340 (20 000), 385 (43 600); FAB$^+$ *m/z* (nature of the peak, relative intensity) 1541 ([M + H]$^+$, 100), 1461 ([M − Br]$^+$, 25), 1462 ([M − Br + H]$^+$, 15). Anal. Calcd for $C_{94}H_{156}O_6Br_2$: C, 73.22; H, 10.20. Found: C, 73.01; H, 9.87.

1-(2-Methyl-3-butyn-2-ol)-4-(2,2′:6′,2″-terpyridine-4-yl-ethynyl)-2,5-didodecyloxybenzene (5). This compound was prepared according to experimental conditions 2, from 0.200 g (0.36 mmol) of 1-(2-methyl-3-butyn-2-ol)-4-ethynyl-2,5-didodecyloxybenzene **3**, 0.381 g (0.44 mmol) of 4′-[[(trifuoromethyl)sulfonyl]oxy]-2,2′:6′,6″-terpyridine, 20 mL of benzene, 0.025 g (0.022 mmol) of [Pd(PPh_3)$_4$], and 3.5 mL of diisopropylamine. The reaction mixture was heated at 60 °C during 40 h. Purification was performed by chromatography on alumina with CH_2Cl_2 as eluant and afforded 0.197 g of **5** (70%): mp 72−3 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (m, CH_3, 6H), 1.27 (m, CH_2, 36H), 1.63 (s, CH_3, 6H), 1.83 (m, CH_2, 4H), 2.39 (s, OH, 1H), 3.99 (td, J = 6.2, 1.2 Hz, OCH_2, 4H), 6.86 (s, Ph, 1H), 6.92 (s, Ph, 1H), 7.34 (ddd, J = 7.4, 5.8, 1.0 Hz, 2H), 7.86 (td, J = 7.8, 1.8 Hz, 2H), 8.59 (s, 2H), 8.64 (d, J = 8.8 Hz, 2H), 8.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 25.9, 26.1, 29.3, 29.4, 29.6, 31.4, 31.8, 65.5, 69.4, 69.6, (78.3, 90.4, 92.5, 99.7, C≡C), 112.9, 114.3, 117.1, 121.1, 122.7, 123.8, 128.3, 128.5, 131.9, 132.1, 133.4, 136.7, 149.0, 153.4, 153.7, 155.4, 155.6; FT-IR (KBr, cm^{-1}) 2924 (s), 2854 (s), 2214 (w, C≡C), 1467 (s), 1390 (s), 1214 (s), 1111 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 245 (16 600), 252 (22 500), 287 (30 100), 311 (14 800), 364 (13 600); FAB$^+$ *m/z* (nature of the peak, relative intensity) 784 ([M + H]$^+$, 100), 724 ([M − $C(CH_3)_2OH$]$^+$, 50), 492 ([M − $C(CH_3)_2OH$-terpy]$^+$, 10). Anal. Calcd for $C_{52}H_{69}N_3O_3$: C, 79.65; H, 8.87; N, 5.36. Found: C, 79.56; H, 8.81; N, 5.30.

1-(2,2′:6′,2″-Terpyridine-4-ylethynyl)-4-ethynyl-2,5-didodecyloxybenzene (6). This compound was prepared according to experimental conditions 4a, from **5** 0.150 g (0.19 mmol), 1 g of NaOH (excess), and 30 mL of benzene. The reaction mixture was heated during 36 h at 80 °C. Purification was performed by chromatography on alumina with CH_2Cl_2 as eluant and affored 0.096 g of **6** (70%): mp 68−9 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (m, CH_3, 6H), 1.28 (m, CH_2, 36H), 1.85 (m, CH_2, 4H), 3.38 (s, C≡CH, 1H), 4.07 (td, J = 6.2, 1.2 Hz, OCH_2, 4H), 6.95 (s, Ph, 1H), 7.05 (s, Ph, 1H), 7.35 (ddd, J = 7.5, 6.0, 1.1 Hz, 2H), 7.87 (td, J = 7.5, 1.1 Hz, 2H), 8.60 (s, 2H), 8.64 (d, J = 8.8 Hz, 2H), 8.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 25.9, 26.1, 29.1, 29.3, 29.4, 29.6, 31.8, 69.5, 69.7, (79.9, 82.6, 90.2, 92.8, C≡C), 113.5, 113.7, 117.1, 117.8, 121.0, 122.7, 123.8, 133.3, 136.7, 149.0, 153.7, 154.0, 155.4, 155.6; FT-IR (KBr, cm^{-1}) 2925 (s), 2851 (s), 2208 (m, C≡C), 1576 (s), 1469 (s), 1391 (s), 1217 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 245 (27 600), 252 (29 800), 287 (61 200), 309 (48 400), 361 (29 600); FAB$^+$ *m/z* (nature of the peak, relative intensity) 726 ([M + H]$^+$, 100), 493 ([M − terpy]$^+$, 15). Anal. Calcd for $C_{49}H_{63}N_3O_2$: C, 81.06; H, 8.75; N, 5.79. Found: C, 80.82; H, 8.53; N, 5.45.

1-(4′-Ethynyl-2,2′:6′,2″-terpyridine)-4-[1-bromo-2,5-(dodecyloxy)benzene-4-ylethynyl]-2,5-didodecyloxybenzene (7). This compound was prepared according to experimental conditions 1 from 0.150 g (0.21 mmol) of **6**, 0.150 (0.25 mmol) of 1,4-dibromo-2,5-(dodecyloxy)benzene, 0.015 g (0.013 mmol) of [Pd(PPh_3)$_4$], and 30 mL of *n*-propylamine. The reaction mixture was heated during 4 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2 as eluant and afforded 0.162 g of **7** (62%): mp 84−5 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (m, CH_3, 12H), 1.25 (m, CH_2, 72H), 1.88 (m, CH_2, 8H), 4.02 (m, OCH_2, 8H), 7.00 (s, Ph, 2H), 7.03 (s, Ph, 1H), 7.06 (s, Ph, 1H), 7.36 (ddd, J = 7.6, 5.9, 1.2 Hz, 2H), 7.87 (td, J = 7.6, 1.2 Hz, 2H), 8.59 (s, 2H), 8.65 (d, J = 8.0 Hz, 2H), 8.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 26.0, 26.1, 29.3, 29.4, 29.6, 31.9, 69.7, (90.6, 91.5, 91.9, 92.8, C≡C), 113.1, 114.3, 117.1, 115.2, 117.3, 117.4, 121.1, 122.7, 123.9, 133.5, 136.8, 149.1, 153.4, 153.5, 153.9, 155.4, 155.7; FT-IR (KBr, cm^{-1}) 2925 (s), 2855 (s), 2208 (m, C≡C), 1274 (s), 1213 (s), 1110 (s); UV−vis (CH_2Cl_2): λ nm (ϵ, M^{-1} cm^{-1}) 244 (37 600), 255 (43 900), 299 (71 300), 385 (72 100); FAB$^+$ *m/z* (nature of the peak, relative intensity) 1250 ([M + H]$^+$, 100), 1251 ([M + 2H]$^+$, 74), 1168 ([M − Br]$^+$, 65), 936 ([M − Br-terpy]$^+$, 12). Anal. Calcd for $C_{79}H_{114}N_3O_4Br$: C, 75.93; H, 9.19; N, 3.36. Found: C, 75.82; H, 8.95; N, 3.25.

1-(2,2′:6′,2″-Terpyridine-4′-ylethynyl)-4-[1-yl-ethynyl--2,5-di(dodecyloxy)benzene-4-[1-yl-ethynyl-2,5-didodecyloxy)-4-(1-yl-ethynyl-2,5-didodecyloxy)benzene-4-bromo)]]-2,5-didodecyloxy)benzene (8). This compound was prepared according to experimental conditions 1, from 0.036 g (0.02 mmol) of **4**, 15 mL of *n*-propylamine, 0.017 g (0.04 mmol) of **6**, and 0.002 g (0.002 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated during 4 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2 as eluant and afforded 0.024 g of **8** (47%): mp 120−1 C; ^{1}H NMR ($CDCl_3$) δ 0.88 (m, CH_3, 24H), 1.26 (m, CH_2, 144H), 1.88 (m, CH_2, 16H), 4.02 (m, OCH_2, 16H), 7.01 (m, Ph, 8H), 7.36 (ddd, J = 7.6, 5.9, 1.2 Hz, 2H), 7.87 (td, J = 7.6, 1.2 Hz, 2H), 8.59 (s, 2H), 8.65 (d, J = 8.0 Hz, 2H), 8.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.3, 22.8, 23.5, 24.3, 25.0, 26.1, 26.3, 29.5, 29.6, 29.8, 32.1, 68.8, 69.8, 70.0, (89.7, 90.0, 90.8, 91.5, 91.7, 91.8, 92.1, 92.9, C≡C), 113.2, 114.1, 114.2, 114.3, 114.5, 114.6, 114.7, 115.4, 116.7, 117.4, 117.5, 117.6, 118.6, 121.3, 122.9, 124.0, 133.7, 137.0, 149.3, 153.0, 153.7, 154.1, 155.6, 155.9; FT-IR (KBr, cm^{-1}) 2959 (s), 2924 (s), 2854 (s), 2209 (w, C≡C), 1264 (s), 1099 (s), 1025 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 298 (24 900), 322 (22 100), 400 (37 700); FAB$^+$ *m/z* (nature of the peak, relative intensity) 2186 ([M]$^+$, 98), 2187 ([M + H]$^+$, 100), 2105 ([M − Br]$^+$, 20), 1873 ([M − Br-terpy]$^+$, <5). Anal. Calcd for $C_{143}H_{218}N_3O_8Br$: C, 78.53; H, 10.05; N, 1.92. Found: C, 78.39; H, 9.80; N, 1.89.

Synthesis of Rigid Rodlike Ligands. Ligand I. This compound was prepared according to experimental conditions 2, from 0.648 g (0.13 mmol) of 1,4-diethynyl-2,5-didodecyloxybenzene **2**, 0.100 g (0.26 mmol) of 4′-[[(trifuoromethyl) sulfonyl]-oxy]-2,2′:6′,6″-terpyridine, 12 mL of benzene, 0.009 g (0.016 mmol) of [Pd(PPh_3)$_4$], and 3 mL of diisopropylamine. The reaction mixture was heated at 60 °C during 3 days. Purification was performed by chromatography on alumina with CH_2Cl_2 as eluant and afforded 0.100 g (80%) of ligand **I**: mp 167−8 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 6.5 Hz, CH_3, 6H), 1.27 (m, CH_2, 36H), 1.93 (m, CH_2, 4H), 4.10 (t, J = 6.5 Hz, OCH_2, 4H), 7.09 (s, Ph, 2H), 7.36 (ddd, J = 7.5, 5.9, 1.1 Hz, 4H), 7.88 (td, J = 7.9, 1.9 Hz, 4H), 8.60 (s, 4H), 8.61 (d, J = 8.9 Hz, 4H), 8.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 26.1, 29.4, 29.6, 31.9, 69.8, (90.4, 93.1, C≡C), 114.0, 117.4, 121.1, 122.8, 123.9, 133.4, 136.7, 149.1, 153.8, 155.5, 155.7; FT-IR (KBr, cm^{-1}) 2922 (s), 2852 (s), 2212 (m, C≡C), 1575 (s), 1466 (s), 1389 (s), 1212 (s); UV−vis (CH_2Cl_2): λ nm (ϵ, M^{-1} cm^{-1}) 244 (45 200), 286 (46 400), 314 (39 700), 327 (37 900), 383 (29 600); FAB$^+$ *m/z* (nature of the peak, relative intensity) 958.0 ([M + H]$^+$, 100), 789 ([M − $C_{12}H_{25}$ + H]$^+$, 6), 647 ([M − terpy-py]$^+$, 13), 619 ([M − 2$C_{12}H_{25}$]$^+$, 58). Anal. Calcd for $C_{64}H_{72}N_6O_2$: C, 80.30; H, 7.58; N, 8.78. Found: C, 80.05; H, 7.29; N, 8.43.

Ligand II$_1$. This ligand was prepared according to experimental conditions 1, from 0.071 g (0.06 mmol) of **7**, 20 mL of *n*-propylamine, 0.018 g (0.07 mmol) of 4′-ethynyl-2,2′:6′,6″-terpyridine, and 0.005 g (0.004 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated for 3 days at 60 °C. Purification was performed by chromatography on alumina with CH_2Cl_2 as eluant and afforded 0.072 g of liagnd **II$_1$** (70%): mp 172−3 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (m, CH_3, 12H), 1.26 (m, CH_2, 72H), 1.90 (m, CH_2, 8H), 4.06 (m, OCH_2, 8H), 7.05 (m, Ph, 4H), 7.36 (ddd, J = 7.5, 5.9, 1.1 Hz, 4H), 7.88 (td, J = 7.9, 1.9 Hz, 4H), 8.61 (s, 4H), 8.65 (d, J = 8.9 Hz, 4H), 8.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 26.1, 26.3, 29.5, 29.8, 32.0, 32.1, 69.9, (90.7, 91.9, 92.9, C≡C), 113.3, 115.3, 117.3, 117.6, 121.3, 122.9, 124.0, 133.7, 137.0, 149.3, 153.6, 154.0, 155.6, 155.9; FT-IR (KBr, cm^{-1}) 2925 (s), 2854 (s), 2205 (m, C≡C), 1576 (s), 1463 (s), 1215 (s), 1107 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 284 (54 600), 323 (44 000), 408 (58 300); FAB$^+$ *m/z* (nature of the peak, relative intensity) 1426 ([M]$^+$, 100), 1340 ([M − C_6H_{13}

+ H]$^+$, 27). Anal. Calcd for $C_{96}H_{124}N_6O_4$: C, 80.86; H, 8.76; N, 5.89. Found: C, 80.53; H, 0.8.47; N, 5.72.

Ligand II$_2$. This compound was prepared according to experiemental conditions 3, from 0.030 g (0.04 mmol) of **6**, 10 mL of acetonitrile, 0.002 g (0.02 mmol) of CuCl, and 0.003 mL (0.02 mmol) of TMEDA. The reaction mixture was stirred under O_2 at room temperature for 5 days. Purification was performed by chromatography on alumina with CH_2Cl_2 as eluant to give 0.022 g of ligand **II$_2$** (74%): mp 102−3 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (m, CH_3, 12H), 1.27 (m, CH_2, 72H), 1.89 (m, CH_2, 8H), 4.05 (t, J = 5.8 Hz, OCH_2, 8H), 7.03 (s, Ph, 2H), 7.05 (s, Ph, 2H), 7.35 (ddd, J = 7.7, 5.9, 1.1 Hz, 4H), 7.89 (td, J = 7.7, 1.9 Hz, 4H), 8.59 (s, 4H), 8.61 (d, J = 8.0 Hz, 4H), 8.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 26.0, 26.2, 29.2, 29.4, 29.7, 31.9, 69.8, (79.6, 90.3, 91.9, 93.4, C≡C), 113.5, 114.3, 117.3, 117.8, 121.2, 122.8, 124.0, 133.4, 136.8, 140.5, 149.2, 153.8, 155.0, 155.5, 155.8; FT-IR (KBr, cm^{-1}) 2923 (s), 2852 (s), 2210 (w, C≡C), 1577 (s), 1389 (s), 1215 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 245 (31 700), 250 (31 800), 299 (52 800), 322 (54 400), 406 (75 800); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 1450 ([M]$^+$, 24), 1112 ([M − 2$C_{12}H_{25}$ + H]$^+$, 7), 958 ([M − 2 $C_{12}H_{25}$ − 2py + 3H]$^+$, 100). Anal. Calcd for $C_{98}H_{124}N_6O_4$: C, 81.17; H, 8.62; N, 5.80. Found: C, 81.07; H, 8.52; N, 5.64.

Ligand III. This ligand was prepared according to experimental conditions 1, from 0.036 g (0.02 mmol) of **4**, 15 mL of *n*-propylamine, 0.014 g (0.06 mmol) of 4′-ethynyl-2,2′:6′,6″-terpyridine, and 0.004 g (0.003 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated during 5 days at 70 °C. Purification was performed by chromatography on alumina with CH_2Cl_2 as eluant to give 0.030 g of ligand **III** (68%): mp 182−3 °C; ^{1}H NMR ($CDCl_3$) δ 0.84 (m, CH_3, 18H), 1.26 (m, CH_2, 108H), 1.90 (m, CH_2, 12H), 4.05 (m, OCH_2, 12H), 6.98 (s, Ph, 2H), 7.00 (s, Ph, 2H), 7.07 (s, Ph, 2H), 7.36 (ddd, J = 7.5, 5.9, 1.1 Hz, 4H), 7.88 (td, J = 7.9, 1.9 Hz, 4H), 8.61 (s, 4H), 8.65 (d, J = 8.9 Hz, 4H), 8.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 26.1, 26.2, 29.4, 29.5, 29.7, 32.0, 69.8, (90.7, 91.5, 92.0, 92.8, C≡C), 113.1, 114.4, 115.3, 117.2, 117.5, 121.2, 122.8, 123.9, 133.6, 136.8, 149.2, 153.5, 153.6, 154.0, 155.5, 155.8; FT-IR (KBr, cm^{-1}) 2924 (s), 2854 (s), (2207 (m), C≡C), 1589 (s), 1464 (s), 1432 (s), 1391 (s), 1108 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 245 (27 500), 251 (28 400), 268 (34 800), 322 (27 000), 419 (45 000); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 1895 ([M + H]$^+$, 100). Anal. Calcd for $C_{128}H_{176}N_6O_6$: C, 81.14; H, 9.36; N, 4.44. Found: C, 80.82; H, 9.13; N, 4.29.

Ligand IV. This ligand was prepared according experimental conditions 1, from 0.020 g (0.01 mmol) of **8**, 15 mL of *n*-propylamine, 0.003 g (0.01 mmol) of 4′-ethynyl-2,2′:6′,6″-terpyridine, and 0.001 g (0.001 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated during 2 days at 70 °C. Purification was performed by chromatography on alumina using CH_2Cl_2/$CH_3CO_2C_2H_5$ (0−10%) as eluant and afforded 0.016 g of **IV** (72%): mp 155−6 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (m, CH_3, 24H), 1.26 (m, CH_2, 144H), 1.90 (m, CH_2, 16H), 4.06 (m, OCH_2, 16H), 7.05 (m, Ph, 8H), 7.36 (ddd, J = 7.5, 5.9, 1.1 Hz, 4H), 7.88 (td, J = 7.9, 1.9 Hz, 4H), 8.61 (s, 4H), 8.65 (d, J = 8.9 Hz, 4H), 8.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 26.1, 26.2, 27.1, 29.4, 29.5, 29.7, 32.0, 69.7, (90.7, 91.5, 91.7, 92.0, 92.8, C≡C), 113.1, 114.3, 114.5, 115.3, 117.3, 117.5, 121.2, 122.8, 124.0, 133.7, 136.9, 149.2, 153.4, 153.5, 153.6, 154.0, 155.5, 155.8; FT-IR (KBr, cm^{-1}) 3417 (s), 2924 (s), 2854 (s), 2208 (w, C≡C), 1627 (s), 1108 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 286 (31 400), 321 (24 900), 424 (45 200); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 2363 ([M + H]$^+$,100), 2177 ([M − $OC_{12}H_{25}$ + H]$^+$, 30), 1992 ([M − 2$OC_{12}H_{25}$ + H]$^+$, 15). Anal. Calcd for $C_{160}H_{228}N_6O_8$: C, 81.31; H, 9.72; N, 3.56. Found: C, 81.02; H, 9.52; N, 3.22.

Ligand V. This ligand was prepared following experimental conditions 1, from 0.050 g (0.03 mmol) of **4**, 20 mL of *n*-propylamine, 0.047 g (0.06 mmol) of **6**, and 0.005 g (0.004 mmol) of [Pd(PPh_3)$_4$]. The reaction mixture was heated during 5 days at 70 °C. Purification was performed by chromatography on alumina using CH_2Cl_2/$CH_3CO_2C_2H_5$ (0−20%) as eluant and afforded 0.064 g of **V** (70%): mp 142−3 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (m, CH_3, 30H), 1.26 (m, CH_2, 180H), 1.89 (m, CH_2, 20H), 4.07 (m, OCH_2, 20H), 7.04 (m, Ph, 10H), 7.38 (ddd, J = 7.5, 5.9, 1.1 Hz, 4H), 7.88 (td, J = 7.5, 1.9 Hz, 4H), 8.59 (s, 4H), 8.61 (d, J = 8.0 Hz, 4H), 8.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 23.0, 23.8, 26.0, 26.2, 28.9, 29.4, 29.5, 29.7, 30.4, 31.9, 38.7, 68.1, 69.7, (90.7, 91.4, 91.6, 92.0, 92.8, 93.5, C≡C), 113.1, 117.3, 121.2, 122.8, 123.9, 127.6, 128.3, 128.6, 130.8, 132.0, 132.2, 133.6, 136.8, 149.2, 153.6, 154.0, 155.5, 155.8; FT-IR (KBr, cm^{-1}) 3472 (s), 3416 (s), 2924 (s), 2853 (s), (2207 (w), C≡C), 1216 (s), 1107 (s); UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 245 (25 900), 252 (26 200), 285 (27 900), 321 (28 000), 433 (43 700); FAB$^+$ *m*/*z* (nature of the peak, relative intensity) 2831.8 ([M + H]$^+$, 100), 2645.8 ([M − $OC_{12}H_{25}$ + H]$^+$, 20), 2459.8 ([M − 2$OC_{12}H_{25}$ + H]$^+$, 10). Anal. Calcd for $C_{192}H_{280}N_6O_{10}$: C, 81.42; H, 9.96; N, 2.97. Found: C, 81.18; H, 9.72; N, 2.82.

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