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Oligomeric Ligands Incorporating Multiple 5,5′-Diethynyl-2,2′-bipyridine Moieties Bridged and End-Capped by 3,4-Dibutylthiophene Units

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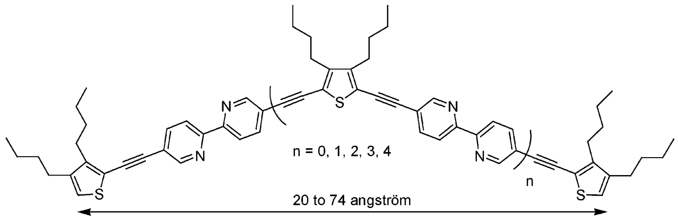

In this work, we detail the synthesis and photophysical properties of a series of soluble polybipyridine ligands comprising one to five bipyridine units sandwiched between rigid carbon−carbon triple bonds substituted by 3,4-dibutylthiophene repeating units. The dual Sonogashira coupling reaction of 5,5′-dibromo-2,2′-bipyridine with TMS- and $(CH_3)_2C(OH)$-protected acetylene allows the synthesis of a dissymmetrically functionalized building block which was selectively deprotected at either the TMS or 2-hydroxyprop-2-yl site. Various combinations allow the interconnection of the terminal alkyne to 3,4-dibutyl-2,5-diiodothiophene or 3,4-dibutyl-2-iodothiophene leading to bipyridine frameworks bearing two acetylene-protected groups or one acetylenethiophene/one acetylene-protected function. It is possible therefore to construct dimeric to pentameric bipyridine ligands where the chelating subunit is bridged by a 3,4-dibutyl-2,5-diethynylthiophene spacer and end-capped by a 3,4-dibutyl-2-ethynylthiophene stopper. All cross-coupling reactions are promoted with palladium(0) tetrakistriphenylphosphine under mild conditions. Spectroscopic data for the new oligomers are discussed in terms of the extent of π-electron conjugation. Upon increasing the number of π-electrons from 24 to 104, there is a progressive lowering in the energy of absorption and fluorescence transitions, while the emission quantum yields remain essentially constant. The LUMO levels of these large molecules, estimated by cyclic voltammetry, lie in the range −3.06 to −3.18 eV.

Introduction

Ligands bearing heteroaromatic moieties have attracted great attention because complexation with ruthenium, osmium, and rhenium, in particular, provides complexes which are luminescent in fluid solution at room temperature.[1,2] Such complexes have been extensively studied in recent decades due not only to their fascinating optical but also to their unusual electronic and redox properties, and they have been long considered likely to have many different applications such as in chemical sensing,[3] electron[4] or photon[5] donation, light harvesting,[6] and electrogenerated luminescence.[7] In many cases, the electronic properties of the metal complexes are sensitive to the nature, substituent patterns, and shape of the surrounding ligands. Grafting unsaturated

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fragments close to the ligands provides a means to easily construct sophisticated units and also to tune the intrinsic properties of the complexes by prolongation of the excited-state lifetimes and by modification of the absorption of the charge transfer state, as well as the redox properties, of one of the peripheral ligands.

Particularly attractive are molecular systems where photoinduced energy or electron-transfer processes can be realized over large distances and in a preferred direction.[8] Earlier discoveries have shown that the nature of the spacing units separating photoactive terminals plays a crucial role in the efficiency and mechanism of information transfer.[9] Here, unsaturated systems have been explored and appear to be the most attractive. Among these systems, *p*-phenylenevinylene oligomers,[10] polyenes,[11,12] polyalkynes,[13−17] polyphenylenes,[18−20] polyphenyl/alkyne,[21,22] and polythiophenes[23−25] units have been extensively studied due to their chemical stability and synthetic accessibility.

The uses of oligothiophenethynylene[26] for the construction of cyclic nanoarrays[27,28] and quasi-linear molecules capped by various stoppers have been reported.[29,30] Furthermore, thiophene-based functional polymers have also attracted significant attention due to their application as conductive and active layers in OLEDs.[31] Oligothiophenes show high conductivity and electroluminescence and have excellent characteristics as organic thin film transistors.[32,33] Based on a thorough understanding of structure−property relationships and the ingenuity of synthetic chemists, ambipolarity, tunability, high quantum efficiencies, and stability have all been achieved.[34]

Our and other investigations have revealed that ethynyl-grafted thiophenes are among the most promising units to connect chromophoric centers and to provide interesting optical properties.[35,36] Although there is considerable literature pertaining to closely coupled binuclear and trinuclear metal complexes, little is known about the more extended systems in which energy hopping processes might be a critical feature. This situation is in marked contrast to that in analogous organic systems, where it is well-known that the optical properties depend on the degree of oligomerization.[37,38]

Unfortunately, the preparation of monodisperse and shape-persistent multitopic ligands is tedious, due to the many synthetic steps and difficulties in purification arising from low solubility. The synthetic protocol presently developed provides a reduction of the number of steps by using a linear synthesis of key intermediates which can be used in an iterative fashion to increase the number of chelating units. To assess subtle differences in electronic effects between the higher oligomers, a novel family of polytopic 5,5′-diethynyl-2,2′-bipyridine based ligands has been designed, each unit being connected or end-capped by a 3,4-dibutylthiophene fragment.[39a] It is anticipated that these molecules will retain both their structural integrity and topological rigidity when complexed with luminescent transition metals and that energy transfer from one site to another is likely to occur. We present here the synthesis of a class of such ligands which, by virtue of their concise and flexible synthesis and their photophysical or redox properties, are promising candidates as effective molecular scale light harvesting devices (a schematic overview is given in Chart 1).

Results and Discussion

Scheme 1 defines the single protocol applicable to the present multitopic ligand syntheses. Clearly, we can

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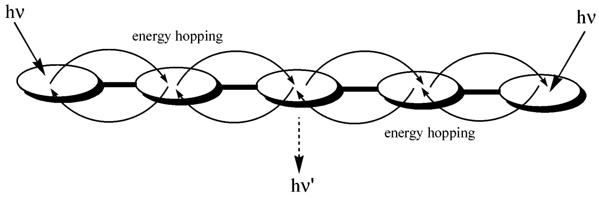
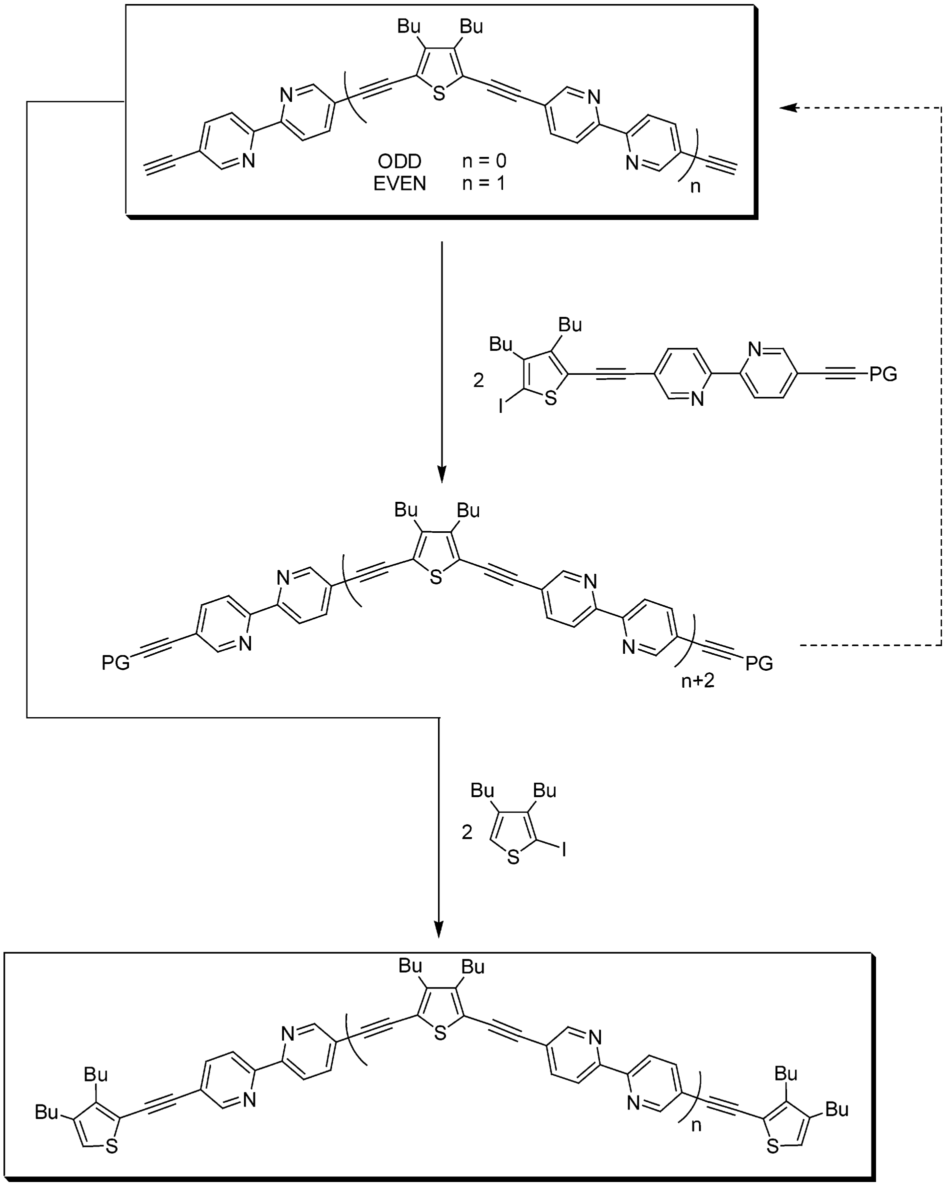
CHART 1



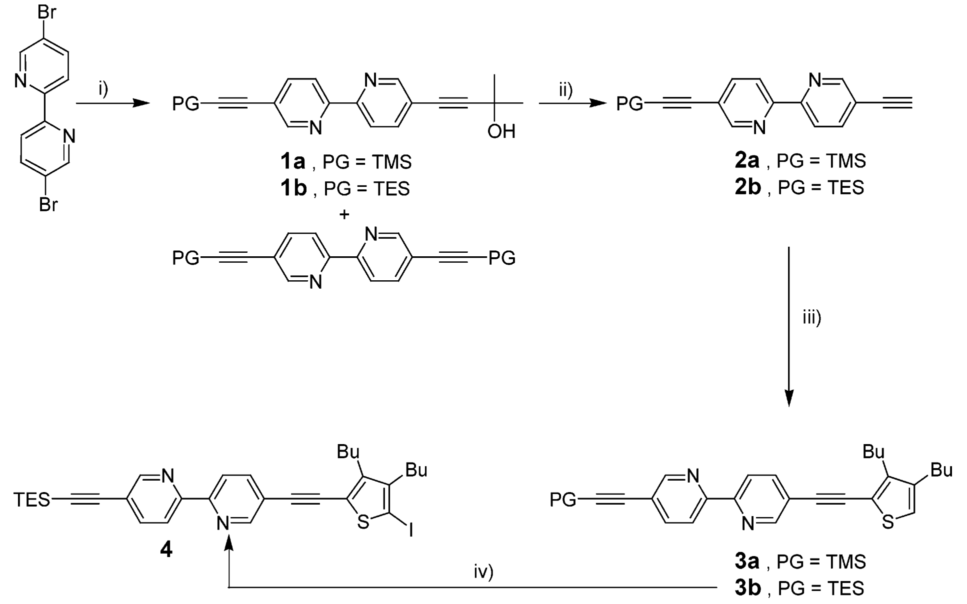
distinguish two main pathways depending of the presence of an odd or even number of bipyridine units. These require two pivotal building blocks constructed around a 5,5′-disubstituted 2,2′-bipyridine core and a thiophene moiety. In the top case, coupling between a synthon carrying two terminal alkynes and a monooiodo-substituted hybrid bpy/thiophene molecule leads to the progressive increase of two bpy links providing the ligands precursors. The final ligands are obtained by cross-linking of these deprotected intermediates with 3,4-dibutyl-2-iodothiophene. The key concept is the provision of the target ligands by an iterative sequence of reactions involving a step-by-step introduction of each extending unit after a facile deprotection reaction. The choice of two solubilizing chains (butyl) was motivated by the relatively easy access to the 3,4-dibutylthiophene starting material.[39b] The presence of one protecting group (triethylsilyl TES) and one reactive iodo function on the second starting material is critical for the success of the proposed reaction scheme. This approach allows an increase in the number of bpy units every two steps. The idea was to start from a 5,5′-dibromo-2,2′-bipyridine moiety which in our hands is easy to produce on the gram scale[40] and has been previously proved to provide transition metal complexes with exceptional photophysical properties. Butyl groups were preferred over longer paraffin chains as substituents on the thiophene units since our experience has been that this leads to better yields in precursor syntheses.

Crucial to the success of the present syntheses was the unsymmetrical functionalization of 2,2′-bipyridine with acetylenic groups bearing different protecting groups. The

SCHEME 1



SCHEME 2[a]



[a] Key: (i) $PdCl_2(PPh_3)_2$, CuI, THF, i-Pr_2NH, rt, HC≡CPG, then $HC{\equiv}CCMe_2OH$, compound **1a**: 33%, compound **1b**: 31%; (ii) NaOH, anhydrous toluene, 130 °C, compound **2a**: 88%, compound **2b**: 97%; (iii) for compound **3a**: 3,4-dibutyl-2-iodothiophene, $PdCl_2(PPh_3)_2$, CuI, THF, i-Pr_2NH, rt, 82%; for compound **3b**: 3,4-dibutyl-2-iodothiophene, $Pd(PPh_3)_4$, benzene, Et_3N, 60 °C, 86%; (iv) LDA, NIS, THF, −78 °C, 80%.

straightforward route leading to these pivotal derivatives is shown in Scheme 2. The use of acetylene protecting groups of different polarity simplifies the isolation of the pure derivatives. The most popular protecting groups for acetylene are the nonpolar silyl groups[41] such as trimethylsilyl (TMS), triethylsilyl (TES), known to be removable with K_2CO_3 in methanol, KF in methanol, or n-Bu_4NF in THF at low temperature, and triisopropylsilyl (TIPS) removed by n-Bu_4NF in THF. As polar protective groups, 2-hydroxyprop-2-yl or hydroxymethyl have been used. For the former, removal of the protecting group as acetone requires heating of the compound with an alkali metal hydroxide or sodium hydride,[42] whereas the latter needs basic and oxidative conditions.[43]

After some experimentation, keeping in mind that regioselective deprotection of a 2-hydroxyprop-2-yl function versus a TMS or TES protecting group could be realized under anhydrous conditions[44] with a mineral base, we decided to react 5,5′-dibromo-2,2′-bipyridine successively with trimethyl- or triethylsilylacetylene (1 equiv) and 2-methylbutyn-2-ol (1 equiv). The low-valent palladium(0) was generated in situ by reduction of palladium(II) with copper(I), and diisopropylamine was used to quench the nascent acid. This base and triethylamine (vide infra) have been currently used in organopalladium chemistry.[45,46] Due to the different polarities imparted by the alcohol function, the resulting molecules **1a** and **1b** could be very easily separated by column chromatography in acceptable yields from the homoprotected derivatives (Scheme 2). The disubstituted side product involving TMS could be isolated in ca. 32% yield and was useful for later in our synthetic strategy. This protocol was inspired by our previous selective monofunctionalization of 3,4-dibutyl-2,5-diiodothiophene.[39a] As expected from previous work,[44,47] derivatives **1a** and **1b** were readily and selectively deprotected from the alcohol side providing the stable mixed diethynyl derivatives **2a** and **2b**. In the next step, a Pd-promoted coupling reaction with 2-iodo-3,4-dibutylthiophene gave compounds **3a** and **3b** in ca. 80% yield.

A critical step in production of the pivotal building blocks **4** or **5a** was the selective functionalization of the thiophene unit to give its iodo derivative. This was achieved by metalation of derivative **3b** with LDA at low temperature, followed by an iodination reaction with NIS in THF. Noteworthy is the case of the TES-protected alkyne **3b**, where the desired compound **4** is produced pure in 80% yield. The characteristic ^{13}C resonance of the C−I group appears at $\delta = 77.4$ ppm in chloroform-d solvent. Surprisingly, a byproduct identified as **5b** (20% yield) was formed using a TMS protecting group. Its ^1H NMR spectrum shows two characteristic singlets at 0.29 and 0.36 ppm for the two different TMS protecting groups and the absence of thiophene H at 6.91 ppm. The formation of this compound can be understood as a nucleophilic attack of the thiophenlithium intermediate on the TMS group of a second molecule causing the formation of the deprotected form of the starting material. This is a rather surprising observation, not previ-

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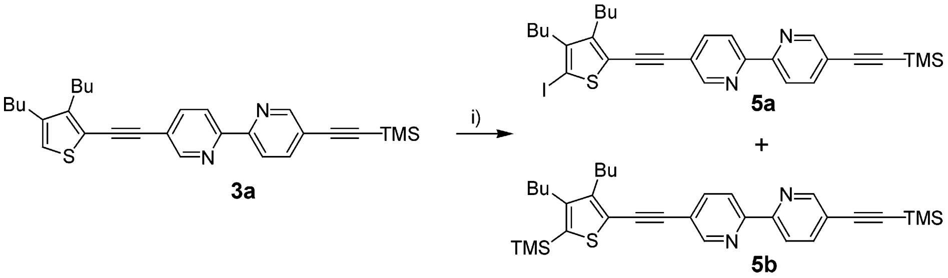
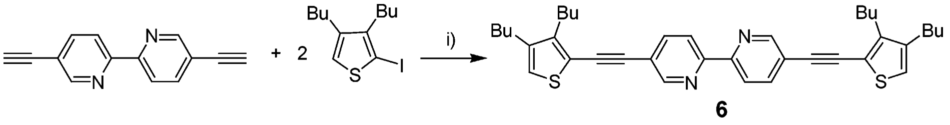
SCHEME 3[a]



[a] Key: (i) LDA, I_2, THF, −78 °C.

SCHEME 4[a]



[a] Key: (i) $Pd(PPh_3)_4$, benzene, Et_3N, 60 °C, 95%.

ously detected during the metalation of 3-ethyl-2-trimethylsilylacetylenethiophene (Scheme 3).[29,48]

To avoid the formation of compound **5b**, we have turned to the use of the TES protecting group instead of TMS. With the dissymmetric moiety **4** in hand, we then turned our attention to the preparation of the symmetrically functionalized target **6**, which has been synthesized in 95% yield, by cross-coupling 2 equiv of 3,4-dibutyl-2-iodothiophene with 5,5′-diethynyl-2,2′-bipyridine (Scheme 4).

As a test of our strategy based on this very efficient reaction, we successfully prepared our first bpy oligomer by treatment of 5,5′-diethynyl-2,2′-bipyridine with derivative **4** under palladium(0)-catalyzed carbon−carbon coupling conditions (Scheme 5).[49] The resulting TES-protected compound **7a** was produced in 93% yield. The deprotection using K_2CO_3 is straightforward and afforded derivative **7b** which possesses several desired features, namely: (i) a terminal alkyne substituent for attachment to a thiophene end-capping unit or additional bpy fragments, (ii) butyl groups ensuring solubility in many organic solvents, and (iii) the desired number of chelating units for complexation of luminescent metal centers. Grafting of 3,4-dibutyl-2-iodothiophene or derivative **4** to the trimer **7b** could be achieved using similar experimental conditions, providing, respectively, the final trimer **7c** or the TES-protected pentamer **8a**. An iterative protocol allowed the preparation of compound **8b** and **8c** in acceptable yield. Efforts to increase the yield of the pentamer were unsuccessful, and it is surmised that, despite the mild experimental conditions, the intermediate **8b** has a high tendency to form insoluble material. This may also apply in the formation of the tetramer (vide infra). From a practical point of view, in the deprotection step of **8a** leading to **8b**, KF is preferred over K_2CO_3 in mixed methanol/tetrahydrofuran.

Since the study of a homologous series of ligands and complexes would need the preparation of the oligomers carrying an even number of bpy modules, we turned our attention to the preparation of the dimer and tetramer (Scheme 6). We planned to use the strategy depicted in Scheme 1 which started from a single thiophene grafted with two bpy modules. The dimer was prepared by treatment of 3,4-dibutyl-2,5-diiodothiophene with the intermediate **2b** under Sonogashira conditions (Scheme 6). The TES protected dimer was isolated pure in 53% yield, while the deprotection step requires K_2CO_3 in protic conditions. End-capping of **9b** with 3,4-dibutyl-2-iodothiophene or with derivative **4** is feasible and gave the desired dimer **9c** and tetramer **10a**. In this latter case, deprotection of the TES group and subsequent cross-coupling with 3,4-dibutyl-2-iodothiophene provides the target tetramer **10c**. Note that the final step during the synthesis of **10c** is less efficient than previously observed but lies in the same range as for the preparation of the pentamer.

The pure ligands and intermediates are soluble in most chlorinated solvents and are isolable as pale-yellow to deep-red powders. All compounds 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 spectroscopy, elemental analysis, and cyclic voltammetry. All spectroscopic data are in keeping with the proposed molecular structures. In particular, the ^{1}H and ^{13}C NMR spectra of the majority of the compounds presented here were free of signal overlap and exhibited the expected coupling patterns. The proton NMR is particularly useful because integration of the thiophene protons at 6.92 ppm and the butylmethylene protons at ca. 2.72 ppm allows the number of grafted units to be counted. The ^{13}C NMR spectra are also useful with respect to identification of the final structures. Increasing the number of bipy subunits resulted in the expected increase in the number of ethynylene carbon signals. The resonances of the ethynylene sp-carbon are readily identified as singlets in the range of 87.2−93.8 ppm and can be used to monitor the number of triple bonds for the monomer **6**, the dimer

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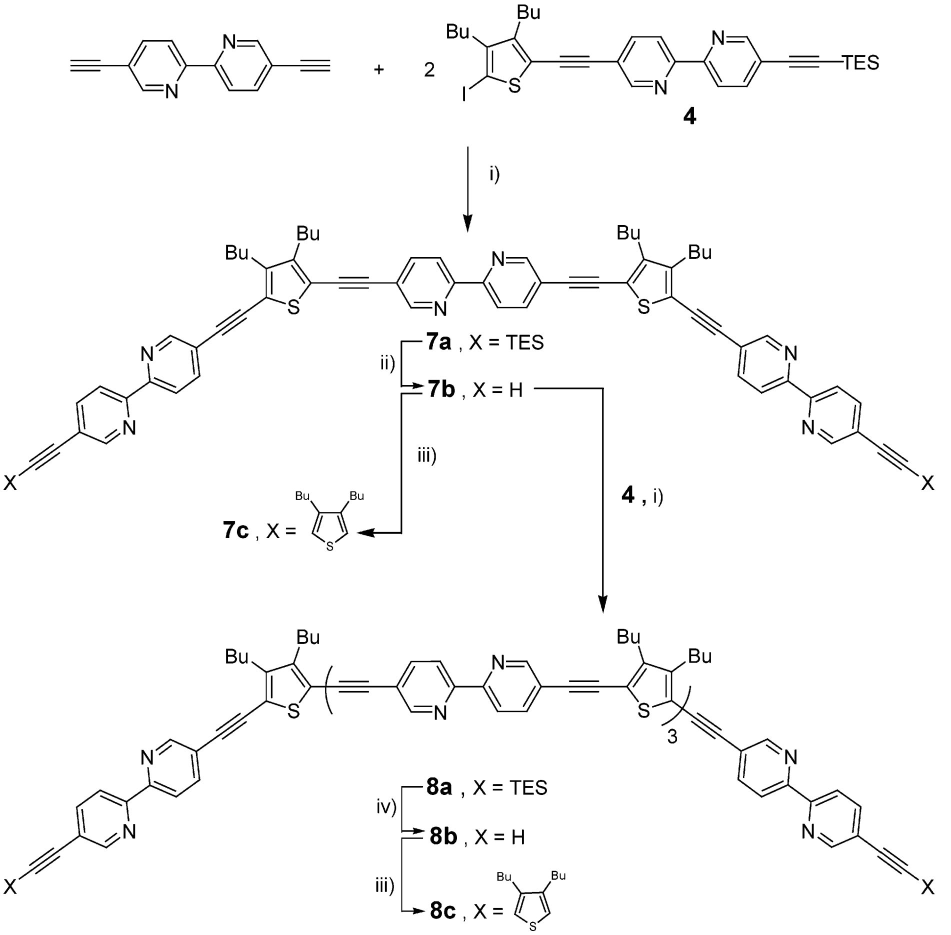
SCHEME 5[a]



[a] Key: (i) Pd(PPh$_3$)$_4$, benzene, Et$_3$N, 60 °C, compound **7a**: 93%, compound **8a**: 86%; (ii) K$_2$CO$_3$, MeOH, THF, 90%; (iii) 3,4-dibutyl-2-iodothiophene, Pd(PPh$_3$)$_4$, benzene, Et$_3$N, 60 °C, compound **7c**: 86%, compound **8c**: 38%; (iv) KF, MeOH, THF, 80%.

9c, and the trimer **7c**. For the two larger ligands we can notice some overlapping resonances of the sp-carbon signals: the tetramer **10c** presents only five different peaks and the pentamer **8c** only three peaks but with different intensities. As the chemical environment is similar for the ethynylene sp-carbons in all the ligands, we can assign the signals at 87−88 ppm to the sp-carbons by the thiophene units and at 92−94 ppm to the sp-carbons by the bpy units. The more external sp-carbons by the thiophenes present always a signal at ca. 88.0 ppm whereas the sp-carbons by the internal thiophenes show a signal at 87.2 ppm. In the same way we can notice two groups of sp-carbons by the bpy units: one group resonating at ca. 92 ppm by the more external bpy and the second group at ca. 93.5 ppm by the internal bpy, except for the pentamer **8c** where all the sp-carbon by the bpy resonate at 93.4 ppm. In this case, the intensity of this peak is five times the intensity of the peak at 88.1 ppm. These chemical shifts are in good agreement with those reported for other ethynylated compounds.[46] For each ligand, the stretching vibrational mode of the ethynylene connecting unit could be resolved about 2200 cm^{-1} in the solid-state IR spectrum and lies in the range expected for such compounds.[46]

Optical Properties

An important issue relating to these series of multitopic ligands concerns the extent of electronic delocalization along the molecular axis. The influence of this factor can be seen in electronic absorption and luminescence spectra, the essential features of which are given in Table 1. Three series of compounds have been thoroughly studied in dichloromethane solution, namely the monomer to tetramer series of the polytopic ligands bearing a thiophene (end-capping unit), the dimer to pentamer TES-protected series (*P*-oligomers), and the dimer- to pentamer-deprotected series (*DP*-oligomers) with, respectively, a C≡CTES or a C≡CH function. The final ligands monomer **6**, dimer **9c**, trimer **7c**, tetramer **10c**, and pentamer **8c** display a pair of intense and well-resolved peaks, the higher energy absorption lying at 280 nm being assigned to essentially unshifted $\pi-\pi^*$ bands of the bipyridine subunits.[50] The lower energy absorption shifts progressively toward lower energy and appears more intense as the number of bipy/thiophene modules increases. For instance, the pentamer with a total of 104 conjugated π electrons exhibits the most red-shifted

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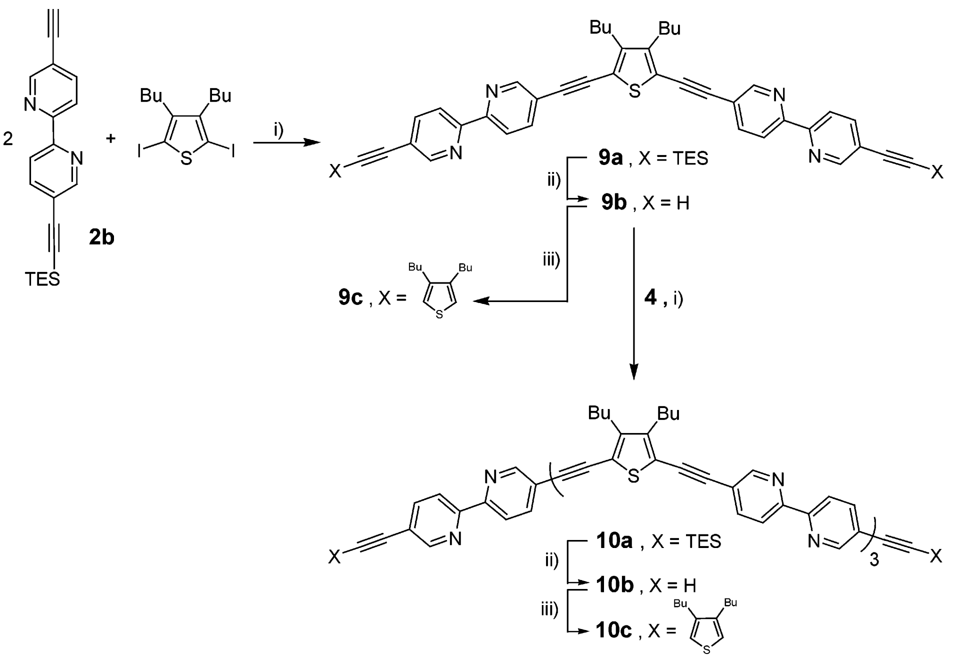
SCHEME 6[a]



[a] Key: (i) $Pd(PPh_3)_4$, benzene, Et_3N, 60 °C, compound **9a**: 53%, compound **10a**: 87%; (ii) K_2CO_3, THF, MeOH, compound **9b**: 96%, compound **10b**: 81%; (iii) 3,4-dibutyl-2-iodothiophene, $Pd(PPh_3)_4$, benzene, Et_3N, 60 °C, compound **9c**: 70%, compound **10c**: 33%.

TABLE 1. Photophysical and Redox Properties of the Thiophene-Substituted Bipyridine Ligands[a]

compd	λ_{max} (nm), [b] (M^{-1} cm^{-1})	λ_{em}[c] (nm)	ϕ_{em}[d] (%)	cathodic potential[e] (V)
monomer **6**	367 (60 000)	426	33	−1.78
P-dimer **9a**	390 (100 000)	450 (474)	38	−1.70
DP-dimer **9b**	395 (85 000)	449 (473)	38	−1.72
dimer **9c**	405 (140 000)	454 (482)	38	−1.71
P-trimer **7a**	410 (165 000)	461 (488)	42	−1.71
DP-dimer **7b**	410 (165 000)	460 (488)	43	−1.69
trimer **7c**	411 (155 000)	462 (488)	43	−1.70
P-tetramer **10a**	417 (270 000)	463 (490)	34	−1.69
DP-tetramer **10b**	417 (240 000)	460 (487)	33	−1.67
tetramer **10c**	416 (260 000)	464 (493)	31	−1.68
P-pentamer **8a**	419 (345 000)	464 (493)	43	−1.66
DP-pentamer **8b**[f]	419 (310 000)	465 (495)	42	−1.68
pentamer **8c**	419 (320 000)	465 (493)	43	−1.69

[a] Measured in aerated dichloromethane solutions at 298 K. [b] Average values measured for three different solutions. [c] Steady-state luminescence maximum with λ_{exc} in the less energetic absorption band;, the value in parentheses corresponds to the additional shoulder. [d] Average values from three measurements under the steady-state conditions using quinine sulfate in 1 N H_2SO_4 as standard; estimated error is ±10%. [e] Calculated by $\Delta(E_c - E_a)/2$ in volts, potentials were standardized using a ferrocene (Fc) internal reference and are converted to SCE scale assuming that $E_{1/2}(Fc/Fc^+) = 0.38$ V. [f] Measured in THF due to its weak solubility in CH_2Cl_2.

absorption maximum located around 419 nm with an ϵ value of 320 000 M^{-1} cm^{-1}. The shift of λ drops from an initial step of $\Delta\lambda_{abs} = 32$ nm (for monomer to dimer) to $\Delta\lambda_{abs} = 6$ nm (from dimer to trimer), to $\Delta\lambda_{abs} = 5$ nm (from trimer to tetramer), and finally to $\Delta\lambda_{abs} = 3$ nm (from tetramer to pentamer). In parallel, the ϵ values progressively increase from 60 000 to 320 000 M^{-1} cm^{-1} from the monomer to the pentamer as the total number of π electrons increases from 24 to 104 (Figure 1a). The linear increase of the ϵ values is in line with the successive addition of a single ethynylbpy/ethynylthiophene module. The attenuation features are in keeping with limited electronic delocalization found in related molecules[37] and metal-capped, wirelike polyynediyl frameworks.[51]

The same trends are observed for the TES-protected dimer to pentamer as well as for the terminal-alkyne-substituted dimer to pentamer precursors (Figure 1b,c). The shift of λ drops from an initial step of $\Delta\lambda_{abs} = 38$ nm (for *P*-monomer to *P*-dimer) to $\Delta\lambda_{abs} = 20$ nm (for *P*-dimer to *P*-trimer) to $\Delta\lambda_{abs} = 7$ nm (from *P*-trimer to *P*-tetramer), and to $\Delta\lambda_{abs} = 2$ nm (from *P*-tetramer to *P*-pentamer), In parallel, the ϵ values progressively increase from 100 000 to 345 000 M^{-1} cm^{-1} from the *P*-monomer to the *P*-pentamer. Similar valuse are found for the *DP* series of oligomers (Table 1).

It is, however, worth pointing out that in both *P* and *DP* series additional absorption bands between 300 and 350 nm are apparent and are probably due to $\pi-\pi^*$ transitions located on the ethynyl fragments.[52] Note that these transitions are not assigned to $n-\pi^*$ transitions of the polypyridine sites,[53] since they should then be evident in the spectra of the final oligomers. From a general point of view, it is surmized that the increases in the size and encumberment of the molecules reduce the planarity of the π systems, dramatically limiting the effective conjugation length. Similar effects have previously been observed in conjugated molecular systems.[37,54] We finally note that, for the oligomers, a pronounced low-energy tail extending some 40 nm was observed for the pentamer (Figure 1a), whereas for the related *P* and *DP* series this tail was not apparent (Figure 1b ,c), as would be expected on decreasing the conjugation length.

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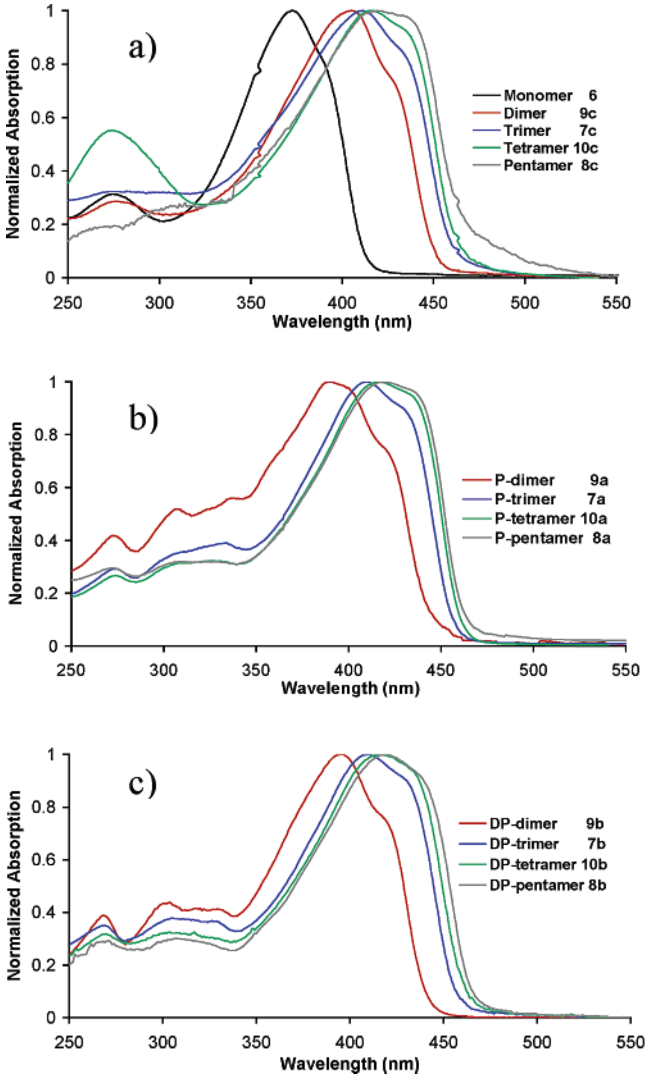

FIGURE 1. Normalized UV−vis absorption spectra measured in aerated dichloromethane (1×10^{-5} M) at room temperature for the ligand series: (a) oligomers, **6**, **9c**, **7c**, **10c**, **8c**; (b) *P*-oligomers **9a**, **7a**, **10a**, **8a**; (c) *DP*-oligomers **9b**, **7b**, **10b**, **8b*** (*measured in tetrahydrofuran).

Parallel behavior is observed by steady-state fluorescence spectrophotometry, where the intense peak of the fluorescence band is shifted progressively toward lower energy upon increasing the number of bipy/thiophene modules. The relative shift in the emission maximum tends toward a plateau for the larger molecules, with $\Delta\lambda_{\mathrm{lum}} = 28$ nm (for monomer to dimer), 8 nm (for dimer to trimer), 2 nm (for trimer to tetramer), and finally 1 nm (for tetramer to pentamer). All emission peaks are broad, and an additional band is clearly evidenced for the higher oligomers on the red side of the emission band (Figure 2a). As in observations of the absorption spectra for the *D* and *DP* series of oligomers, similar trends and features are observed (Figure 2b,c).

Variations of the absorption, primary, and secondary emission bands for the oligomer generation are summarized in Figure 3a and clearly highlight formation of the plateau. Similar plots could be generated for the *P*-oligomer and *DP*-oligomer series of ligands (Figure 3b,c).

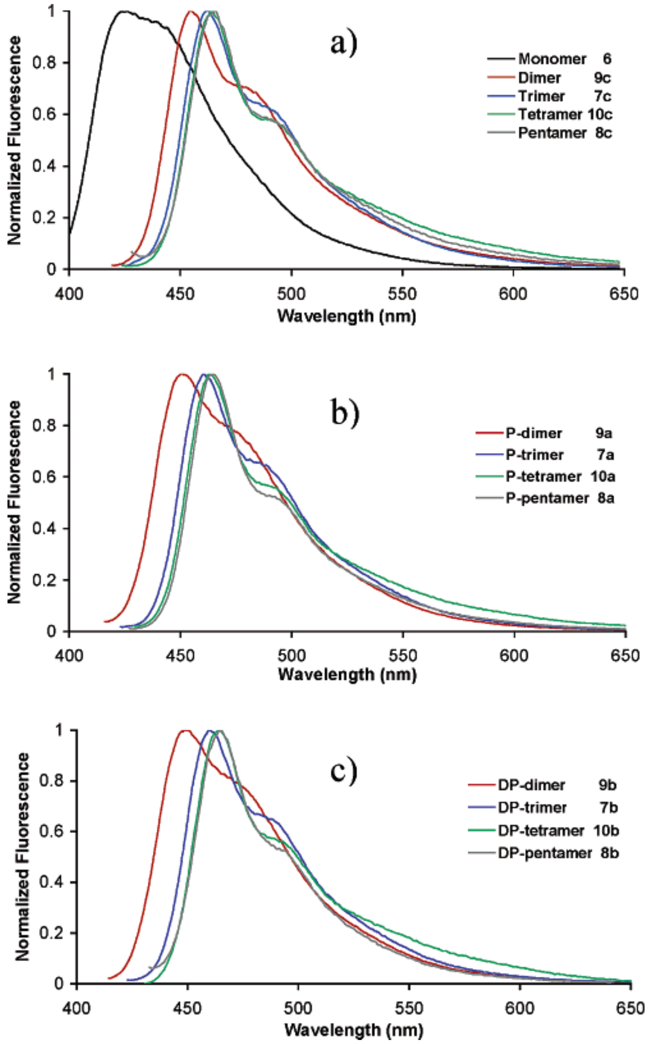

FIGURE 2. Normalized fluorescence emission spectra measured in aerated dichloromethane (1×10^{-7} M) at room temperature for the ligand series: (a) oligomers **6**, **9c**, **7c**, **10c**, **8c**; (b) *P*-oligomers **9a**, **7a**, **10a**, **8a**; (c) *DP*-oligomers **9b**, **7b**, **10b**, **8b*** (*measured in tetrahydrofuran).

It is noteworthy that the fluorescence quantum yields are high and lie in the same range ($\phi = 33$ to 43%) within the series of oligomers. This is an interesting situation because increasing the size and the dynamic motion of the molecule seems not to facilitate nonradiative deactivation of the excited state as previously found in wirelike, metal-based molecules.[37] Furthermore, in all cases the fluorescence spectra show poor mirror symmetry with the lowest-energy absorption band, and they indeed look very different. However, excitation spectra performed under the same conditions match the absorption spectra and partially confirm that the emitted light originates from the lower energy absorption band (Figures S1 and S4, Supporting Information). The apparent Stokes shifts, varying from 3770 cm^{-1} for the monomer to 2360 cm^{-1} for the pentamer, are in keeping with a highly polarized charge transfer (CT) state and not with a classical S_0−S_1 transition from a π−π^* emitting state. The progressively larger Stokes shifts imply that the oligomeric backbone becomes less rigid as the number

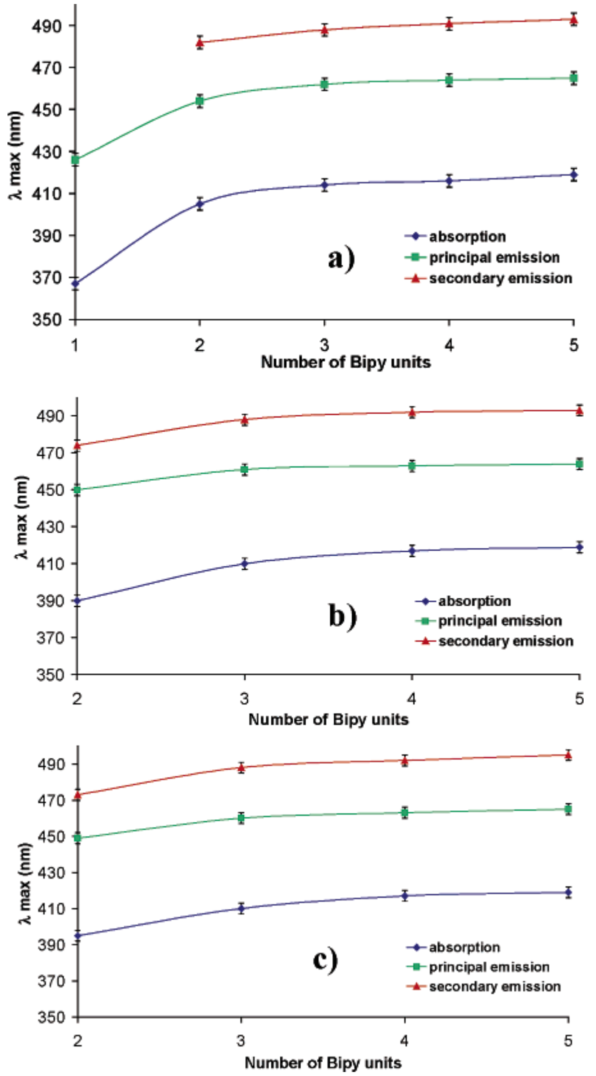

FIGURE 3. Dependence of the maximum of the wavelength for the absorption, principal emission, and secondary emission band versus the oligomer generation for (a) oligomers **6**, **9c**, **7c**, **10c**, **8c**; (b) *P*-oligomers **9a**, **7a**, **10a**, **8a**; (c) *DP*-oligomers **9b**, **7b**, **10b**, **8b*** (*measured in tetrahydrofuran).

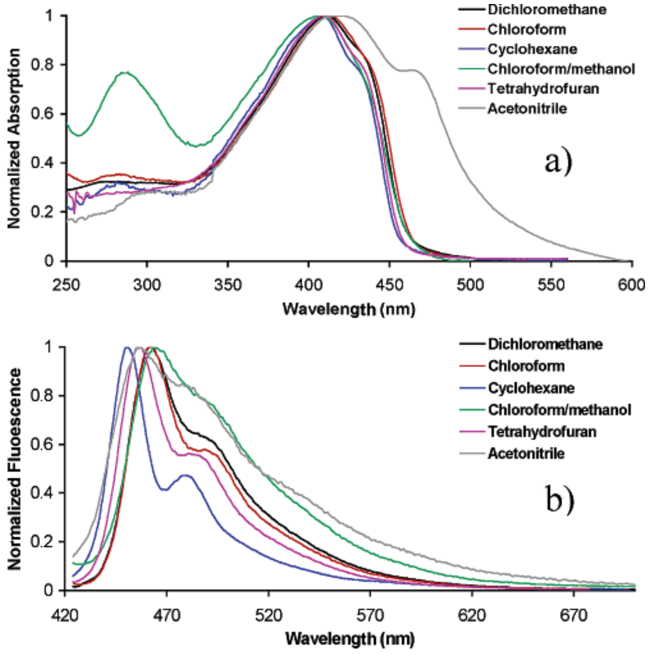

FIGURE 4. (a) Normalized absorption spectra measured at room temperature in various air-equilibrated solvents (2×10^{-5} M) for the trimer **7c**. (b) Normalized fluorescence emission spectra measured in aerated solvents (1×10^{-7} M) at room temperature for the trimer **7c**. Quantum yields measured are as follows: 43% in dichloromethane, 31% in chloroform, 20% in cyclohexane, 26% in chloroform/methanol (50/50, v/v), 39% in tetrahydrofuran, 4% in acetonitrile.

of bipy/thiophene modules increases, but it is not detrimental to the luminescence efficiency.

A confirmation of the plausibility of the involvement of a charge transfer state is found by varying the polarity of the solvent (Figure 4). By increasing the polarity of the solvent a significant bathochromic shift is found for the trimer **7c** ($\Delta\lambda_{abs} = +14$ nm), with the appearance of a new band at 463 nm in acetonitrile (Figure 4a). For the other solvents, similar spectra were observed, whereas the addition of methanol (50% v/v) in chloroform causes a hypsochromic shift ($\Delta\lambda_{abs} = -5$ nm) and a significant decrease of the intensity of the CT band. The fluorescence profiles becomes more structured and blue shifted in cyclohexane versus a mixture of chloroform and methanol. Such behavior has been previously observed for ethynylated aromatic compounds and suggests a close interaction of $\pi-\pi^*$ and charge-transfer excited singlet states.[55] Furthermore, a nice vibronic sequence was observed at room temperature in cyclohexane where the 0.0, 0.1, and 0.2 transitions in the emission spectrum are separated by ca. 1300 cm^{-1}. In addition, the presence of an emissive triplet excited state is excluded on the basis of the absence of any oxygen effect[56] in the steady-state emission quantum yields and the absence of long-lived excited state ($\tau < 2$ nanosecond). This observation is in keeping with the fact that a CT state would be more susceptible to change in the size, the polarizability and the topology of the molecular framework as in the oligomer series of compounds.

To localize the LUMO orbitals of these oligomers, cyclic voltammetry was carried out in a three-electrode cell setup with 0.1 M n-Bu$_4$PF$_6$ as a supporting electrolyte in anhydrous THF (Figure 5). All the potentials reported are referenced to Fc/Fc$^+$ standard (0.38 V versus SCE in THF), and the results are gathered in Table 1. All the oligomers are inactive in the cathodic window of the voltammograms showing the absence of thiophene oxidation in keeping with previous observations made with thiophene-based ruthenium complexes.[57,58] On the other hand, the oligomers exhibit a single reduction wave at relatively negative potential, which corresponds to the reduction of the bipyridine fragments. The reduction of the monomer is facilitated relative to unsubstituted

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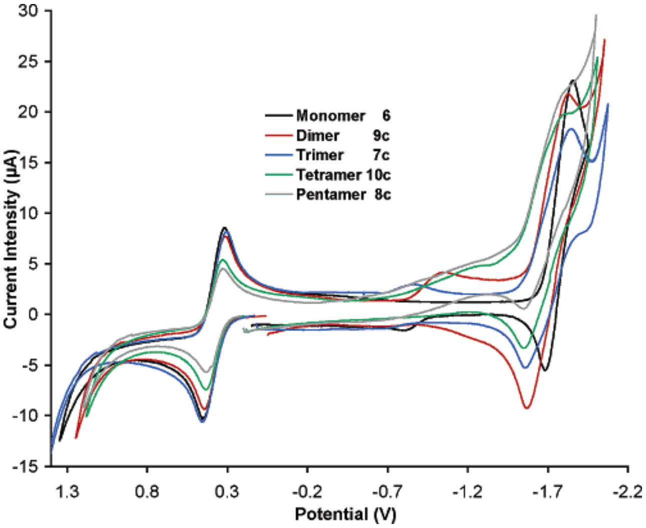

FIGURE 5. CV of the ligands series **6**, **9c**, **7c**, **10c**, and **8c** in anhydrous THF containing 0.1 M *n*-Bu_4NPF_6 under a N_2 atmosphere, scan rate 200 mV s^{-1}, Pt working electrode, reference Fc/Fc^+.

bipyridine by ca. 460 mV[59] due to the presence of two ethynyl connectors, known to behave as σ-electron withdrawing entities.[60] However, the monomer **6** is more difficult to reduce versus other oligomers, owing to the limited delocalization effect induced by the extended π system. Dimer **9c** and trimer **7c** are reduced at the same potential and are easier to reduce than the monomer by ca. 70 mV. Moreover, tetramer **10c** and pentamer **8c** are also reduced at similar potentials and are easier to reduce by ca. 27 mV than the trimer or dimer. These reductions are irreversible in the electrochemical sense and the voltammetric waves show asymmetry suggestive of the simultaneous reduction of several near-equivalent bpy centers. For these reasons, no attempt to deduce the number of exchanged electrons has been initiated. This apparently weak coupling of the bpy units is consistent with the attenuation of the red shift in the absorption and emission spectra within the series of oligomers. Similar observations were made for the *D* and *DP* series of oligomers (Figures S5 and S6, Supporting Information). Calculated LUMO values for all these compounds lies in the −3.06 eV for the monomer **6** to −3.18 eV for the *P*-pentamer **8a**.[61]

Conclusion

The present work describes a logical and convenient synthetic protocol for the construction of quasilinear polybipyridine ligands. Each chelating frame is connected to two 2,5-diethynyl-3,4-dibutylthiophene units. To prepare the key building block **4** bearing a reactive iodothiophene and a TES-protected acetylene function, two dissimilar acetylene precursors with different polarities were selected in order to allow a facile separation of the compounds by chromatography. An overall yield of 21% was obtained for the preparation of compound **4**. This is a key compound for the tailoring of the larger architectures, allowing the preparation of linear ligands with an odd number of bpy units by sequential deprotection−coupling steps. It may also be used for the synthesis of ligands with an even number of bpy units by Pd-promoted cross coupling with a 3,4-dibutylthiophene symmetrically substituted with two bpy units. The good yields obtained for the syntheses of these extended ligands underline the versatility of the synthetic protocol. It is anticipated that this procedure will be useful for the synthesis of larger systems because only slightly decreasing yields have been detected as a function of chain length for the various compounds obtained so far.

The ligands bearing one to five chelating centers are of nanometric dimensions and lie within the range of 2.2 to 7.4 nm, taking into account the edge-to-edge distance between the two external thiophene rings. Spectrophotometric studies have revealed that, by increasing the number of π-electrons from 24 to 104, a significant bathochromic shift occurs for the absorption and emission maxima. This effect is attenuated upon increasing the number of chelating sites. This saturation effect of the effective conjugation length (ECL) which originates from π-electron confinement related to structural factors such as rotational disorder or resonance stabilization energy has previously been found in related π-conjugated oligomers based on thiophene,[62] triacetylene,[63] phenylenevinylene,[64] phenyleneethynylene,[65] and thiopheneethynylene.[66] All ligands fluoresce strongly in solution at room temperature likely from localized charge transfer states when excited in the less energetic absorption band, with the fluorescence quantum yield increasing from 31 to 43% with increased molecular length. These results are interesting compared to previous series of related compounds bearing 1,4-diethynyl-2,3-didodecyloxybenzene spacers where the fluorescence quantum yield progressively increase from a few percent to a maximum value of 31% for five bipyridine units.[54] Also worth noting is the continuous decrease of the fluorescence quantum yield from 30% to a few percent by increasing the number of 2,5-diethynyl-3,4-dibutylthiophene subunits from one to five in the spacer spanning back-to-back terpyridine ligands.[39a] It is surmised that in the present series of polybipyridine ligands the fluorescence quantum yield is kept constant due to the absence of dissymmetry along the main molecular axis. The fact that each bipyridine subunits is bridged and end-capped by identical 3,4-dibutylthiophene units is certainly at the origin of the observed phenomenon and in keeping with charge transfer states localized at very close energy.

The first reduction potential (or LUMO level) of the oligomers does not change significantly along the series of oligomers. The thermal and photostabilities of these rigid-rod platforms make them attractive for the engi-

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neering of luminophoric d^8-transition metal centers where each metallic dot might act as a relay station in a photon shuttling processes. The whole array might be expected to operate as an artificial photon-harvesting system. The dibutyl fragment's ability to markedly increase solubility and the presence of thiophene subunits are additional tools for micromanipulation.

Experimental Section

5-(3-Hydroxy-3-methylbutynyl)-5′-(trimethylsilyl)-ethynyl-2,2′-bipyridine (1a). To a solution of 5,5′-dibromo-2,2′-bipyridine (1.00 g, 3.18 mmol) in a mixture of THF (80 mL) and diisopropylamine (15 mL) were added $Pd(PPh_3)_2Cl_2$[67] (223 mg, 0.32 mmol) and CuI (63 mg, 0.32 mmol). The solution was argon-degassed for 30 min. The trimethylsilylacetylene (344 mg, 3.50 mmol) was then added, and after 4 h, the 2-methylbutyn-3-yn-2-ol (535 mg, 6.36 mmol) was added. The solution was stirred overnight at room temperature, and then the solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water and then brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina, eluting with dichloromethane−hexane (v/v 20/80) to dichloromethane to give 340 mg (33%) of **1a** as a white solid: mp 83−85 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.71 (m, 2H), 8.35 (m, 2H), 7.83 (m, 2H), 2.58 (s, 1H), 1.63 (s, 6H), 0.27 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.1, 152.1, 151.7, 139.8, 139.5, 120.7, 120.5, 120.4, 120.0, 101.7, 99.5, 98.4, 79.1, 65.6, 31.4, −0.1; IR (KBr, cm^{-1}): 3535, 2981, 2893, 2158, 2072, 1637, 1589, 1531, 1460; FAB$^+$ *m/z* (nature of the peak, relative intensity) 335.1 ($[M + H]^+$, 100), 261.2 ($[M - TMS]^+$, 15). Anal. Calcd for $C_{20}H_{22}N_2OSi$: C, 71.82; H, 6.63; N, 8.38. Found: C, 71.60; H, 6.31; N, 8.20.

5-Ethynyl-5′-(trimethylsilyl)ethynyl-2,2′-bipyridine (2a). To a solution of **1a** (910 mg, 2.81 mmol) in anhydrous toluene (50 mL) was added sodium hydroxide (124 mg, 3.10 mmol). The mixture was refluxed (130 °C) for 5 h. The solvent was removed by rotary evaporation. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water and then brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane to give 660 mg (88%) of **2a** as a white solid: mp 93−95 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.73 (m, 2H), 8.36 (m, 2H), 7.87 (m, 2H), 3.30 (s, 1H), 0.28 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.5, 154.0, 152.2, 152.0, 139.9, 139.7, 120.5, 120.4, 119.2, 101.8, 99.4, 81.6, 80.6, −0.2; IR (KBr, cm^{-1}) 3300, 3053, 2936, 2159, 2109, 1638, 1588, 1532, 1458; FAB$^+$ *m/z* (nature of the peak, relative intensity) 277.1 ($[M + H]^+$, 100), 203.2 ($[M - TMS]^+$, 20). Anal. Calcd for $C_{17}H_{16}N_2Si$: C, 73.87; H, 5.83; N, 10.13. Found: C, 73.71; H, 5.78; N, 10.10.

5-[(3,4-Dibutylthien-2-yl)ethynyl]-5′-(triethylsilyl)ethynyl-2,2′-bipyridine (3b). A Schlenk flask was charged with **2b** (382 mg, 1.20 mmol), 3,4-dibutyl-2-iodothiophene (425 mg, 1.32 mmol), $Pd(PPh_3)_4$[68] (83 mg, 0.07 mmol), and finally with argon-degassed benzene (20 mL) and triethylamine (5 mL). The yellow solution was heated at 60 °C until complete consumption of the starting material (determined by TLC), and then the solvent was evaporated under vacuum. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water and then brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina, eluting with dichloromethane−hexane (v/v 10/90) to give 528 mg (86%) of **3b** as a yellow viscous liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.73 (m, 2H), 8.39 (m, 2H), 7.86 (m, 2H), 6.91 (s, 1H), 2.74 (m, 2H), 2.53 (m, 2H), 1.50 (m, 8H), 1.03 (m, 9H), 0.96 (m, 6H), 0.70 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.2, 153.8, 152.2, 151.2, 147.9, 142.2, 139.7, 138.7, 122.3, 120.8, 120.6, 120.4, 120.3, 117.8, 103.1, 97.1, 91.8, 87.9, 32.2, 31.9, 28.7, 28.0, 22.7, 22.6, 14.0, 13.9, 7.5, 4.3; IR (KBr, cm^{-1}) 3048, 2956, 2931, 2873, 2858, 2200, 2156, 1630, 1587, 1529, 1463; FAB$^+$ *m/z* (nature of the peak, relative intensity) 513.2 ($[M + H]^+$, 100), 397.2 ($[M - TES]^+$, 10). Anal. Calcd for $C_{32}H_{40}N_2SSi$: C, 74.95; H, 7.86; N, 5.46. Found: C, 74.75; H, 7.61; N, 5.24.

5-[(3,4-Dibutyl-5-iodothien-2-yl)ethynyl]-5′-(triethylsilyl)ethynyl-2,2′-bipyridine (4). To a solution of diisopropylamine (76 mg, 0.75 mmol) in THF (2 mL) at −78 °C was added dropwise *n*-butyllithium (0.45 mL, 0.63 mmol, 1.53 M in hexanes). After 15 min, **3b** (176 mg, 0.34 mmol) in THF (1.5 mL) was added dropwise via a cannula; the solution turned dark green. Still at −78 °C, NIS (110 mg, 0.49 mmol) in THF (1.5 mL) was added dropwise via a cannula. The decolorization was instantaneous. The mixture was quenched with a saturated solution of NH_4Cl. The aqueous layer was extracted with dichloromethane. The organic extracts were washed with water and then brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina, eluting with hexane−dichloromethane−ethyl acetate (v/v 98.4/0.8/0.8) to give 175 mg (80%) of **4** as a brownish viscous liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.73 (m, 2H), 8.39 (m, 2H), 7.88 (m, 1H), 7.84 (m, 1H), 2.77 (m, 2H), 2.53 (m, 2H), 1.50 (m, 8H), 1.06 (m, 9H), 0.97 (m, 6H), 0.71 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.9, 153.8, 152.0, 151.0, 147.1, 146.1, 139.5, 138.4, 123.1, 120.5, 120.3, 120.2, 103.0, 96.9, 93.6, 86.7, 77.4, 32.4, 31.8, 30.7, 28.7, 22.6, 22.6, 13.9, 13.8, 7.4, 4.3; IR (KBr, cm^{-1}) 2956, 2930, 2873, 2858, 2198, 2157, 1619, 1587, 1530, 1462, 1403; FAB$^+$ *m/z* (nature of the peak, relative intensity) 639.1 ($[M + H]^+$, 100), 523.1 ($[M - TES]^+$, 20). Anal. Calcd for $C_{32}H_{39}IN_2SSi$: C, 60.17; H, 6.15; N, 4.39. Found: C, 59.81; H, 5.82; N, 4.06.

5-[(3,4-Dibutyl-5-iodothien-2-yl)ethynyl]-5′-(trimethylsilyl)ethynyl-2,2′-bipyridine (5a). To a solution of diisopropylamine (51 mg, 0.50 mmol) in THF (1 mL) at −78 °C was added dropwise *n*-butyllithium (0.30 mL, 0.23 mmol, 1.66 M in hexanes). The solution was warmed to 0 °C for 10 min and then recooled to −78 °C. Compound **3a** (153 mg, 0.33 mmol) was then added dropwise via a cannula, and the solution was stirred at −30 °C for 1 h. The solution was then recooled to −78 °C and stirred for 30 min. Iodine (124 mg, 0.49 mmol) was added to the solution as a solid. The mixture was stirred at −78 °C for 1 h and quenched with a saturated solution of NH_4Cl. The aqueous layer was extracted with dichloromethane. The organic extracts were washed with a saturated solution of sodium thiosulfate, water, and then brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography on alumina, eluting with dichloromethane−hexane (v/v 7/93) to give 50 mg (26%) of **5a** as a brown viscous liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.73 (m, 2H), 8.39 (m, 2H), 7.88 (m, 1H), 7.84 (m, 1H), 2.77 (m, 2H), 2.53 (m, 2H), 1.50 (m, 8H), 0.97 (m, 6H), 0.29 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.2, 154.0, 152.1, 151.2, 147.3, 146.3, 139.8, 138.7, 123.1, 120.7, 120.4, 120.3, 101.8, 99.5, 93.6, 86.8, 77.4, 32.5, 32.0, 30.7, 28.9, 22.8, 22.7, 14.1, 13.9, −0.1; IR (KBr, cm^{-1}) 2956, 2932, 2875, 2854, 2196, 2162, 1623, 1587, 1538, 1462, 1408; FAB$^+$ *m/z* (nature of the peak, relative intensity) 597.1 ($[M + H]^+$, 100), 523.0 ($[M - TMS]^+$, 25). Anal. Calcd for $C_{29}H_{33}IN_2SSi$: C, 58.38; H, 5.57; N, 4.70. Found: C, 58.09; H, 5.38; N, 4.48.

5-[(3,4-Dibutyl-5-trimethylsilylthien-2-yl)ethynyl]-5′-(trimethylsilyl)ethynyl-2,2′-bipyridine (5b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.73 (m, 2H), 8.39 (m, 2H), 7.87 (m, 1H), 7.85 (m, 1H), 2.72 (m, 2H), 2.60 (m, 2H), 1.64 (m, 4H), 1.45 (m, 4H), 1.06 (m, 9H), 0.97 (m, 6H), 0.36 (s, 9H), 0.29 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.3, 153.8, 152.1, 151.2, 149.7,

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149.1, 139.8 138.7, 137.1, 122.3, 121.0, 120.7, 120.4, 120.3, 101.9, 99.4, 92.9, 88.0, 34.2, 32.8, 29.7, 29.4, 23.2, 23.0, 14.1, 14.0, 1.0, 0.4; IR (KBr, cm^{-1}) 2957, 2925, 2854, 2198, 2159, 1622, 1587, 1530, 1460; FAB$^+$ *m/z* (nature of the peak, relative intensity) 543.3 ([M + H]$^+$, 100). Anal. Calcd for $C_{32}H_{42}N_2SSi_2$: C, 70.79; H, 7.80; N, 5.16. Found: C, 70.52; H, 7.63; N, 5.00.

5,5′-Bis[[3,4-dibutyl-5-[(5′-ethynyl-2,2′-bipyridin-5-yl)ethynyl]thien-2-yl]ethynyl]-2,2′-bipyridine (7b). To a solution of **7a** (385 mg, 0.31 mmol) in THF (20 mL) and methanol (20 mL) was added K_2CO_3 (434 mg, 3.14 mmol) as a solid. The mixture was stirred at room temperature until the complete consumption of the starting material (determined by TLC), and then the solvent was evaporated under vacuum. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water and then brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by chromatography (alumina, hexane−dichloromethane) to give in 90% yield **7b** as a orange solid: mp >265 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.77 (m, 6H), 8.56 (m, 6H), 7.91 (m, 6H), 3.31 (s, 2H), 2.75 (m, 8H), 1.54 (m, 16H), 0.99 (m, 12H); IR (KBr, cm^{-1}) 3045, 2952, 2926, 2871, 2857, 2200, 2100, 1638, 1526, 1461; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}) 269 (65 000), 410 (165 000); FAB$^+$ *m/z* (nature of the peak, relative intensity) 997.2 ([M + H]$^+$, 100). Anal. Calcd for $C_{66}H_{56}N_6S_2$: C, 79.48; H, 5.66; N, 8.43. Found: C, 79.37; H, 5.52; N, 8.38.

5,5′-Bis[[3,4-dibutyl-5-[[5′-[[3,4-dibutyl-5-[(5′-ethynyl-2,2′-bipyridin-5-yl)ethynyl]thien-2-yl]ethynyl]-2,2′-bipyridin-5-yl]ethynyl]thien-2-yl]ethynyl]-2,2′-bipyridine (8b). To a solution of **8a** (147 mg, 0.07 mmol) in 50 mL of THF and 4 mL of methanol was added KF (42 mg, 0.72 mmol) as a solid. The mixture was stirred at room temperature until the complete consumption of the starting material (determined by TLC). The solvent was partially evaporated, and the precipitate was centrifuged to give 108 mg (83%) of **8b** as a dark orange solid: mp >265 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.78 (m, 10H), 8.42 (m, 10H), 7.91 (m, 10H), 3.31 (s, 2H), 2.75 (m, 16H), 1.52 (m, 32H), 0.99 (m, 24H); UV−vis (THF) λ nm (ϵ, M^{-1} cm^{-1}) 419 (310 000); IR (KBr, cm^{-1}) 3042, 2953, 2926, 2870, 2856, 2194, 2110, 1636, 1586, 1529, 1460; FAB$^+$ *m/z* (nature of the peak, relative intensity) 1790.2 ([M + H]$^+$, 100). Anal. Calcd for $C_{118}H_{104}N_{10}S_4$: C, 79.16; H, 5.82; N, 7.82. Found: C, 78.83; H, 5.49; N, 7.64.

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Supporting Information Available: Experimental procedures and characterization data for the new compounds **1b**, **2b**, **3a**, **6**, **7a**,**c**, **8a**,**c**, **9a**−**c**, and **10a**−**c**; excitation spectra for the dimer series **9a**−**c**, the trimer series **7a**−**c**, the tetramer series **10a**−**c**, and the pentamer series **8a**−**c** (Figures S1−S4); cyclic voltammograms for the protected and deprotected series of compounds (Figures S5 and S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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