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A Concise Modular Synthesis of 2,5-Diethynyl-3,4-dibutyl-thiophene-Bridged Back-to-Back Terpyridine Ligands

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The efficient synthesis of soluble and rigid terpyridine-based ditopic ligands bearing an increasing number of 2,5-diethynyl-3,4-dibutylthiophene (DEDBT) modules has demonstrated the advantages of a single convergent strategy based on a double coupling in a final step of monoterpyridine building blocks carrying the adequate number of thiophene modules with a diiodo-substituted thiophene subunit. This protocol enjoys the advantages of both efficiency and versatility and requires pivotal intermediates, which were produced by a step-by-step implementation of monoterpyridine fragments with a key thiophene intermediate carrying an iodo function, a propargylic-protecting group, and two butyl-solubilizing fragments. One set of experimental conditions is required to produce all the intermediates and the final ligands. Oxidative dimerization of monosubstituted terpyridine skeletons bearing one or two thiophene substituents and a terminal alkyne function, in the presence of cupric salts and oxygen, afforded the homotopic ligands with a central dithienylbutadiyne spacer. Optical properties for the new oligomers have been investigated and are discussed in terms of effective conjugation length and π-electron conjugation. Upon increasing the number of interspersed DEDBT units, a significant lowering in energy of absorption and fluorescence transitions as well as of the quantum yields is observed.

Introduction

The optical properties of compounds containing d^6 transition metals, particularly those based on ruthenium(II), osmium(II), and rhenium(I), continue to attract a widespread interest because of their potential applications in diverse areas such as solar energy conversion,[1] luminescence sensing,[2] electroluminescence displays,[3] biotechnology,[4] molecular machines,[5] and molecular electronics.[6] Despite these special features, in many cases the photoluminescence and the target property depend on both the way the ligands are engineered and how various components are interlocked around the metal centers. Particularly attractive are artificial systems where photoinduced energy transfer can be realized over large distances and in preferred directions and those where the tethering of suitable polyaromatic fragments results in a spectacular increase in the excited-state lifetime. Because these photochemical characteristics are ultimately governed by the topology of the ligands, their fabrication hinges on the tailoring of productive molecular architectons, which enable the step-by-step construction of the target molecules. The use of well-defined materials makes it easier to establish firm structure−property relationships. For this purpose, significant efforts have been devoted to the engineering of artificial multicomponent arrays with a particular emphasis on those involving terpyridine complexes.[7]

Most noteworthy among them are the donor−acceptor complexes based on polyethynyl-bis-terpyridine ligands where extremely fast electron exchange has been observed taking place along the alkynylene bridges, with the rate of transfer being almost insensitive to the length of the spacer.[8] The alkynyl connectors are particularly

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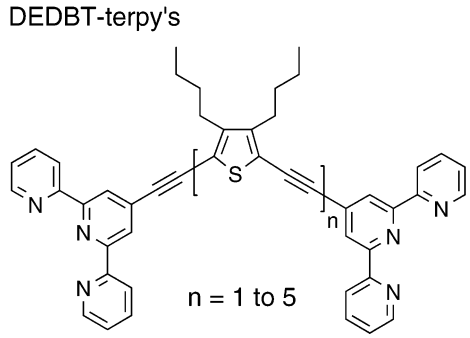
serviceable driving forces to decrease significantly the LUMO level of the spacer because of their pronounced σ-withdrawing character and their ease of tailoring.[9] This is especially true when the connection is united in the para position of the central pyridine ring of a terpyridine template.[10] We recently discovered that the use of a central thiophene unit in such ditopic ligands is resistant to attack by singlet molecular oxygen and improves electronic communication between terminal chromophores at the triplet level.[11] The related dinuclear complexes possess significantly better photophysical properties than are exhibited by other complexes.[12] Critical comparison with the corresponding 1,4-diethynylated-phenylene-bridged complexes shows that the central thiophene fragment provides for improved stabilization of the triplet state. This very interesting behavior is interpreted in terms of the relative ability of the ligand to adopt cumulene-type structures.[11] Prior to this work, the use of oligothiophenethynylene for the construction of cyclic nanoarrays[13,14] and larger quasi-linear molecules capped by various stoppers has been elegantly documented.[15,16] Thiophene-based functional polymers have also attracted significant attention because of their application as conductive and active layers in OLEDs.[17] On the basis of a thorough understanding of structure−property relationships and the ingenuity of synthetic chemists, color tunability, quantum efficiencies, and stability have been achieved.[18]

Surprisingly, up to now only the backbone of the thiophene polymer has been modified, but it has not been further modified with chromophoric subunits. However, very recently poly(3-octylthiophene) alternating with Ru− and Os−bipyridine complexes has been studied.[19,20] The progressive implementation of an increasing number of diethynyldibutyl−thiophene modules will allow scientists to study the influence of the length on the rate of triplet energy or electron transfer. This piece of information expressed as an attenuation factor is especially critical if larger systems are envisaged. To scrutinize subtle differences in electronic effects between polyphenyl and thiophene units, a novel family of bis-terpyridine-bridged ligands has been designed in which it is anticipated that these molecules retain both structural integrity and topological rigidity during the study of energetic information transfer. We wish to present here a new class of rigid ligands which, by virtue of their concise and flexible synthesis and their photophysical properties, are promising candidates as effective molecular-scale wires (Chart 1).

CHART 1



Results and Discussion

A single synthetic approach to α-conjugated 2,5-diethynyl-3,4-dibutylthiophene (DEDBT)-terpy's oligomers could be envisaged. The strategy is reported in the synthetic Scheme 1 and clearly distinguishes two main pathways depending of the presence of an odd or even number of thiophene modules but also highlights the need for pivotal monoterpy intermediates. In the first case, direct coupling between a terpy fragment bearing one or two ethynylthiophene fragments or a single ethynyl function with a diiodo-substituted dibutylthiophene would provide the back-to-back terpy ligands with respectively $n = 5$, 3, and 1 modules. For the ligands with an even number of modules, cross-coupling of the 4′-ethynylthienyl-terpy or 4′-ethynyl-terpy with an acetylene-bridged diiododithiophene would afford, respectively, the ligands with $n = 4$ and 2 modules. The key intermediate depicted in the inset of Scheme 1 would be produced by an iterative sequence of reaction involving a step-by-step implementation of the diethynylthiophene fragment and a deprotection reaction. The first molecule would be produced by a cross-coupling reaction of 4′-ethynyl-terpy with the tetrasubstituted thiophene derivative bearing two solubilizing chains (butyl), one protecting group (propargylic alcohol), and one reactive iodo function (Scheme 1).

To achieve these syntheses, key building blocks have to be designed to harness the beneficial solubility and electronic attributes of both dibutylthiophene and alkynyl connectors. A crucial role is played by mono- and disubstituted iodothiophene derivatives. Besides contributing one or two leaving groups, these compounds bear two alkyl chains, which are needed to increase the solubility of the final product. The butyl groups have been preferred over longer paraffinic chains because they afford better yields during the synthesis of the precursors.[21] The straightforward route leading to these pivotal derivatives is reported in Scheme 2. The commercially available 3,4-dibromothiophene **1** was converted into the corresponding 3,4-dibutylthiophene derivative **2** via a Kumada alkylation catalyzed by a nickel(II) complex.[21] This compound was subjected to reaction with iodine and mercury oxide,

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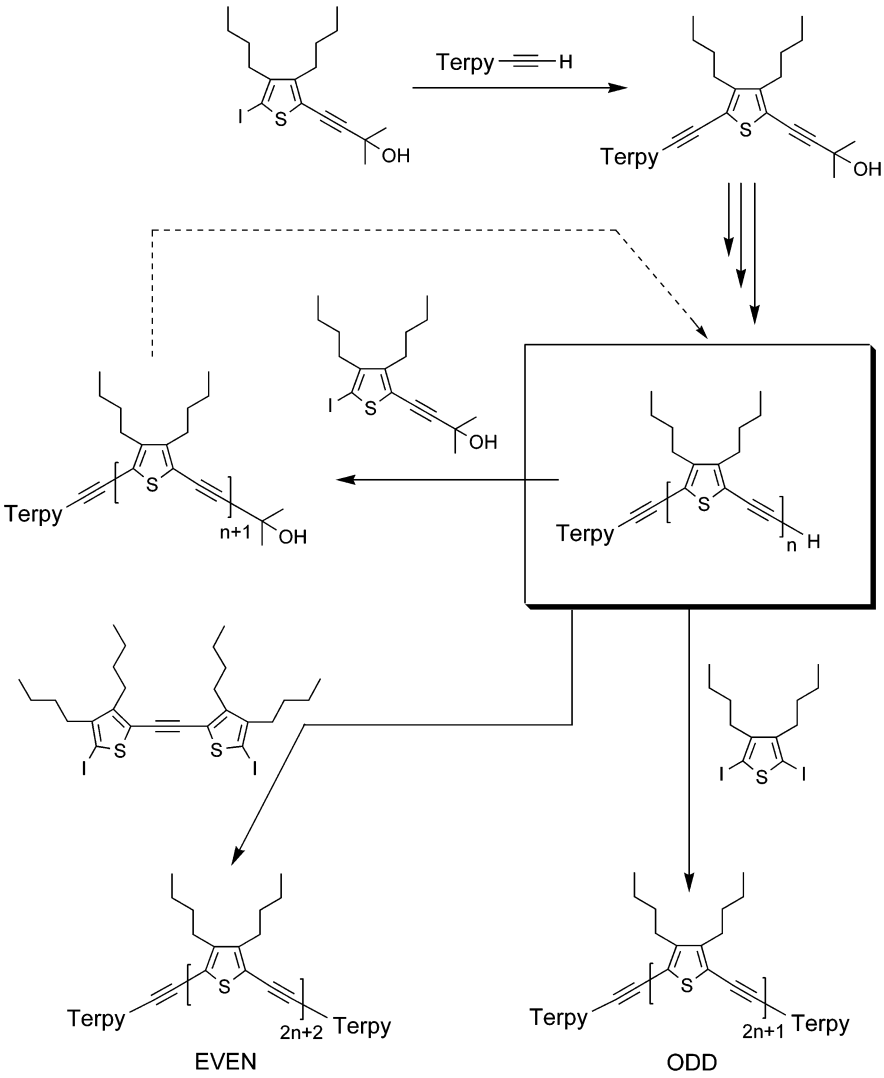
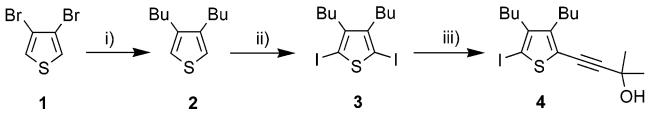
SCHEME 1



SCHEME 2[a]



[a] (i) *n*-BuMgBr, Ni(dppp)Cl_2, Et_2O, rt, 92%; (ii) I_2, HgO, CH_2Cl_2/toluene, rt, 93%; (iii) HC≡$CCMe_2OH$, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 45%.

leading to **3** by adopting a procedure reported by Minnis.[22] Monosubstitution of one iodo function of **3** with propargylic alcohol giving derivative **4** was achieved in 45% isolated yield, using a slight excess of the starting material under mild conditions. The side product resulting from a double substitution was isolated in less than 10%, and the starting material **3** could be recovered (35%) and recycled. Compound **4** was connected to 4′-ethynylterpy **5** via a Sonogashira−Hagihara reaction promoted by low-valent palladium complexes, affording compound **6a** in good yield (Scheme 3).[23] Deprotection giving rise to **6b** was performed in refluxing toluene under basic conditions. With these building blocks in hand, it was readily possible to apply the synthetic protocol outlined in Scheme 1. The synthetic protocol consists of cross-coupling derivative **5** with 2,5-diiodo-3,4-dibutylthiophene **3** in a "one pot" procedure leading to the ditopic ligand **7** with $n = 1$. Similarly, reacting ligand **6b** with **3** provided ligand **8** with $n = 3$ in fair yield.

The extension of the conjugated system present in larger molecules, such as in ligand **11** with $n = 2$ or in ligand **12** with $n = 5$, was carried out according to the retrosynthetic Scheme 1 by using a homologation reaction between derivatives **6b** and **4**, leading to compound **9a** (Scheme 4). Compound **9b** was readily prepared in conditions similar to those used for the previous deprotection. This iterative homologation process was applied to the third generation of building blocks, leading to derivative **10**. At this stage, it should be noticed that, by increasing the number of modules, the chromatographic separation between the unreacted starting material and the target compounds was becoming tedious because of the increase in lipophilicity imposed by the increasing number of the butyl chains. Indeed, we were unable to purify the analogue of compound **10** with four and five thiophene-based modules. Furthermore, when the num-

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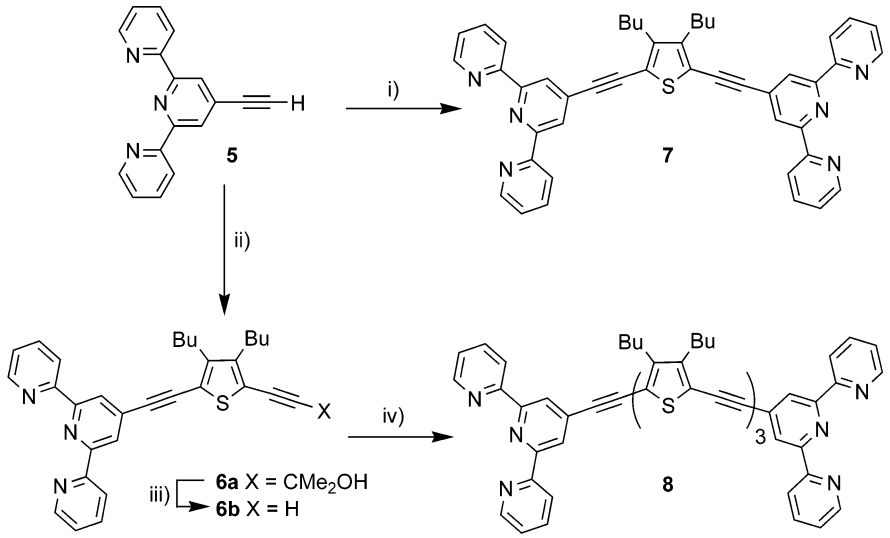
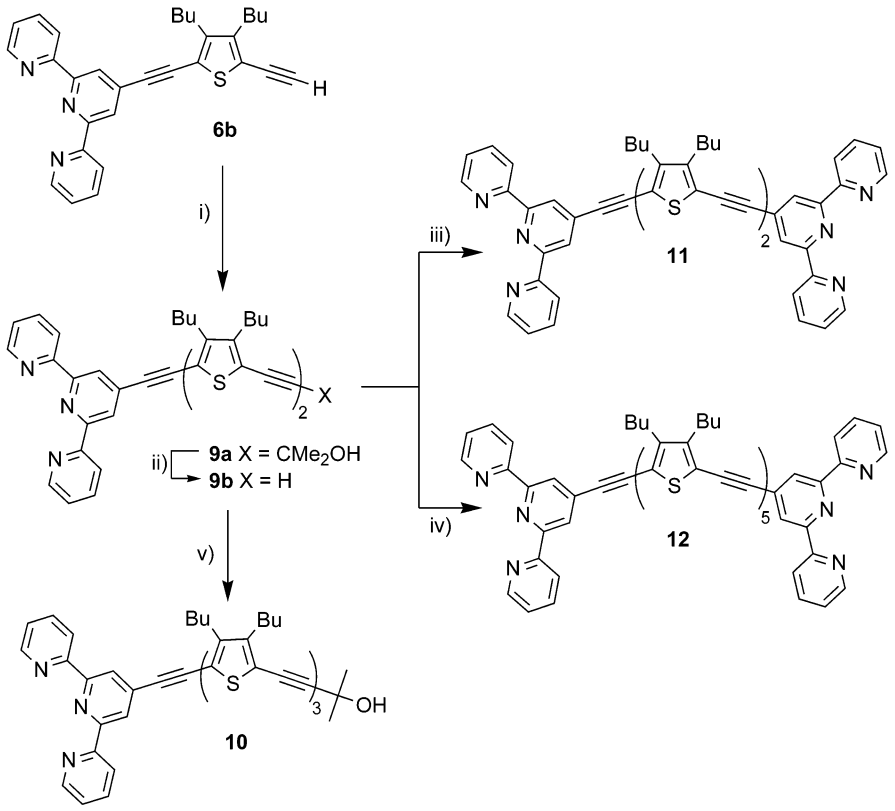
SCHEME 3[a]



[a] (i) **3**, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 72%; (ii) **4**, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 82%; (iii) KOH, toluene, reflux, 97%; (iv) **3**, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 84%.

SCHEME 4[a]



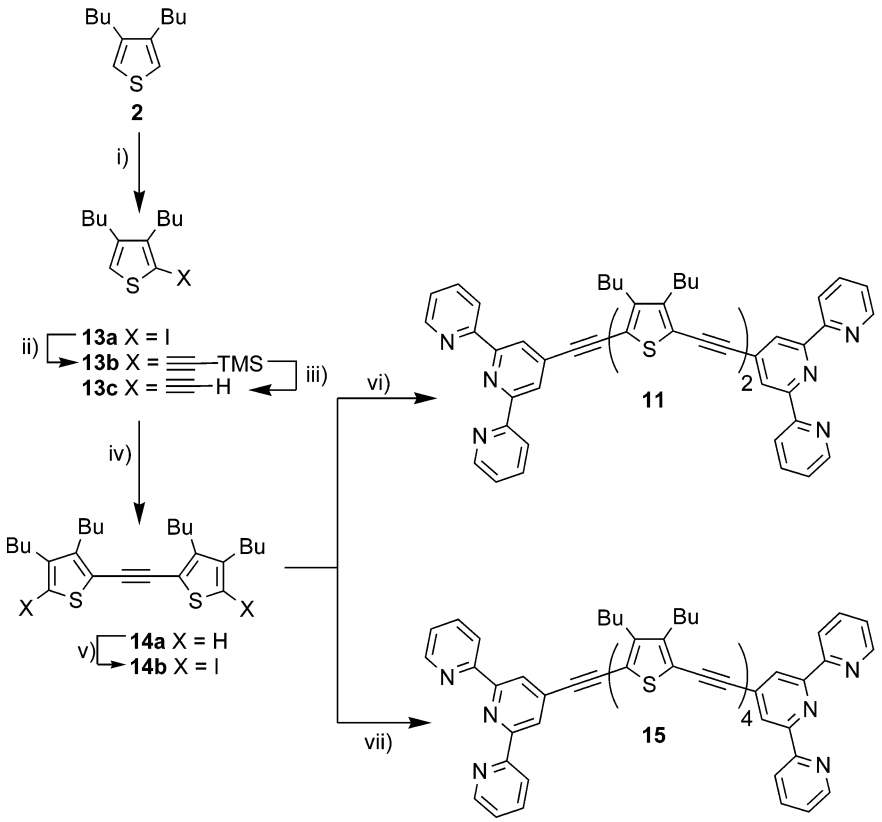
[a] (i) **4**, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 90%; (ii) KOH, toluene, reflux, 86%; (iii) terpy-OTf, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 60%; (iv) **3**, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 73%; (v) **4**, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 48%.

ber of DEDBT modules was increasing, the deprotection step required drastic conditions ($T > 130$ °C), which also favored the decomposition of the samples. It is worth noting that ligand **11** with $n = 2$ could be prepared in 60% yield at the early stage of this program by cross-coupling derivative **9b** with terpy-OTf[24] in the presence of low-valent palladium(0) complexes (Scheme 4). Furthermore, the synthesis of ligand **12** with $n = 5$ was achieved in 73% yield by cross-coupling derivatives **9b** with **3** under similar conditions.

According to the retrosynthetic analysis and to the fact that the preparation of the building block with four diethynylthiophene modules failed, the construction of ligand **15** with $n = 4$ was undertaken with the acetylene-

(24) Potts, K. T.; Konwar, D. *J. Org. Chem.* **1991**, *56*, 4815.

SCHEME 5[a]



[a] (i) HgO, I_2, benzene, rt, 21%; (ii) HC≡CTMS, $PdCl_2(PPh_3)_2$, CuI, THF, rt, 98%; (iii) K_2CO_3, MeOH, rt, 94%; (iv) **14a**, $PdCl_2(PPh_3)_2$, CuI, THF, rt, 80%; (v) LDA, I_2, THF, −78 °C, 89%; (vi) **5**, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 55%; (vii) **6b**, $Pd(PPh_3)_4$, *n*-$PrNH_2$, 60 °C, 58%.

bridged starting material **14b** (Scheme 5). The preparation of this synthon started from 2-iodo-3,4-dibutylthiophene **13a**, which was prepared by iodation of **2** with iodine and mercury salts, followed by a combination of careful chromatography and fractional distillation.[25] Compound **13a** was subjected to a coupling reaction with trimethylsilylacetylene in the presence of palladium complexes, affording after deprotection and under weakly basic conditions the corresponding derivative **13c**. The latter was allowed to react with **13a** to provide with good yield the acetylene-bridged thiophene molecule **14a**. Deprotonation of **14a** at low temperature, followed by reaction with iodine, afforded compound **14b** in excellent yield. Finally, the reaction reported in Scheme 5 highlights an additional feature of our strategy. Indeed, by double cross-coupling of derivatives **14b** with **6b**, the preparation of oligomer **15** with $n = 4$ modules was possible. It is worth noting that this convergent approach is further emphasized by conversion of **14b** with 2 equiv of the 4′-ethynyl-terpy **5**, leading to ligand **11** with $n = 2$. This latter compound has already been described in Scheme 4 using a variation of our synthetic protocol.

Finally, it has previously been observed that the construction of ligands and complexes bearing a central butadiyne fragment allows high-fluorescence quantum yields and long-lived excited states to be obtained because of a better blending of the orbitals along the linear backbone.[26,27] Therefore, we prepared with very good yields from building blocks **6b** and **9b** the corresponding ditopic ligands **16** and **17** (Scheme 6). The best experimental conditions we found for this oxidative homocoupling reaction is the use of cupric salts in oxygenated DMF solutions. This reaction is efficient in the absence of additional *N*,*N*,*N*′,*N*′-tetramethylethylenediamine usually required in similar reactions.[28,29]

Optical Properties. The electronic spectra were measured under ambient conditions, and solvent for spectroscopy was used as received. The most striking findings are gathered in Figures 1−3 and Table 1. We first studied the monosubstituted terpyridine derivatives **6a** ($n = 1$), **9a** ($n = 2$), and **10** ($n = 3$). The absorption spectra display a quasi-symmetrical band at 280 nm and an unsymmetrical band at lower energy: 367 ($n = 1$), 392 ($n = 2$), and 410 nm ($n = 3$), respectively, at ca. 3.01, 2.82, and 2.70 eV, attributed to $\pi-\pi^*$ transitions (not to $n-\pi$ transitions).[30] These absorption bands are bathochromically shifted with respect to λ_{abs} of 4-ethynylterpyridine (λ_{max} at 326 nm, ca. 3.39 eV).[27] By increasing the number of DEDBT modules, the less-energetic absorption band is red-shifted (Figure 1a), whereas the molar absorption coefficient remained almost constant within the margins of error for **6a**, **9a**, and **10**, showing

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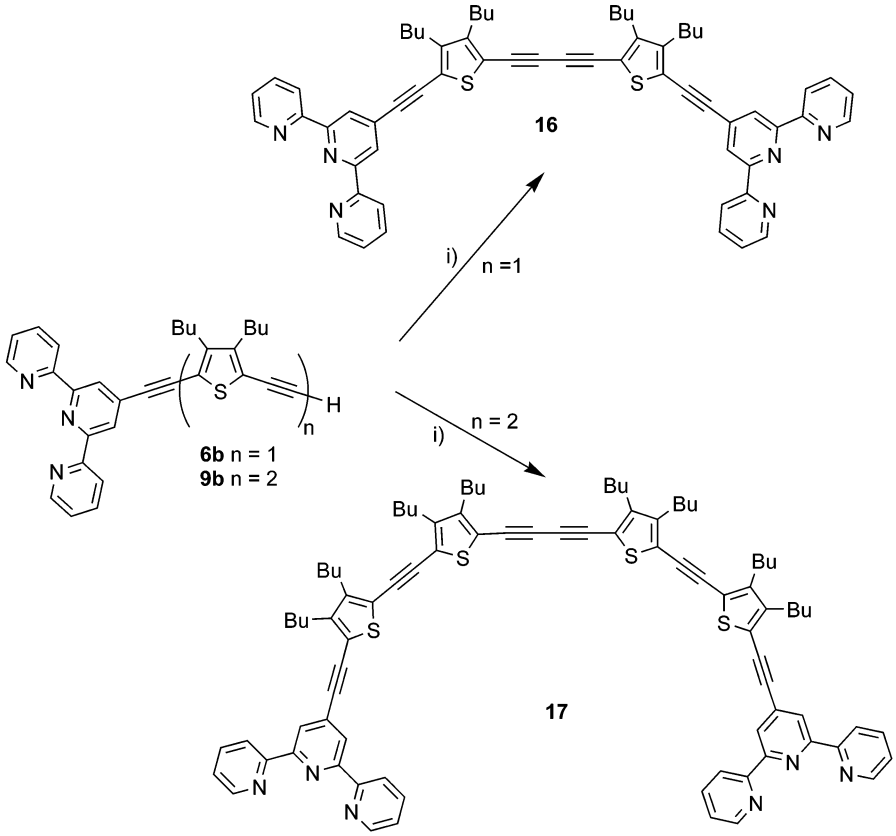
SCHEME 6[a]



[a] (i) CuCl, $CuCl_2$, O_2, DMF, rt, compd **16**: 82%, compd **17**: 60%.

a relatively weak contribution of the thiophene fragment to the global absorption (Table 1). All three compounds are luminescent in solution at room temperature, with fluorescence maxima progressively shifted by 50 and 25 nm respectively for **9a** and **10** versus the model compound **6a** (Figure 1b).

As anticipated by substitution of the propargylic unit with a second terpy fragment, the lowest-energy absorption band is red-shifted (Table 1). Both the λ_{abs} and λ_{em} maxima are dependent on the length of the spacer with a bathochromic shift to lower energy as the number of DEDBT moieties is extended (Figure 2a and b). This shift is more pronounced for the shorter systems with an initial step of $\Delta\lambda_{abs} = 35 \pm 2$ nm (from $n = 1$ to $n = 2$), $\Delta\lambda_{abs} = 20 \pm 2$ nm (from $n = 2$ to $n = 3$), $\Delta\lambda_{abs} = 6 \pm 2$ nm (from $n = 3$ to $n = 4$), and $\Delta\lambda_{abs} \approx 0$ nm (from $n = 4$ to $n = 5$). It is interesting to note that the absorption maximum for the longer molecules is close to that of polythiophene polymers ($\lambda_{max} \approx 450$ nm).[31] Similar trends have been observed with ethynyl−phenylene spacers with comparable substituent arrangements. These observations have accounted for an increase in steric interaction, reducing the planarity of the π systems during the increase in the size of the spacer.[32] For the series of ditopic ligands, the most energetic absorption band at ca. 280 nm remains almost unshifted. Interestingly, these highly soluble ligands exhibit strong photoluminescence with fluorescence quantum yields being measured in an undergassed dichloromethane solution (ca. 10^{-6} M) using quinine bisulfate dihydrate in 1 N H_2SO_4 solution as standard, which absorbs at 347 nm and emits at 448 nm with a known quantum yield of $\Phi_F = 0.546$.[33] The calculation of the fluorescence quantum yield of a solution sample (Φ_s), relative to the reference sample of known quantum yield (Φ_r), is given by $\Phi_s = \Phi_r[(A_r/A_s) \times (I_s/I_r)][n_s/n_r]^2$ where A_s and A_r are the absorbencies of the sample and the reference solutions, I_s and I_r are the corresponding relative integrated fluorescence intensities, and n_s and n_r are, respectively, the measured refractive indexes of dichloromethane ($n_s = 1.4224$) and 1 N H_2SO_4 ($n_r = 1.3414$) at 296 K.[34] The highest quantum yield is found for ligand **7** ($n = 1$), which has the highest oscillator strength for the corresponding absorption. Although the protected series of compounds have an almost-constant quantum efficiency of 13 to 17% (for $n =$ **6a**, **9a**, and **10**), a very significant decrease was found for the elongated oligomers (30% for ligand **7**, $n = 1$, to 7% for ligand **12**, $n = 5$). The fact that the molar extinction coefficient measured for the series of ligands remains almost constant could not account for the decrease of the quantum yield. It is likely that the strong reduction in the fluorescence quantum yield is due to the dynamic motion of the spacer, which might facilitate nonradiative deactivation of the excited states.[35] Another noteworthy feature in the optical properties is the relative

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TABLE 1. Photophysical Properties of the Thiophene-Substituted Terpyridine Ligands[a]

compd	λ_{max} (nm), ϵ (M^{-1} cm^{-1})	λ_{em} (nm)[b]	ϕ_{em} (%)[c]
6a	286 (33 300) 348 (31 400) 367 (32 000)	413	17
9a	283 (29 500) 392 (36 600) 425 (sh, 25 000)	463	15
10	286 (24 500) 410 (35 000) 459 (sh, 16 100)	488	13
7	285 (47 800) 373 (49 000) 391 (sh, 42 800)	421	30
8	284 (46 700) 428 (56 200)	492	13
11	285 (92 200) 408 (88 400) 444 (sh, 58 500)	472	9
12	279 (91 000) 433 (47 500)	510	7
15	284 (64 200) 346 (sh, 36 700) 434 (81 700)	504	9
16	279 (49 300) 399 (62 800)	466	8
17	283 (59 000) 425 (70 730)	502	7

[a] Measured in argon degassed dichloromethane at 298 K. [b] Steady-state luminescence maximum with λ_{exc} in the less energetic absorption band. [c] Measured under the steady-state conditions using quinine sulfate in 1 N H_2SO_4 as standard; estimated error is ±10%.

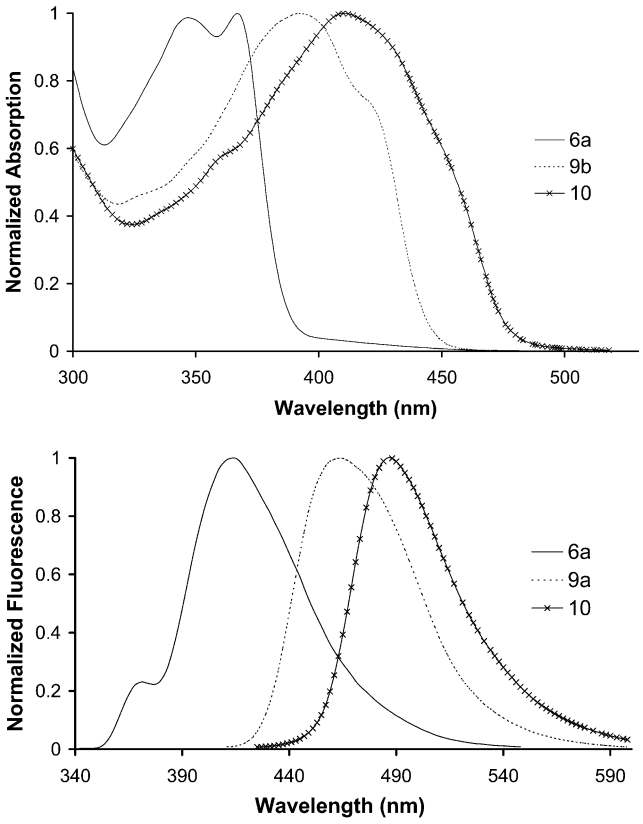

FIGURE 1. (a) Normalized absorption spectra measured in dichloromethane (1×10^{-5} M) at room temperature for **6a** ($n = 1$), **9a** ($n = 2$), and **10** ($n = 3$) where n accounts for a monoethynyldibutylthiophene module. (b) Normalized fluorescence emission spectra measured under the same conditions but using a 10-fold dilution of the solutions, all ligands were excited by irradiation in the less-energetic aborption band.

red shift of the emission maxima when the molecules become larger. A progressive decrease of $\Delta\lambda_{em}$ of 51 nm (for ligand **7**, $n = 1$, to ligand **11**, $n = 2$), $\Delta\lambda_{em}$ of 20 nm (for ligand **11**, $n = 2$ to ligand **8**, $n = 3$), and $\Delta\lambda_{em}$ of 12 nm (for ligand **8**, $n = 3$ to ligand **15**, $n = 4$) to only 6 nm (for ligand **15**, $n = 4$ to ligand **12**, $n = 5$) was found along the series. Interestingly, the emission spectrum for all ditopic ligands (Figure 2b), and to a lesser extent for the monosubstituted terpy derivatives (Figure 1b), exhibits a pronounced long-wavelength emission tail spanning above 650 nm for the larger molecules. This is probably due to a better conjugation between the terpy and the thiophene−acetylenic moieties. In most cases, the fluorescence spectra show very poor mirror symmetry with the lowest-energy absorption band, and they indeed look very different. Excitation spectra performed under similar conditions partially confirmed that the emitted light does not originate from a classical singlet excited-state $S_0 \rightarrow S_1$ transition.[36] The presence of a triplet excited state is excluded on the basis of the absence of any oxygen effect in the steady-state emission quantum yields and by the fact that very short excited-state lifetimes were measured.[37] In fact, the broad and structureless absorption bands are reminiscent of charge-transfer (CT) transitions, and it is noteworthy that these ligands contain electron-donating groups (the alkyl chain) and electron-accepting fragments such as the terpys, the acetylenic, and thiophene subunits. The latter groups promote CT along the molecular axis.

The apparent Stokes shifts from 48 nm for the shorter to 77 nm for the longer systems are in keeping for a CT state and not for a $\pi-\pi^*$ emitting state. The progressively larger Stokes shifts imply that the oligomeric backbone becomes less rigid[38,39] as the number of DEDBT modules is increased. Furthermore, all the fluorescence spectra possess a distinct shoulder or second maxima on the red side. This fine structure is more pronounced for the shorter systems (for ligand **7**, $n = 1$, and for ligand **16**) possibly due to a more favorable ongoing planarization of the conjugated backbone. Furthermore, it is not excluded that the observation of shoulders on the red side of the absorption and emission spectra could also be due to *s*-cis and *s*-trans rotamers induced by the central thiophene fragments. The 2,5-disubstituted thiophene subunits generate bent bonds, likely to give zigzag or curved dynamic conformations in solution. Some of them

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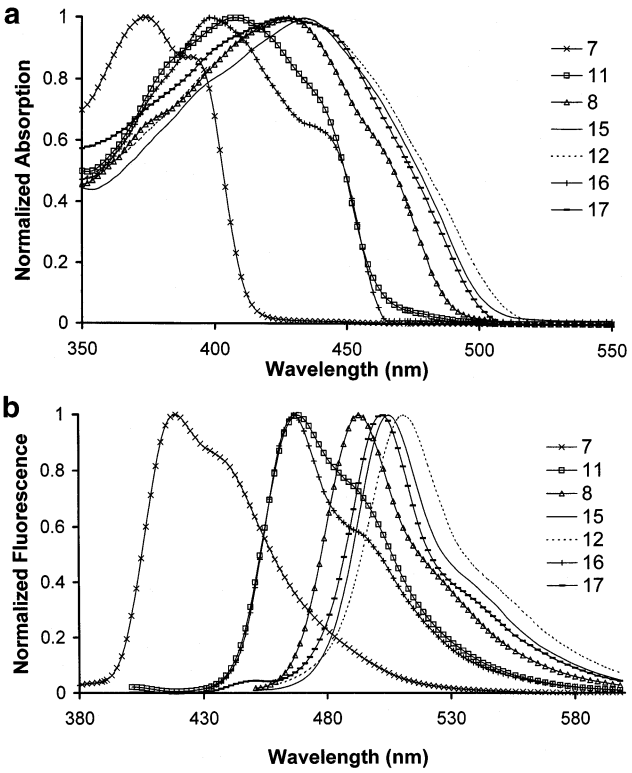

FIGURE 2. (a) Normalized absorption spectra measured in dichloromethane (1×10^{-5} M) at room temperature for ditopic ligands from left to right, respectively, for **7, 16**, **11**, **8**, **15**, **17**, **12**. (b) Normalized fluorescence emission spectra measured under the same conditions but using a 10-fold dilution of the solutions; all ligands from **7, 16**, **11**, **8**, **15**, **17** to **12** were excited by irradiation in the less-energetic aborption band.

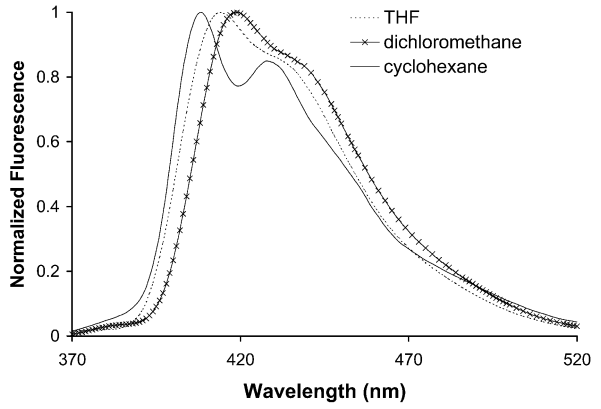

FIGURE 3. Normalized steady-state fluorescence emission spectra of ligand **7** measured at room temperature in various solvents (1×10^{-6} M).

might favor a better blending of the orbitals, inducing a better delocalization over the entire backbone.

As shown in Figure 3, the fluorescence profile becomes more structured and undergoes a blue shift while decreasing the polarity of the solvent. Such behavior has been noted for other ethynylated aromatic compounds and is attributed to close interaction of π,π^* and charge-transfer excited singlet states.[40] In addition, in cyclohexane, a nice vibronic sequence could be seen (Figure 3), where the 0.0, 0.1, and 0.2 transitions in the fluorescence spectrum are separated by ca. 1200 cm^{-1}. Finally, for all ditopic ligands, the excited lifetime measured in degassed dichloromethane is shorter than 2 ns.

Conclusions

Strongly fluorescent and highly soluble monodisperse bis-terpyridine oligomers with one to five diethynyl-3,4-dibutylthiophene modules have been synthesized by following a hybrid synthetic approach, which combines the advantages of a linear methodology previously used for related compounds and the synthetic efficiency of the convergent approach. For example, ligand **11** with $n = 2$ could be prepared either from building blocks **9b** or **14b** and the requested terpy-OTf or from terpy-C≡C−H modules. This convergent protocol offers a convenient entry to larger systems bearing six to eight-bridging DEDBT subunits by coupling the pivotal diiodo intermediates **3** and **14b** with, respectively, the mono-, di-, and trisubstituted thiophene building blocks **9b** and deprotected form of **10**. This convergent strategy, which is based on the combinatorial coupling of a series of ethynyl-grafted fragments, enjoys the advantages of both efficiency and diversity. Only one set of reaction conditions based on palladium(0)-promoted Sonogashira cross-coupling reactions is required for the entire iterative synthetic sequence.

The use of an acetylenic spacer not only has a therapeutic effect on the electronic properties of the bridge[41] but also enhanced conjugation due to reduction of steric effects imposed by the alkyl pendants. This assumption has recently been invoked for polyethynylthiophenes.[42] Alternatively, it is to be expected because of the vibration of the molecular backbone, rotation around the sp−sp^2 linkage, and out-of-plane bending[43] that the so-called molecular wires will not be planar. However, it is believed, on the basis of previous observation, that fractional planarity of neighboring fragments might be sufficient to provide fast and efficacious triplet- or electron-transfer processes favored by a hopping mechanism.[35,44] Disruption of the conjugation along the molecular bridge is also a way to raise its triplet energy. A low-energy state would favor detrimental, nonradiative relaxation processes. Finally, a small degree of solvatochromism in the absorption and a significant responsiveness of the emission to the solvent dielectric constant indicate intramolecular CT in the excited state. Because of the short lifetimes of the excited states, the nature of the emitting state is clearly a singlet. The 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,[45] triacety-

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lene,[46] phenylenevinylene,[47] phenyleneethynylene,[48] and thiopheneethynylene.[49] The design and engineering of more planar and less aromatic oligomeric templates may exhibit improved π-electron delocalization and a better ECL. We are currently using these strategies for the synthesis of a complete library of compounds that contains larger systems and different chelating templates to screen them in molecular energy and electron-transfer processes.

Experimental Section

General Methods. The 200.1 (^{1}H) and 50.3 MHz (^{13}C) NMR spectra were recorded at room temperature using predeuterated solvents as internal standards: δ (H) in ppm relative to residual protiated solvent; δ (C) in ppm relative to the solvent. A fast-atom bombardment ZAB-HF-VB-analytical apparatus in positive mode was used with a *m*-nitrobenzyl alcohol (*m*-NBA) as matrix. FT-IR spectra were recorded on the neat liquids or as thin films, prepared with a drop of dichloromethane, and evaporated to dryness on KBr pellets. Melting points were obtained on a capillary melting point apparatus in open-ended capillaries and are uncorrected. Chromatographic purification was conducted using 40−63 μm silica gel or aluminium oxide 90 standardized. Thin layer chromatography (TLC) was performed on silica gel or aluminium oxide plates coated with fluorescent indicator. Deactivated plates were previously treated with 90:10 CH_2Cl_2−Et_3N. All mixtures of solvents are given in *v*/*v* ratio. The experimental procedures for each reaction were tested several times to optimally find the best conditions.

Materials. CH_2Cl_2 was distilled from CaH_2. THF was dried over Na-benzophenone prior to distillation. CH_3CN was filtered over aluminium oxide and distilled over P_2O_5, and *n*-bromobutane was distilled over K_2CO_3. $[Pd(PPh_3)_2Cl_2]$ was recrystallized from hot DMSO. Et_3N and EtOH were used as purchased. $[Pd(PPh_3)_2Cl_2]$[50] and $[Pd(PPh_3)_4]$[51] were prepared and purified according to the literature procedures. All reactions were carried out under dry argon by using Schlenk tube techniques.

General Procedure Following Experimental Conditions 1. A Schlenk flask was charged with the iodo and ethynyl derivatives, $Pd(PPh_3)_4$ (6 mol %), and finally with argon-degassed *n*-propylamine. 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 aqueous layer was extracted with dichloromethane, and 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 for terpyridine derivatives and silica gel for terpyridine-free derivatives).

General Procedure Following Experimental Conditions 2. To a mixture of 1 equiv of the ethynyl and 1.1 equiv of the iodo derivatives in a Schlenk flask equipped with a septum were added THF, CuI, diisopropylamine, and $PdCl_2(PPh_3)_2$. The solution was argon-degassed for 30 min and stirred overnight at room temperature before being poured into water. The aqueous layer was extracted with ether, and 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 (silica gel, hexane).

General Procedure for the Removal of the 2-Propanol Group Conditions 3. To a solution of the 2-propanol-protected compound in toluene was added KOH (5 equiv) as a solid. The mixture was refluxed until the complete consumption of the starting material (determined by TLC). The solution was neutralized by an aqueous solution of ammonium chloride. 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 (alumina, hexane−dichloromethane).

3,4-Dibutylthiophene (2). To magnesium turnings (562 mg, 23.1 mmol) in ether (15 mL) was added dropwise 1-bromobutane (4.64 g, 33.9 mmol) at room temperature, and an ice bath was used to maintain a mild reflux. The mixture was stirred at room temperature until the disappearance of the magnesium and transferred via a cannula to a solution of 3,4-dibromothiophene (2.01 g, 8.31 mmol) and [1,3-bis(diphenylphosphino)propane]-nickel(II)chloride (89 mg, 0.16 mmol) in ether (30 mL) at 0 °C. The mixture was then refluxed for 16 h before being poured into a solution of hydrochloric acid 10%. The aqueous layer was extracted with ether and the organic extracts were washed with water and then brine and dried over magnesium sulfate. The solvent was removed, and the residue was purified by chromatography (silica gel, hexane) and by distillation under reduced pressure (0.2 mmHg, 80 °C) to afford 1.493 g (92%) of **2** as colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.89 (s, 2H), 2.51 (t, J = 7.7 Hz, 4H), 1.61 (m, 4H), 1.41 (m, 4H,), 0.92 (t, J = 7.1 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.8, 119.9, 31.9, 28.5, 22.7, 14.0; IR (neat, cm^{-1}): 2892, 1637, 1465, 1378; EI *m*/*z* (relative intensity): 196 ([M], 100); Anal. Calcd for $C_{12}H_{20}S$: C, 73.41; H, 10.27. Found: C, 73.16; H, 9.89.

3,4-Dibutyl-2,5-diiodothiophene (3). To a solution of **2** (1.44 g, 7.36 mmol) in toluene (200 mL) and dichloromethane (80 mL) at 0 °C were added mercuric oxide (3.42 g, 15.8 mmol) and iodine (6.71 g, 26.5 mmol). The mixture was stirred at room temperature overnight before filtration through Celite. The solvent was removed by rotary evaporation. After addition of water and ether, the aqueous layer was extracted with ether, and 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 (silica gel, hexane) to afford 3.07 g (93%) of **3** as a colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.56 (m, 4H), 1.40 (m, 8H), 0.94 (t, J = 6.9 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 146.2, 77.8, 32.1, 31.3, 22.7, 13.9; IR (neat, cm^{-1}): 2955, 2858, 1464, 1378, 1079, 915; EI *m*/*z* (relative intensity): 448 ([M], 100), 321 (20), 194 (10); Anal. Calcd for $C_{12}H_{18}I_2S$: C, 32.16; H, 4.05. Found: C, 31.90; H, 3.81.

3,4-Dibutyl-2-(3-hydroxy-3-methylbutynyl)-5-iodothiophene (4): prepared following exptl conditions 1; from **3** (1.500 g, 3.35 mmol), 2-methylbut-3-yn-2-ol (394 mg, 4.68 mmol) and $Pd(PPh_3)_4$ (232 mg, 0.20 mmol) in 60 mL of *n*-propylamine for 5 days; chromatography on silica, eluting first with hexane and then hexane−ethyl acetate (*v*/*v* 90/10) to give 585 mg (45%) of **4** as a viscous liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.79 (s, 1H), 2.66 (t, J = 7.7 Hz, 2H), 2.49 (m, 2H), 1.61 (s, 6H), 1.42 (m, 8H), 0.94 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 146.5, 145.9, 123.2, 101.0, 75.7, 75.1, 65.8, 32.3, 31.9, 31.9, 30.7, 28.6, 22.7, 22.6, 13.9; IR (neat, cm^{-1}): 3343, 2956, 2931, 2851, 2216, 1458, 1377, 1259, 1163; EI *m*/*z* (relative intensity): 404 ([M], 100), 277 (30); Anal. Calcd for $C_{17}H_{25}IOS$: C, 50.50; H, 6.23. Found: C, 50.30; H, 5.96.

3,4-Dibutyl-2-(3-hydroxy-3-methylbutynyl)-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]thiophene (6a): prepared following exptl conditions 1; from **4** (150 mg, 0.38 mmol), **5** (138 mg, 0.54 mmol), and $Pd(PPh_3)_4$ (27 mg, 2.3 10^{-2} mmol) in 30 mL

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of *n*-propylamine for 2 days; chromatography on alumina, eluting initially with dichloromethane and then increased to dichloromethane−ethyl acetate (*v*/*v* 75/25) to give 163 mg (82%) of **6a** as yellowish solid: mp 113−114 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.68 (m, 2H), 8.57 (d, J = 7.8 Hz, 2H), 8.48 (s, 2H), 7.83 (td, ^3J = 7.7, ^4J = 1.9 Hz, 2H), 7.32 (ddd, ^3J =7.5 Hz, ^3J = 4.8 Hz, ^4J =1.3 Hz, 2H), 2.87 (s, 1H), 2.71 (t, J = 7.5 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 1.63 (s, 6H), 1.41 (m, 8H), 0.93 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.6, 155.4, 148.1, 147.7, 146.8, 136.9, 133.1, 124.0, 122.2, 121.2, 120.2, 118.0, 101.0, 93.8, 87.2, 75.3, 65.7, 32.4, 32.1, 31.4, 28.3, 28.1, 22.7, 22.6, 14.0, 13.9; IR (KBr, cm^{-1}): 3436, 2956, 2930, 2198, 1583, 1567, 1466, 1391; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 286 (33 300), 348 (73 300), 367 (31 500); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 534 ([M + H]$^+$, 100). Anal. Calcd for $C_{34}H_{35}N_3OS$: C, 76.51; H, 6.61; N, 7.87. Found: C, 76.24; H, 6.32; N, 7.53.

3,4-Dibutyl-2-ethynyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)-ethynyl]thiophene (6b): prepared following exptl conditions 3; from **6a** (202 mg, 0.39 mmol) and KOH (108 mg, 1.93 mmol) in 30 mL of toluene; chromatography on alumina; no further purification to give 173 mg (97%) of **6b** as orange solid: mp 118−119 °C; ^{1}H NMR (200M Hz, $CDCl_3$): δ 8.70 (m, 2H), 8.58 (d, J = 8.1 Hz, 2H), 8.50 (s, 2H), 7.85 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 2H), 7.34 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J = 1.3 Hz, 2H), 3.50 (s, 1H), 2.70 (m, 4H), 1.48 (m, 8H), 0.95 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.6, 155.6, 149.2, 148.0, 147.7, 136.9, 133.1, 124.0, 122.3, 121.2, 119.5, 118.6, 93.8, 87.0, 84.3, 76.8, 32.4, 32.2, 28.4, 28.2, 22.7, 22.6, 14.0, 13.9; IR (KBr, cm^{-1}): 3300, 3053, 2959, 2861, 2200, 2100, 1584, 1567, 1467, 1391, 1265, 1071; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 287 (60 200), 343 (68 500), 361 (66 100); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 476 ([M + H]$^+$, 100); Anal. Calcd for $C_{31}H_{29}N_3S$: C, 78.28; H, 6.15; N, 8.83. Found: C, 78.02; H, 6.03; N, 8.77.

3,4-Dibutyl-2,5-bis[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]-thiophene (7): to a mixture of **5** (305 mg, 1.18 mmol) and **3** (190 mg, 0.42 mmol) in 10 mL of THF were added $PdCl_2(PPh_3)_2$ (34 mg, 0.05 mmol, 11 mol %), CuI (22 mg, 0.11 mmol), and 350 μL (0.11 mmol) of diisopropylamine. The solution was argon-degassed for 30 min and stirred at room temperature for 23 h. The solvent was evaporated. The crude product was treated by 100 mg of KCN in 20 mL of methanol. After 2 h, the solution was poured into 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, dichloromethane) and recrystallized (hexane, dichloromethane, and methanol) to afford 216 mg (72%) of **7** as yellowish solid: mp 251−252 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.73 (m, 4H), 8.63 (d, J = 8.1 Hz, 4H), 8.51 (s, 4H), 7.89 (td, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 4H), 7.37 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J = 1.3 Hz, 4H), 2.79 (m, 4H), 1.54 (m, 8H), 1.01 (t, J = 7.1 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.7, 155.6, 149.2, 148.1, 137.0, 133.1, 124.2, 124.1, 122.4, 121.3, 94.6, 87.1, 32.5, 28.4, 22.7, 14.1; IR (KBr, cm^{-1}): 2918, 2856, 2198, 1597, 1580, 1446, 1262, 1067, 883; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 285 (47 800), 373 (49 000), 391 (42 800); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 707 ([M + H]$^+$, 100), 474 ([M − terpy]$^+$, 20); Anal. Calcd for $C_{46}H_{38}N_6S$: C, 78.16; H, 5.42; N, 11.89. Found: C, 77.88; H, 5.18; N, 11.62.

3,4-Dibutyl-2,5-bis{3,4-dibutyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]thienylethynyl}thiophene (8): prepared following exptl conditions 1; from **6b** (104 mg, 0.21 mmol), **3** (39 mg, 0.09 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in 20 mL of *n*-propylamine for 24 h; chromatography on alumina; eluting initially with dichloromethane−hexane (*v*/*v* 10/90) and then increased to dichloromethane−hexane (*v*/*v* 50/50) to give 84 mg (84%) of **8** as bright orange crystals: mp 200−201 °C; ^{1}H NMR (200M Hz, $CDCl_3$): δ 8.73 (m, 4H), 8.63 (d, J = 8.1 Hz, 4H), 8.53 (s, 4H), 7.88 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 4H), 7.37 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J = 1.3 Hz, 4H), 2.74 (m, 12H), 1.44 (m, 24H), 0.99 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.7, 155.6, 149.2, 148.0, 146.8, 146.7, 136.9, 133.2, 124.0, 122.2, 121.3, 120.7, 119.6, 117.8, 94.4, 89.7, 89.4, 87.3, 32.5, 28.5, 22.8, 22.3, 14.0; IR (KBr, cm^{-1}): 2955, 2928, 2856, 2196, 1583, 1566, 1466, 1390, 1264; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 284 (46 700), 428 (56 200); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 1143 ([M + H]$^+$, 100), 910 ([M − terpy]$^+$, 10); Anal. Calcd for $C_{74}H_{74}N_6S_3$: C, 77.72; H, 6.52; N, 7.35. Found: C, 77.53; N, 6.28; N, 7.09.

1-[3,4-Dibutyl-5-(3-hydroxy-3-methylbutynyl)thienyl]-2-{3,4-dibutyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]-thienyl}ethyne (9a): prepared following exptl conditions 1; from **6b** (220 mg, 0.47 mmol), **4** (205 mg, 0.52 mmol), and $Pd(PPh_3)_4$ (33 mg, 0.03 mmol) in 30 mL of *n*-propylamine for 3 days; chromatography on alumina; eluting with dichloromethane−ethyl acetate (*v*/*v* 95/5) to give 309 mg (90%) of **9a** as yellowish solid: mp 117−118 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.67 (m, 2H), 8.56 (d, J = 7.8 Hz, 2H), 8.47 (s, 2H), 7.81 (td, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 2H), 7.30 (ddd, ^3J = 7.2 Hz, ^3J = 6.1 Hz, ^4J = 1.1 Hz, 2H), 2.92 (s, 1H), 2.64 (m, 8H), 1.58 (s, 6H), 1.43 (m, 16H), 0.92 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.6, 155.5, 149.1, 148.0, 146.8, 146.5, 136.9, 133.1, 124.0, 122.2, 121.2, 120.7, 119.2, 118.7, 100.7, 94.4, 89.6, 88.7, 87.2, 75.4, 65.7, 32.4, 32.1, 31.4, 28.4, 28.1, 22.74, 22.69, 22.6, 14.0, 13.9; IR (KBr, cm^{-1}): 3400, 2956, 2929, 2858, 2196, 1567, 1466, 1391, 1263, 1165; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 283 (29 500), 3932 (36 600), 425 (25 000); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 752 ([M + H]$^+$, 100), 668 ([M − C≡CC(CH$_3$)$_2$OH]$^+$, 30). Anal. Calcd for $C_{48}H_{53}N_3OS_2$: C, 76.66; H, 7.10; N, 5.59. Found: C, 76.30; H, 6.75; N, 5.20.

1-(3,4-Dibutyl-5-ethynylthienyl)-2-{3,4-dibutyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl] thienyl}ethyne (9b): prepared following exptl conditions 3; from **9a** (183 mg, 0.25 mmol) and KOH (70 mg, 1.3 mmol) in 30 mL of toluene; chromatography on alumina; eluting with dichloromethane−hexane (*v*/*v* 50/50) to give 145 mg (86%) of **9b** as red solid: mp 70−71 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.70 (m, 2H), 8.60 (d, J = 8.1 Hz, 2H), 8.51 (s, 2H), 7.80 (td, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 2H), 7.33 (ddd, ^3J = 7.8 Hz, ^3J = 4.7 Hz, ^4J = 1.1 Hz, 2H), 3.48 (s, 1H), 2.70 (m, 8H), 1.50 (m, 16H), 0.94 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.5, 155.4, 149.1, 147.9, 147.8, 146.6, 146.4, 136.8, 133.0, 123.9, 122.1, 121.1, 120.5, 119.2, 118.8, 118.5, 94.4, 89.4, 88.7, 87.1, 84.1, 76.8, 32.4, 32.2, 28.4, 28.1, 22.7, 22.7, 22.6, 22.6, 14.0, 13.8; IR (KBr, cm^{-1}): 3307, 2950, 2926, 2855, 2192, 2093, 1583, 1465, 1384, 1262, 1116, 1069; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 284 (28 600), 389 (37 600); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 694 ([M + H]$^+$, 100); Anal. Calcd for $C_{45}H_{47}N_3S_2$: C, 77.88; H, 6.83; N, 6.05. Found: C, 77.63; H, 6.62; N, 5.83.

3,4-Dibutyl-2-[3,4-dibutyl-5-(3-hydroxy-3-methylbutynyl)thienylethynyl]-5-{3,4-dibutyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]thienylethynyl}thiophene (10): prepared following exptl conditions 1; from **9b** (180 mg, 0.27 mmol), **4** (116 mg, 0.29 mmol), and $Pd(PPh_3)_4$ (19 mg, 0.02 mmol) in 30 mL of *n*-propylamine for 5 days; chromatography on alumina; eluting with dichloromethane−hexane (*v*/*v* 90/10) first and then with dichloromethane to give 60 mg (33%) of the starting material **9b** and 120 mg (48%) of **10** as orange solid: mp 79−80 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.73 (m, 2H), 8.62 (d, J = 8.01 Hz, 2H), 8.52 (s, 2H), 7.87 (td, ^3J = 7.9 Hz, ^4J = 1.6, 2H), 7.36 (ddd, ^3J = 6.7 Hz, ^3J = 6.2 Hz, ^4J = 1.1 Hz, 2H), 2.68 (m, 12H), 1.63 (s, 6H), 1.40 (m, 24H), 0.92 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.6, 155.5, 149,2, 148.0, 146.8, 146.7, 146.6, 146.5, 146.4, 136.9, 124.0, 122.2, 121.3, 120.7, 119.7, 119.3, 119.1, 118.81, 118.75, 100.6, 94.4, 89.7, 89.4, 89.3, 88.8, 87.2, 75.5, 65.8, 32.5, 32.2, 31.4, 28.4, 28.1, 22.8, 22.75, 22.68, 19.9, 19.78, 19.77, 14.0, 13.9; IR (KBr, cm^{-1}): 3437, 2957, 2930, 2859, 2197, 1599, 1584, 1466, 1391, 1264, 1163, 1120, 1067, 1042; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 286 (24 500), 410 (35 000), 459 (sh, 16 000); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 970 ([M + H]$^+$, 100), 886

([M − C≡CC(CH$_3$)$_2$OH]$^+$, 35); Anal. Calcd for $C_{62}H_{71}N_3OS_3$: C, 76.74; H, 7.37; N, 4.33. Found: C, 76.40; H, 7.01; N, 3.97.

Bis{3,4-dibutyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]-thienyl}ethyne (11): prepared following exptl conditions 1; from **9b** (50 mg, 0.07 mmol), (2,2′:6′,2″-terpyridin-4′-yl) triflate (34 mg, 0.09 mmol), and Pd(PPh$_3$)$_4$ (9 mg, 7 10^{-3} mmol) in 10 mL of *n*-propylamine for 24 h; chromatography on alumina; eluting with dichloromethane to give 41 mg (60%) of **11** as orangish solid. Or prepared following exptl conditions **1**; from **14b** (80 mg, 0.12 mmol), **5** (67 mg, 0.26 mmol), and Pd(PPh$_3$)$_4$ (10 mg, 7 10^{-3} mmol) in 30 mL of *n*-propylamine for 5 days; chromatography on alumina; eluting with dichloromethane−hexane (*v*/*v* 50/50) first and then with dichloromethane to give 60 mg (55%) of **11**: mp 188−189 °C; ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.72 (m, 4H), 8.61 (d, J = 7.8 Hz, 4H), 8.52 (s, 4H), 7.87 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 4H), 7.35 (m, 4H), 2.75 (m, 8H), 1.55 (m, 16H), 0.87 (m, 12H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 155.7, 155.6, 149.2, 148.0, 146.8, 136.9, 133.2, 124.0, 122.3, 121.3, 120.6, 118.9, 94.5, 89.6, 87.3, 32.5, 28.5, 28.4, 22.8, 22.7, 14.0; IR (KBr, cm^{-1}): 2956, 2929, 2861, 2196, 1583, 1567, 1466, 1391, 1263, 1092, 888, 791; UV−vis (CH$_2$Cl$_2$) λ nm (ϵ, M^{-1} cm^{-1}): 285 (92 200), 347 (44 800), 408 (88 400); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 925 ([M + H]$^+$, 100), 692 ([M − terpy]$^+$, 10); Anal. Calcd for $C_{60}H_{56}N_6S_2$: C, 77.89; H, 6.10; N, 9.08. Found: C, 77.55; H, 5.84; N, 8.74.

3,4-Dibutyl-2,5-bis(3,4-dibutyl-5-{3,4-dibutyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]-thienylethynyl}thienylethynyl)thiophene (12): prepared following exptl conditions 1; from **9b** (128 mg, 0.19 mmol), **3** (43 mg, 0.09 mmol), and Pd(PPh$_3$)$_4$ (13 mg, 0.01 mmol) in 25 mL of *n*-propylamine for 3 days; purified by recrystallization from dichloromethane−methanol to give 110 mg (73%) of **12** as a reddish solid: mp 74 °C; ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.73 (m, 4H), 8.63 (d, J = 7.8 Hz, 4H), 8.53 (s, 4H), 7.88 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 4H), 7.37 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J = 1.0 Hz, 4H), 2.71 (m, 20H), 1.49 (m, 40H), 1.01 (m, 30H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 156.1, 156.0, 149.6, 148.5, 147.2, 147.1, 137.3, 133.6, 124.4, 122.66, 121.7, 121.1, 120.1, 120.0, 119.9, 119.2, 94.9, 90.2, 90.0, 89.9, 89.8, 87.7, 28.9, 28.9, 23.2, 23.1, 14.4, 14.4; IR (KBr, cm^{-1}): 2956, 2931, 2859, 2197, 1583, 1567, 1466, 1391, 1262, 1092, 889; UV−vis (CH$_2$Cl$_2$) λ nm (ϵ, M^{-1} cm^{-1}): 278 (81 000), 433 (47 500); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 1581/1580/1579 ([M + H]$^+$, 100), 1348 ([M − terpy]$^+$, 15); Anal. Calcd for $C_{102}H_{110}N_6S_5$: C, 77.52; H, 7.02; N, 5.32. Found: C, 77.36; H, 6.70; N, 5.80.

3,4-Dibutyl-2-iodothiophene (13a). To a solution of **2** (1.257 g, 6.4 mmol) in 1.5 mL of benzene were added alternatively, in a small portion, mercuric oxide (1.284 g, 5.9 mmol) and iodine (1.667 g, 6.60 mmol) at 0 °C. The mixture was stirred at room temperature for 6 h before filtration on Celite. The filtrate was poured into water, and the aqueous layer was extracted with ether. 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 chromatography (silica gel, hexane) of the residue gave three fractions. The distillation at reduced pressure (0.2 mmHg, 100 °C) of the main fraction (821 mg) afforded 397 mg (21%) of pure **13a** as colorless oil, 91 mg of **3**, and 314 mg of a mixture **13a**−**3** (86/14); ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.05 (s, 1H), 2.55 (m, 4H), 1.41 (m, 8H), 0.92 (m, 6H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 145.9, 141.8, 125.2, 74.6, 31.8, 30.4, 22.8, 22.5, 14.0; IR (neat, cm^{-1}): 2959, 2932, 2861, 1466, 1265, 740, 705; EI *m*/*z* (relative intensity): 322 ([M], 100), 195 (10); Anal. Calcd for $C_{12}H_{19}IS$: C, 44.73; H, 5.94. Found: C, 44.49; H, 5.71.

3,4-Dibutyl-2-(trimethylsilyl)ethynylthiophene (13b): prepared following exptl conditions 2; from **13a** (207 mg, 0.64 mmol), trimethylsilylacetylene (89 mg, 0.90 mmol), PdCl$_2$(PPh$_3$)$_2$ (22 mg, 0.03 mmol), and CuI (3 mg, 1.6 10^{-2} mmol) in 15 mL of THF and 0.13 mL (97 mg, 0.96 mmol) of diisopropylamine to give 184 mg (98%) of **13b** as colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.79 (s, 1H), 2.64 (t, J = 7.5 Hz, 2H), 2.48 (t, J = 7.7 Hz, 2H), 1.46 (m, 8H), 0.95 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.1 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 148.0, 141.8, 121.2, 118.5, 100.2, 98.4, 32.0, 31.9, 28.7, 27.9, 22.7, 22.5, 14.0, 13.9, 0.0; IR (neat, cm^{-1}): 2958, 2860, 2143, 1465, 1249, 842, 759; EI *m*/*z* (relative intensity): 292 ([M], 100); Anal. Calcd for $C_{17}H_{28}SiS$: C, 69.79; H, 9.65. Found: C, 75.01; H, 9.05.

3,4-Dibutyl-2-ethynylthiophene (13c). To a solution of **13b** (178 mg, 0.60 mmol) in methanol (10 mL) was added potassium carbonate (253 mg, 1.8 mmol). The solution was allowed to stir for 1.5 h before being poured into water and neutralized by a solution of hydrochloric acid (10%). The aqueous layer was extracted with ether. The organic extracts were washed with water and then brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation. No further purification was necessary to afford 126 mg (94%) of the title compound as a colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.82 (s, 1H), 3.41 (s, 1H), 2.66 (t, J = 7.7 Hz, 2H), 2.49 (td, J = 7.7 Hz, ^2J = 0.9 Hz, 2H), 1.49 (m, 8H), 0.95 (t, J = 6.7 Hz, 3H), 0.94 (t, J = 6.7 Hz, 3H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 148.0, 141.9, 121.5, 117.3, 82.7, 77.5, 32.1, 31.9, 28.7, 27.9, 22.7, 22.6, 13.9; IR (neat, cm^{-1}): 3311, 2957, 2930, 2860, 2100, 1465, 1378; EI *m*/*z* (relative intensity): 220 ([M], 100); Anal. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15. Found: C, 76.04; H, 8.74.

Bis(3,4-dibutylthienyl)ethyne (14a): prepared following exptl conditions 2; from **13c** (112 mg, 0.51 mmol), **13a** (180 mg, 0.56 mmol), PdCl$_2$(PPh$_3$)$_2$ (18 mg, 2.5 10^{-2} mmol), and CuI (3 mg, 1 10^{-2} mmol) in 10 mL of THF and 0.11 mL (77 mg, 0.76 mmol) of diisopropylamine to give 168 mg (80%) of **14a** as colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.87 (s, 2H), 2.72 (t, J = 7.4 Hz, 4H), 2.54 (t, J = 7.7 Hz, 4H), 1.52 (m, 16H), 0.98 (t, J = 7.1 Hz, 6H), 0.97 (t, J = 7.1 Hz, 6H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 146.4, 142.0, 121.3, 118.8, 88.3, 32.4, 31.9, 28.7, 28.1, 14.0, 14.0; IR (KBr, cm^{-1}): 2956, 2930, 2871, 2859, 2192, 2134, 1465, 1377, 740; EI *m*/*z* (relative intensity): 414 ([M], 100); Anal. Calcd for $C_{26}H_{38}S_2$: C, 75.30; H, 9.24. Found: C, 75.02; H, 9.05.

Bis(3,4-dibutyl-5-iodothienyl)ethyne (14b). To a solution of diisopropylamine (123 mg, 1.22 mmol) in 1 mL of THF at −78 °C was added dropwise *n*-butyllithium (0.77 mL, 1.14 mmol, 1.48 M in hexanes). The solution was warmed to 0 °C for 10 min and then recooled to −78 °C. **14a** (169 mg, 0.41 mmol) in THF (1 mL) 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 (227 mg, 0.89 mmol) was added in the solution as a solid. The mixture was stirred at −78 °C for 1 h, then quenched with a solution of 10% hydrochloric acid at 0 °C. The aqueous layer was extracted with ether. 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, and the residue was purified by column chromatography (silica gel, hexane) to provide 241 mg (89%) of **14b** as colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$): δ 2.74 (t, J = 7.5 Hz, 4H), 2.54 (t, J = 7.5 Hz, 4H), 1.43 (m, 16H), 0.97 (m, 12H); ^{13}C NMR (50 MHz, CDCl$_3$): δ 146.2, 146.1, 123.7, 122.8, 89.2, 32.6, 32.0, 31.8, 28.9, 22.8, 22.7, 14.0, 14.0; IR (neat, cm^{-1}): 2955, 2929, 2858, 2186, 2134, 1457, 1377, 1264, 1104, 1081; EI *m*/*z* (relative intensity): 666 ([M], 100); Anal. Calcd for $C_{26}H_{36}I_2S_2$: C, 46.85; H, 5.44. Found: C, 46.65; H, 5.30.

Bis(3,4-dibutyl-5-{3,4-dibutyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]thienylethynyl} thienyl)ethyne (15): prepared following exptl conditions 1; from **6b** (97 mg, 0.21 mmol), **14b** (70 mg, 0.10 mmol), and Pd(PPh$_3$)$_4$ (7 mg, 6.2 10^{-3} mmol) in 5 mL of *n*-propylamine for 19 h; purified by recrystallization from dichloromethane−methanol; eluting with dichloromethane−hexane (*v*/*v* 50/50) to give 82 mg (58%) of **15** as a red solid: mp 180−181 °C; ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.73 (m, 4H), 8.62 (d, J = 8.1 Hz, 4H), 8.53 (s, 4H), 7.87 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 4H), 7.36 (ddd, ^3J = 4.8 Hz, ^3J = 7.5 Hz,

^4J = 1.1 Hz, 4H), 2.74 (m, 16H), 1.49 (m, 32H), 0.99 (m, 24H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.6, 149.2, 148.0, 146.8, 146.6, 136.9, 133.1, 124.0, 122.2, 121.2, 120.7, 119.7, 119.4, 118.8, 94.4, 89.7, 89.5, 89.3, 87.2, 32.5, 28.5, 22.8, 22.7, 14.0; IR (KBr, cm^{-1}): 2956, 2929, 2860, 2196, 1583, 1566, 1466, 1391, 1262, 1091, 888, 791; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 284 (64 200), 346 (36 700), 434 (81 700); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 1362/1361 ([M + H]$^+$, 100). Anal. Calcd for $C_{88}H_{92}N_6S_4$: C, 77.61; H, 6.81; N, 6.17. Found: C, 77.49; H, 6.67; N, 5.93.

Bis[3,4-dibutyl-5-(2,2′:6′,2″-terpyridin-4′-yl)ethynylthienyl]butadiyne (16). To a stirred solution of ethynyl derivative **6b** (57 mg, 0.12 mmol) in 5 mL of DMF were added CuCl (120 mg, 1.2 mmol) and $CuCl_2$ (82 mg, 0.61 mmol) as a solid. The solution was satured with oxygen and stirred at room temperature for 4 days. After evaporation of the solvent, addition of KCN in water (5 mL) led to the copper decomplexation. The free ligand was extracted with dichloromethane, and 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 recrystallization from dichloromethane−hexane to afford 46 mg (82%) of **16** as an orange solid: mp 225−226 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.74 (m, 4H), 8.63 (m, 4H), 8.53 (s, 4H), 7.88 (td, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 4H), 7.37 (ddd, ^3J = 7.4 Hz, ^3J = 4.9 Hz, ^4J = 1.1 Hz, 4H), 2.72 (m, 8H), 1.55 (m, 16H), 0.99 (t, J = 7.2 Hz, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.70, 155.65, 150.0, 149.2, 147.9, 136.9, 133.0, 124.1, 122.4, 121.3, 120.2, 119.5, 94.5, 87.0, 81.1, 77.2, 32.4, 28.5, 28.4, 22.7, 14.0, 13.9; IR (KBr, cm^{-1}): 2953, 2926, 2857, 2190, 2132, 1581, 1564, 1467, 1392, 1263, 1151, 1097, 1042, 884; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 279 (140 300), 399 (62 800), 444 (38 300); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 949 ([M + H]$^+$, 100), 476 ([M/2 + H]$^+$, 20); Anal. Calcd for $C_{62}H_{56}N_6S_2$: C, 78.45; H, 5.95; N, 8.85. Found: C, 78.18; H, 5.73; N, 8.71.

Bis(3,4-dibutyl-5-{3,4-dibutyl-5-[(2,2′:6′,2″-terpyridin-4′-yl)ethynyl]thienylethynyl} thienyl)butadiyne (17): prepared by the procedure described for **16**; from **9b** (61 mg, 0.09 mmol), CuCl (90 mg, 0.91 mmol), and $CuCl_2$ (77 mg, 0.57 mmol) in 10 mL of DMF for 6 h; chromatography on alumina; eluting with dichloromethane−hexane (*v*/*v* 50/50) to afford 36 mg (60%) of **17** as an orange solid: mp 90−91 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.73 (m, 4H), 8.62 (m, 4H), 8.53 (s, 4H), 7.85 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 4H), 7.37 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J = 1.3 Hz, 4H), 2.71 (m, 16H), 1.48 (m, 32H), 0.94 (m, 24H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.7, 155.6, 149.9, 149.2, 148.0, 146.9, 146.7, 136.9, 133.2, 128.8, 124.0, 122.3, 121.3, 119.0, 118.6, 94.5, 89.6, 87.2, 81.0, 78.3, 77.2, 34.4, 32.5, 31.9, 30.4, 28.9, 28.4, 22.8, 22.7, 14.0, 13.9; IR (KBr, cm^{-1}): 2956, 2928, 2870, 2858, 2197, 2129, 1583, 1567, 1540, 1465, 1391, 1263, 1093, 1070, 1042, 995; UV−vis (CH_2Cl_2) λ nm (ϵ, M^{-1} cm^{-1}): 283 (59 000), 426 (70 700); FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 1386/1385 ([M + H]$^+$, 100), 694 ([M/2 + H]$^+$; Anal. Calcd for $C_{90}H_{92}N_6S_4$: C, 77.99; H, 6.69; N, 6.06. Found: C, 77.73; H, 6.39; N, 5.83.

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