



Stepwise construction of novel zig-zag shaped thiophene-based back-to-back terpyridine ligands with acetylenic tethers

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Abstract—A series of structurally well-defined molecular-scale wires bearing one to five 2,5-diethynyl-3,4-dibutylthiophene spacers and 2,2':6',2''-terpyridine capping units were synthesized by a combination of cross-coupling reactions and deprotection steps. Palladium-catalyzed cross-coupling of halogenated thiophene units with acetylene grafted terpyridine effectively yields ethynylated thiophenes. Deprotection of the propargylic fragment provides additional building blocks, which could be used in an iterative sequence of reactions. Reliable and practical synthetic routes are now available for the construction of very large polytopic frameworks. © 2002 Elsevier Science Ltd. All rights reserved.

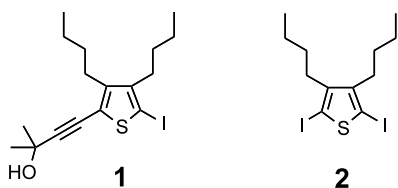
The design and engineering of synthetic molecular materials with a precise architecture is an area of great interest. In some of these multicomponent arrays intramolecular information transfer undergoes over very long distances and via exergonic gradient.^{1,2} Dyads, triads, and higher-order scaffoldings have been synthesized in attempts to mimic and better understand the photosynthetic reaction center but also with views to provide, in the future, new molecular-based storage devices.^{3,4} It is therefore tempting to design and develop new molecules in which the different constituting building blocks are well oriented and directed in such a way to favor unidirectional information transfer. Excellent examples of such predesigned molecular materials are the back-to-back terpyridine ligands carrying either polyethynylene⁵ or polyphenylene/ethynylene⁶ spacers which both possess the ability to work as effective molecular-scale wires. In addition, the use of fast photochemical methods is an increasingly valuable method for the measurements of energy or electron transfer rates, among them transient absorption spectroscopy allow to localize excited states in complex molecules. At the core of these artificial systems lie the use of ethynyl spacers which have been recognized to provide exceptional fast transfer rate and very weak attenuation factors when the size of the spacer is increasing.^{2,7}

Furthermore, various series of conjugated oligothiophenes have been investigated as model compounds for conducting polymers.⁸ Moreover, some of these polymers exhibit well defined optical properties and have recently been successfully used as active components in organic field-effect transistors,⁹ light-emitting devices¹⁰ or photovoltaic solar cells.¹¹ In addition to their use as advanced materials for electronic and photonic applications, these compounds were intensively investigated to model the electronic and electrochemical properties of the parent polydisperse polymers.^{12–14} Recently, regioregular oligothiophenes and novel oligo(2-ethynylpyridines) building blocks were prepared via palladium promoted coupling reactions.^{15,16}

In addition, sensitizers suitable for spectroscopic applications must meet the minimum requirements of stability, rigidity, chemical accessibility and versatility.¹⁷ In the present account we put together two ideas consisting in the use of diethynylthiophene templates to promote electronic communication between two chelating terpyridine fragments. The new class of ditopic ligands which by virtue of their concise and flexible synthesis and their photochemical properties are promising candidates to act as efficient molecular scale wires when complexed with adequate metal centers. As such, 2,5-diethynyl-3,4-dibutylthiophene linked to a 2,2':6',2''-terpyridine fragment represent viable alternatives to some polyphenyl bridged back-to-back terpyridine ligands, that are currently being investigated as second generation scaffoldings for intramolecular energy transfer systems¹⁸ and are significant advancement over the

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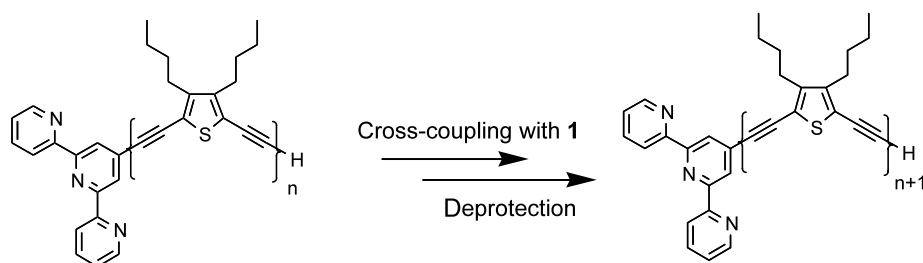
corresponding hardly soluble polyynes bridged systems.¹⁹



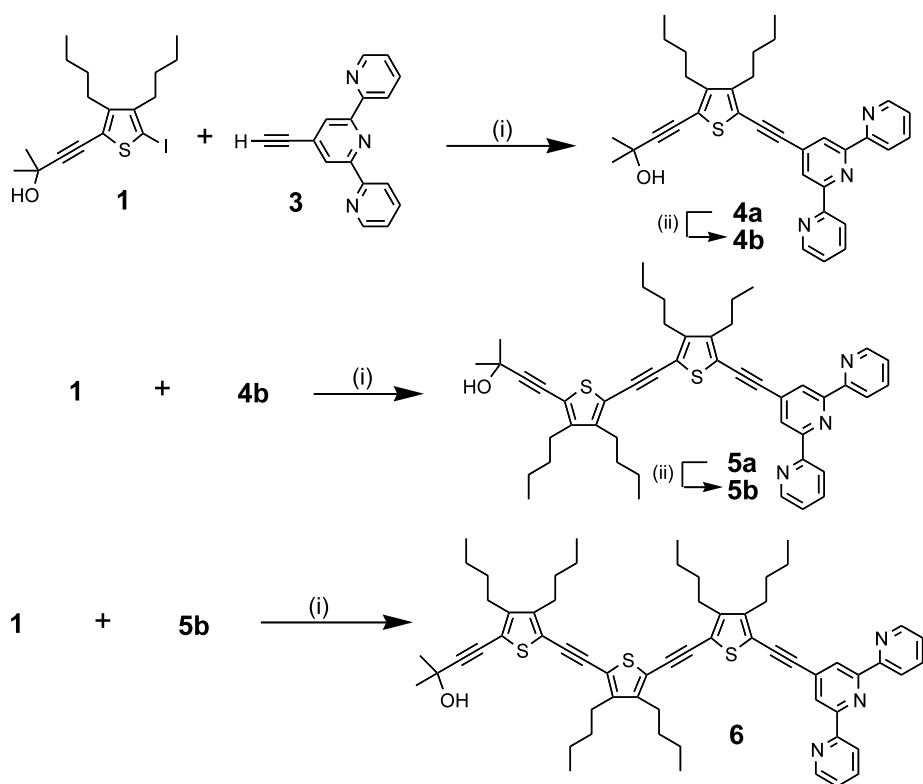
While preparing thiophene-substituted derivatives,²⁰ we came across with the 3,4-dibutylthiophene derivative **1**, substituted in the 2-position with an iodo function and in the 5-position with a propargylic protecting group. This compound was readily prepared in one step from **2** and propargylic alcohol by a reaction mediated by $[Pd(PPh_3)_4]$ under basic conditions. Construction of the target ditopic ligands can be envisaged by a step-by-step implementation of a terpy building block grafted with a single thiophene subunit carrying a terminal

acetylenic function, with the key building block **1**. Afterwards, deprotection of the propargylic group and the use of an iterative sequence of reactions involving cross-coupling/deprotection, would provide the molecules with the requested number of modules (Scheme 1). In a final step cross-coupling of these molecules with a triflate or bromide substituted terpyridine would access to the target ditopic ligands.

Recognizing that this pivotal molecule **1** would be the simplest way for the progressive implementation of the thiophene modules, we decided to investigate its reactivity in solution towards 4'-ethynyl-2,2':6',2''-terpyridine **3**⁵ under Sonogashira–Hagihara cross-coupling reaction conditions (Scheme 2).²¹ The first cross coupling reaction is straightforward when catalyzed by low valent palladium complexes and provide the protected derivative **4a** in 82% yield. *N*-Propylamine is utilized to quench the nascent acid. Deprotection was carried out under basic conditions providing compound **4b** in 97%



Scheme 1. Synthetic protocol used to implement one thiophene unit.



Scheme 2. Reagents and conditions: (i) $[Pd(PPh_3)_4]$ (6 mol%), $nPrNH_2$, 60°C; (ii) KOH, toluene, reflux.

yield. The same sequence of reactions provide the two module compound **5b** in 77% (for the two steps) and the three module derivative **6** in 49%. In principle this protocol could be further applied to larger systems but we were hampered by tedious separation of the final compounds. Indeed, we were unable to pursue this strategy with $n=4$ and $n=5$ modules.

These desired building blocks were photostable, highly soluble in most organic solvents and characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR, FAB $^+$ -MS, UV-vis, IR spectroscopies and all data were consistent with the proposed structures. Selected data are given in Table 1.

With these key building blocks in hands it was then possible to prepare the final ditopic ligands as sketched in Schemes 3 and 4. At this stage we have to distinguish between the series of ligands bearing one, three and five thiophene modules (Scheme 3) and the ligand carrying two modules (Scheme 4). In the first series the protocol was inspired by the use of a single starting material **2**. In all cases the cross-coupling reaction is straightforward and afforded the target ligands **7** to **9** in fair yields. This is a convenient and versatile method because for the larger molecules the required ligands precipitate during the reaction and the use of mild reaction conditions avoids side reactions.

Table 1. Selected data for the novel thiophene molecules

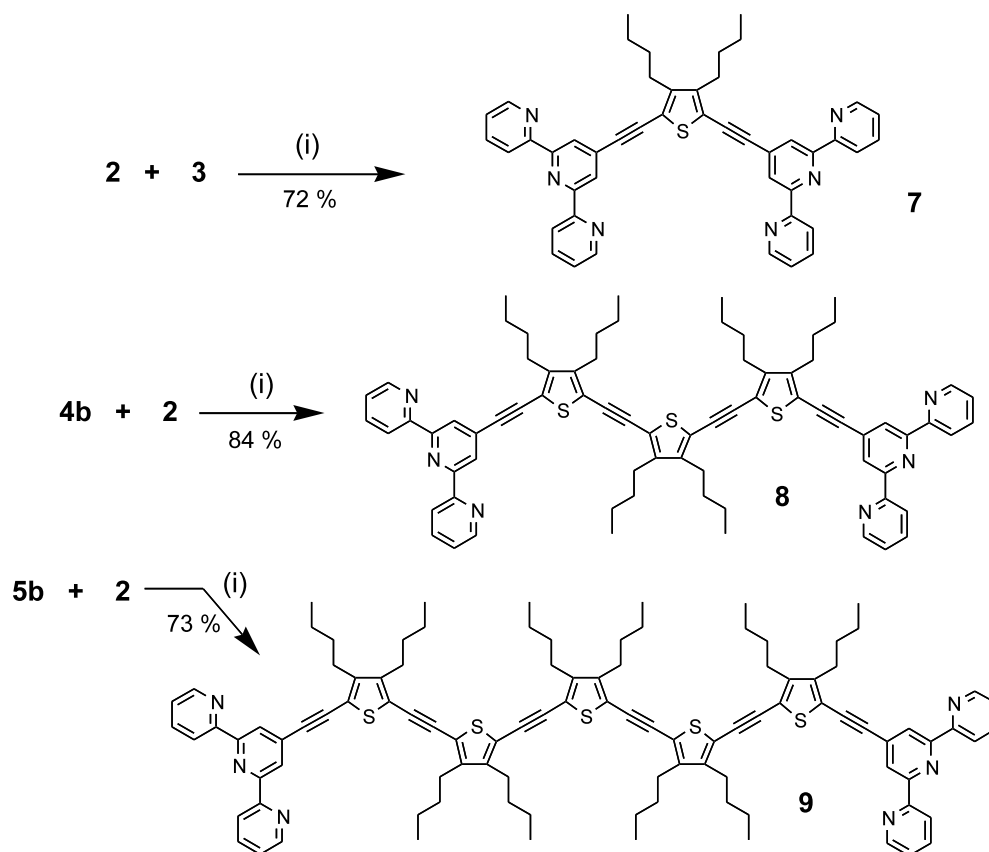
Product	Yield (%)	IR (cm $^{-1}$) ^a	UV-vis: λ/nm (ϵ , M $^{-1}$ cm $^{-1}$) ^b	MS ^c	$^{13}\text{C}\{^1\text{H}\}$ $\delta_{\text{C}\equiv\text{C}}$ (ppm) ^d
4a	82	2198	367 (31,920)	534.2	101.0; 93.8; 87.2; 75.3
4b	97	2200/2100	361 (66,070)	476.2	93.8; 87.0; 84.3; 76.8
5a	90	2197	425 (24,920)	752.2	100.7; 94.4; 89.6; 88.7; 87.2; 75.5
5b	86	2192/2093	425 (22,470)	694.3	94.4; 89.4; 88.7; 87.1; 84.1; 76.8
6	48	2197	410 (34,930)	970.2	100.6; 94.4; 89.7; 89.4; 89.3; 88.9; 87.2; 75.5
7	72	2198	391 (42,800)	707.2	94.6; 87.1
8	84	2196	428 (56,150)	1143.2	94.4; 89.7; 89.4; 87.3
9	73	2197	433 (47,500)	1581.3	94.9; 90.2; 90.0; 89.9; 89.8; 87.7
11	60	2196	409 (99,360)	925.3	94.4; 89.6; 87.3

^a $\nu_{\text{C}\equiv\text{C}}$ Stretching vibration measured in KBr pellets.

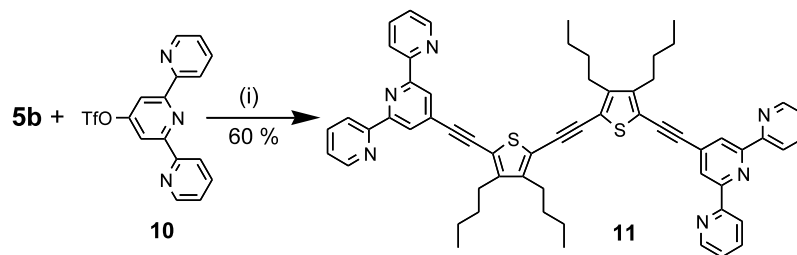
^b Less energetic absorption band measured in CH_2Cl_2 .

^c Obtained by FAB $^+$ using *meta*-nitrobenzyl alcohol as matrix and corresponds to the most intense mass peak and $[\text{M}+\text{H}]^+$.

^d In CDCl_3 .



Scheme 3. Reagents and conditions: (i) $[\text{Pd}(\text{PPh}_3)_4]$ (6 mol%), $n\text{PrNH}_2$, 60°C .



Scheme 4. Reagents and conditions: (i) $[\text{Pd}(\text{PPh}_3)_4]$ (6 mol%), $n\text{PrNH}_2$, 60°C .

The preparation of compound **11** was performed by a different way using a reaction between the building block **5b** and the triflate substituted derivative **10** (Scheme 4).²²

As might be expected, the *sp*-hybridized C atoms tend to give signals lying at similar chemical shifts as the chain grows longer but the expected number of signals is always reflected in the spectrum. The ^{13}C NMR spectra appear to be the finger-print of the resulting molecules and diagnostic for the purity. Furthermore, the observed carbon chemical shifts for all precursors and final ligands are in good agreement with those reported for other ethynylated derivatives. FT-IR spectra remain similar throughout the series, with the most pronounced bands occurring at $\nu=3000$, $1650\text{--}1100$, and between 850 and 620 cm^{-1} . The spectrum is dominated by vibrations associated with the aromatic rings but the acetylene stretching vibration, although rather weak, can be resolved and at about 2200 cm^{-1} in each case (see Table 1). Interestingly, for all novel compounds a very intense mass peak corresponding to the protonated form is observed which unambiguously confirmed the molecular structure of the thiophene based ligands. Upon increasing the number of inter-spread thiophene modules a significant lowering in energy of the less energetic absorption transition is always observed either for the mono-terpy derivatives or for the ditopic ligands. However, a clear saturation effect of the effective conjugation length is observed.

From the above results, we conclude that a homologous series of butylated α -conjugated oligothiophene back-to-back terpyridine ligands can be usefully elaborated. The use of a single tetra-substituted thiophene starting material allows the preparation of the ligands with an odd number of modules. For the series of ligands bearing an even number of modules the first molecule with $n=2$ was prepared via the use of a terpy template grafted with two thiophene modules and a terminal acetylenic function. While the preparation of higher oligomers remains a challenge we might envisage to use a synthetic protocol based on an acetylene bridged diiodo-dithiophene starting material. Due to their excellent solubility and stability, the characterization of the photophysical properties in dependence of the chain length leads to excellent structure–property relationships. This will be reported in the due course. Finally, this convergent synthetic strategy en route to multinuclear transition metal complexes paves the way

for a new generation of photoactive molecular-scale wires in which directional information transfer is expected. We are now developing a research program along these lines.

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