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Stepwise construction of rigid rod-like terpyridine ligands based on alternating ethynyl/phenyl modules

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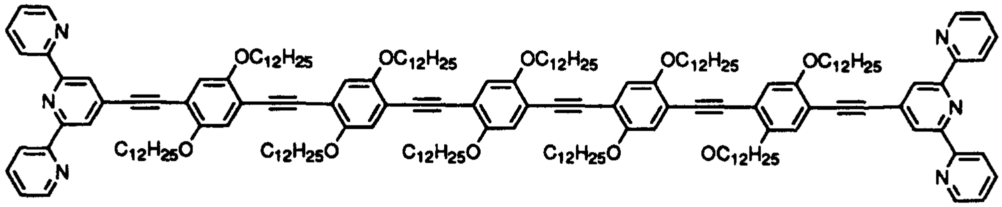
Abstract

We report the synthesis of novel soluble ditopic terpyridine ligands bearing an alternance of acetylenic/phenyl modules (one to five) built in the centre. The protocol is based on sequential Pd-promoted cross-coupling reaction between selected mono-terpy fragments and either mono-protected 1,4-diethynyl-2,5-di(dodecyloxy)benzene or 1,4-diethynyl-2,5-di(dodecyloxy)benzene synthons. The ligand bearing a central diethynyl spacer was prepared by an oxidative self-coupling reaction promoted by copper salts and O_2. © 1999 Elsevier Science Ltd. All rights reserved.

The increasing interest in molecule-based components for technologies has stimulated extensive research on nanoscale devices capable of performing useful light-induced functions.[1] Some 10 years ago we pursued a research program which had objectives to develop synthetic tools for the engineering of photoactive molecular-scale wires.[2] Since then we have demonstrated that polyacetylene spacers operate as extremely effective pathways for transporting electronic charge between photoactive terminals.[3] By careful design we have introduced directionality and selectivity into the photoactive dyads and consequently we were able to modulate the rate of triplet energy transfer by several orders of magnitude.[4]



Similar effects can be obtained with polycyclic hydrocarbons built into the spacer and in such cases, the energetics of the bridge can also be tuned over a wide range by varying the extent of conjugation in the aromatic moiety.[5,6] A special case can be identified where the polycycle itself possesses coordinating sites which on complexation can modulate the energy of the bridge.[7] An emerging problem of increasing the

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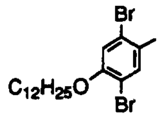
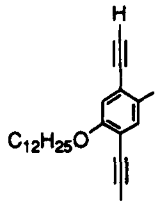
size of the system is the lowering of solubility. Therefore it is desirable to design soluble multicomponent molecules of nanometric dimension without loss of the effectiveness of the electronic conductivity. Solubility and tunability can be achieved for an increasing number of substituted diethynylphenyl subunits by functionalizing with two dodecyloxy moieties and spanning two back-to-back terpyridines.

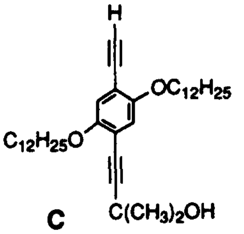
Here we show that this strategy is succesful in generating a family of rigid multitopic ligands where the edge-to-edge distance between the two central pyridine rings varies from 16 to 44 Å. The use of palladium promoted coupling reactions of terminal alkynes with pyridinic halides is a straightforward method for the synthesis of pyridinealkynes,[8] and a subsequent selective deprotection sequence allows the synthesis of the key intermediates **B** to **D** using 1,4-dibromo-2,5-di(dodecyloxy)benzene **A** as a starting material.[9]



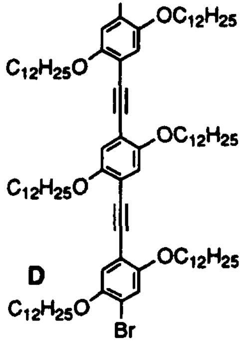
A



B

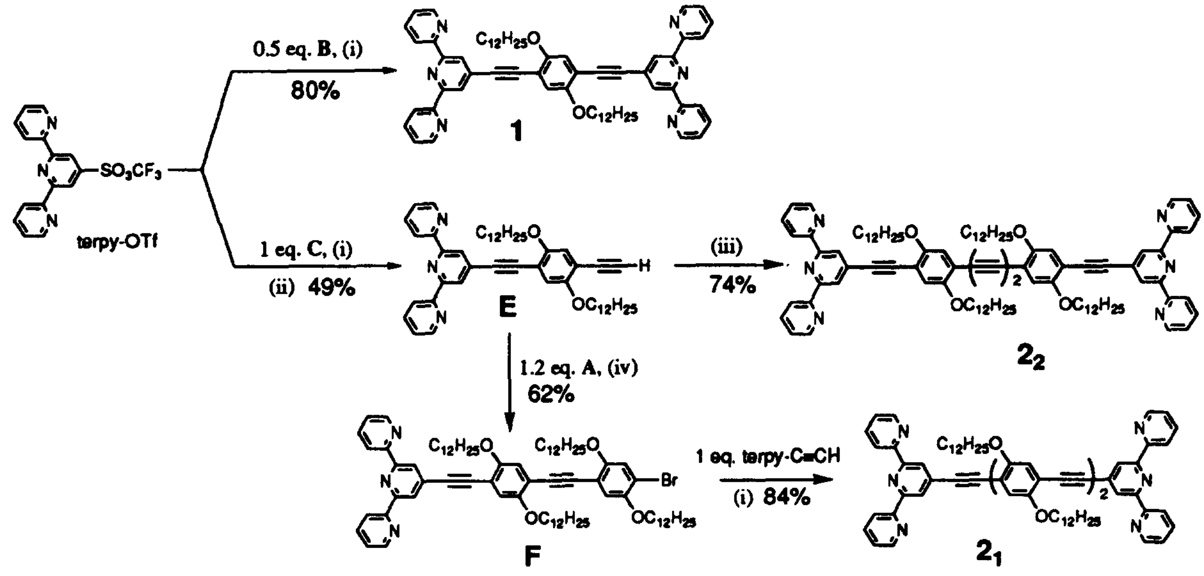


C



D

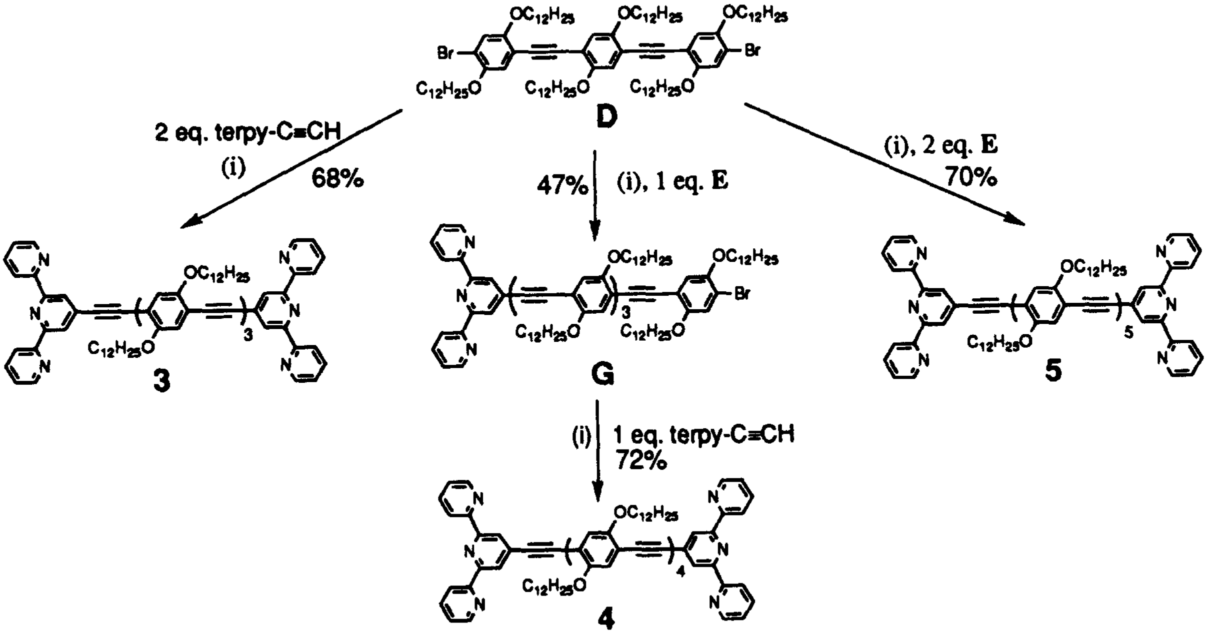
Ditopic ligand **1** bearing one diethynylphenyl module was prepared in good yield, according to Scheme 1, by the double cross-coupling reaction of **B** and two equiv. of the 4′-[{(trifluoromethyl)sulfonyl}oxy]-2,2′:6′,6″-terpyridine (terpy-OTf)[10] using [Pd^0(PPh$_3$)$_4$] (6 mol%) as catalyst and excess ^{i}Pr$_2$NH as base.[11]



Scheme 1. (i) [Pd(PPh$_3$)$_4$], benzene, ^{i}Pr$_2$NH, 60°C; (ii) NaOH excess, benzene, 80°C, 70%; (iii) 0.5 equiv. CuCl, 0.5 equiv. TMEDA, CH$_3$CN, O$_2$, rt; (iv) [Pd(PPh$_3$)$_4$], ^{n}PrNH$_2$, 70°C

Reaction of terpy-OTf with **C** afforded, after deprotection in basic conditions, intermediate **E**. This compound was then allowed to react with **A** to give a second intermediate **F**. Then cross-coupling of **F** with 4′-ethynyl-2,2′:6′,6″-terpyridine (terpy-C≡CH)^{12} afforded ligand $\mathbf{2_1}$. Oxidative self-coupling of **E** with CuCl, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and molecular oxygen^{13} afforded ligand $\mathbf{2_2}$ in fair yield as outlined in Scheme 1.

This rational design has been extended to the construction of longer rod-like ditopic ligands as sketched in Scheme 2. Here, the pivotal synthon **D** [prepared from 2 equiv. **A** and 1 equiv. **B** in 81% isolated yield] was allowed to react, under Pd-catalyzed conditions, with 2 equiv. of terpy-C≡CH to produce ligand **3**. Cross-coupling of compound **D** with **E** afforded under stoichiometric conditions and after tedious chromatography separation intermediate **G** in modest yield. When an analogous reaction was carried out with 2 equiv. of **E** and 1 equiv. of **D**, ligand **5** was isolated in good yield.



Scheme 2. (i) [Pd(PPh$_3$)$_4$], ^{n}PrNH$_2$, 70°C

The desired products obtained in satisfactory yields were highly soluble in most common solvents and photostable and characterized by ^{1}H, ^{13}C{^{1}H} NMR, FAB$^+$MS, UV–vis and IR spectroscopies. All data was consistent with the proposed structures (see Table 1 for selected analytical data). A typical NMR spectrum for compound **5** is given in the References.^{14}

The observed carbon and proton chemical shifts for all the precursors and the ligands **1**, $\mathbf{2_1}$, $\mathbf{2_2}$, **3**–**5** are in good agreement with those reported for other ethynyl-derivatives.^{8,11,15} By progressive increase of the number of ethynyl/phenyl modules, a bathochromic shift of the less energetic absorption band was observed. It is worth noting that with the diethynyl spacing unit a hyperchromic behaviour is simultaneously observed. This substantiates the conclusion that based on UV–vis absorption spectroscopy the energetic level of the spacer will not significantly perturb the photophysical properties of the external transition metal chromophores.

In conclusion, we have designed and synthesized novel rigid rod-like ditopic ligands by sequential deprotection coupling steps leading to appropriate intermediates. The availability of these molecules makes them ideal building blocks for the preparation of luminescent transition metal complexes. These complexes will be highly soluble in non-polar solvents and are susceptible to segregation into organized microstructures. We believe that this system has sufficient simplicity and versatility to be the object of a

Table 1
Selected data for the novel back-to-back terpyridine ligands

Product	Overall Yield (%)$^{a)}$	m.p. (°C)	IR (cm^{-1})$^{b)}$	UV-Vis λ nm, (ε, M^{-1} cm^{-1})$^{c)}$	MS$^{d)}$	$^{13}C\{^1H\}$ $\delta_{C\equiv C}$ (ppm)$^{e)}$
1	80	167/168	2212	383 (29 600)	958.0	93.1, 90.4
2_1	26	172/173	2205	408 (58 300)	1426.0	92.9, 91.9, 90.7
2_2	36	102/103	2210	406 (75 800)	1112.0	93.4, 90.3, 79.6
3	55	182/183	2207	419 (45 000)	1895.0	92.8, 92.0, 91.5, 90.7
4	27	155/156	2208	424 (45 200)	2362.7	92.8, 92.0, 91.7, 91.5, 90.7
5	57	142/143	2207	433 (43 700)	2831.8	93.5, 92.8, 92.0, 91.6, 91.4, 90.7

a) Calculated from the successive steps from the starting compounds terpy-OTf or **A**; b) $\nu_{C\equiv C}$ stretching vibration measured in KBr pellets; c) less energetic absorption band measured in CH_2Cl_2; d) obtained by FAB$^+$ using *meta*-nitrobenzylalcohol as matrix and correspond to $[M+H]^+$ except for **2_1** and **2_2** which correspond to $[M]^+$; e) in $CDCl_3$.

systematic study of the influence of the length of the spacer on information transfer along the molecular axis. The study of their photophysical and electrochemical properties and extension of this methodology to even larger compounds is currently under active investigation and will afford ample opportunity to verify their efficiency as electronic mediators.

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9. Prepared from 1,4-di(dodecyloxy)benzene and Br_2 (4 equiv.) under reflux in CCl_4: ^1H NMR ($CDCl_3$, 20°C): δ 7.09 (s, 2H), 3.91 (t, $^3J_{H-H}$=6.3 Hz, OCH_2, 4H), 1.80 (m, 4H), 1.26 (m, 36H), 0.85 (t, $^3J_{H-H}$=6.6 Hz, CH_3, 6H).
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