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Photoactive Molecular-scale Wires: Synthesis of Carotene/Terpyridine Ditopic Ligands

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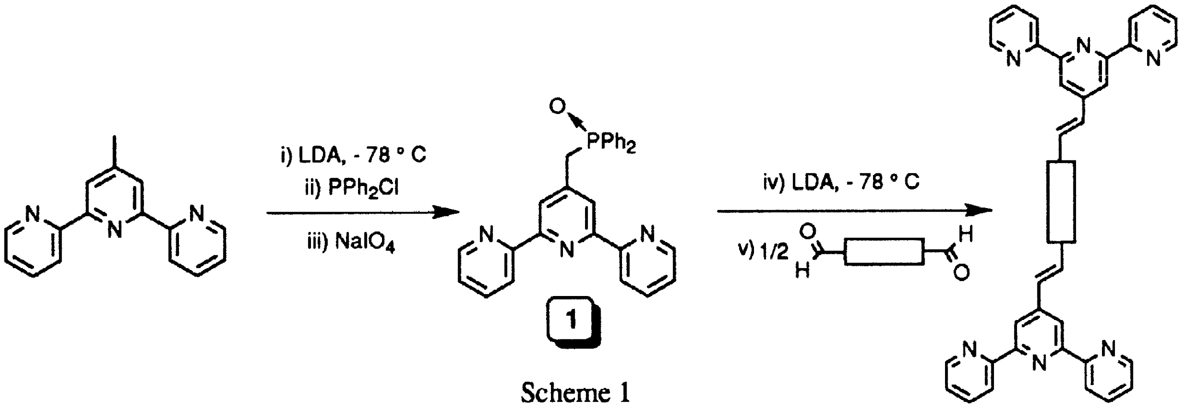
Abstract: We report the preparation of multi-component molecules based on carotene-substituted 2,2':6',6"-terpyridine ligands. The synthetic protocol based on a double Wittig-Horner coupling reaction uses 4'-methyldiphenylphosphinoxide-2,2':6',2"-terpyridine and the relevant carotene bis-aldehyde. The all-*trans* conformation of the double bonds is confirmed by proton NMR. Highly colored and redox-active ruthenium(II) dinuclear complexes have also been prepared and characterized.

The preparation of multi-component molecular systems comprising discrete redox and/or photoactive moieties separated by well-defined spacer groups have been widely studied over the last decade.[1-4] The integration of polyacetylenes into multi-site ligands[5] has been shown to produce extremely effective photoactive molecular-scale wires for conducting electronic charges between redox-active terminals and is now considered as a major corner-stone of this subject.[1,3,6] Furthermore, we have shown that joining ethynylene groups into a short polyacetylene wire causes only a small attenuation in the electronic conductivity with incremental numbers of acetylenic functions.[7]

The effect of hybridization of carbon bridges, in terpyridine (terpy) based systems, on the electronic properties is comparable for a double bond and a triple bond but is essentially non existent in the saturated bridges.[8] Bipyridine systems constructed with double bonds have received some attention in the past.[9,10] As part of our continuing interest in the engineering of larger molecules we have now designed and prepared novel systems in which the spacers consist of carotenes spanning two terpyridine fragments.



Scheme 1

The synthetic protocol described here allows the preparation of ligands bearing five, seven or nine double bonds (**2** to **4**) and four or six double bonds attached symmetrically to a central triple bond (**5** and **6**).

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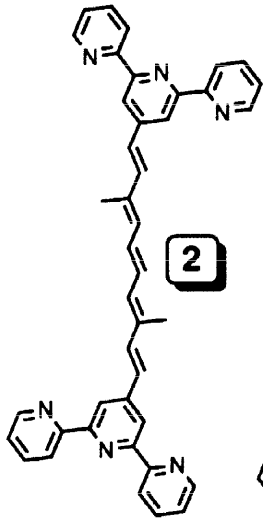
These *caro-terpy* ligands were prepared by a double Wittig-Horner coupling reaction from 4'-methyldiphenylphosphinoxide-2,2':6',2"-terpyridine derivative **1** as outlined in Scheme 1. During the course of the reaction the desired ditopic ligands precipitate from the reaction mixture, driving the reaction to completion within a couple days. The pure ligands were obtained, in excellent yields, after centrifugation, and were characterized using classical techniques including elemental analyses. On the basis of spectroscopic evidence, the molecular structures of the multi-component molecules were unequivocally authenticated (see Table I for selected data). In particular, the ^{1}H-NMR spectra for all five ligands exhibit in the aromatic region five well-defined patterns corresponding to the pyridinic hydrogen atoms, an AB quartet for the vinylic hydrogen adjacent to the central pyridine and additional vinylic hydrogens at lower frequency (6.7 to 5.9 ppm). The methyl groups resonnate as singlets at ca 2.10 ppm. A typical NMR spectra is given in ref 11.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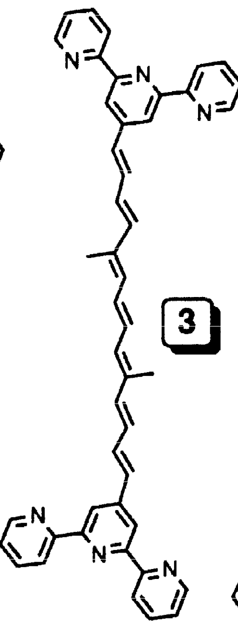
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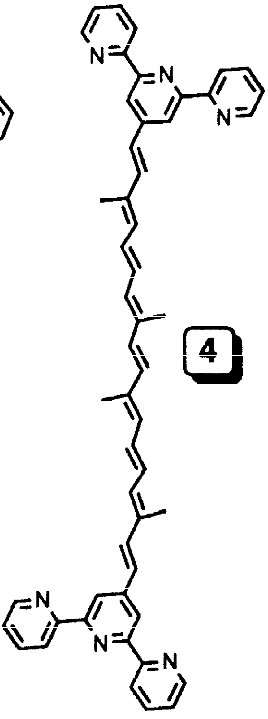
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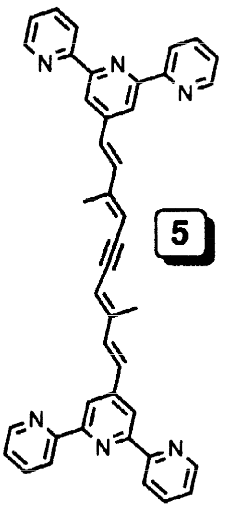
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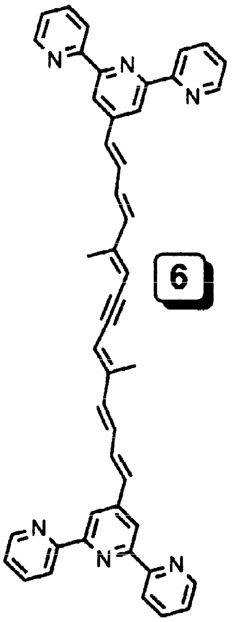
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^{1}H-NMR analyses showed that, as expected by the type of coupling reaction which has been used, the ligands have an all-*trans* conformation of the polyenic framework with a characteristic coupling constant found between 15 and 16 Hz for the vinylic protons attached to the terpy subunit.[12] The UV-Vis. absorption spectra of the *caro-terpy* ligands show clearly the features of their terpy and carotene moieties. The high energy absorption band are due to π-π* transitions of the protonated terpy units and the less energetic absorption bands due to π-π* transitions of the conjugated polyenic bridge. A significant bathochromic shift estimated to *ca* 20 nm per incremental double bonds have been found. When a triple bond is present in the spacer a hypsochromic shift in the range of 65 to 50 nm is observed which is representative of a weakening of the electronic conjugation between both chelating centres. The corresponding ruthenium(II) dinuclear complexes are prepared by reaction of the free ligand with a silver dehalogenated solution of

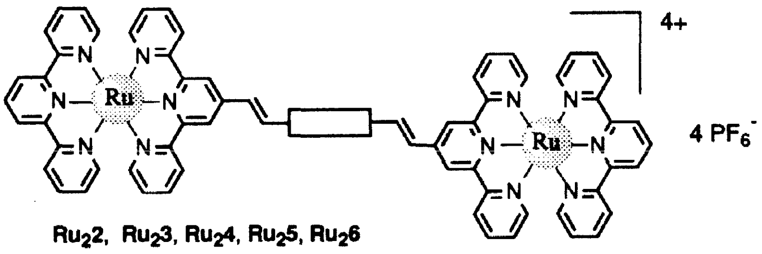
$[Ru(DMSO)_4Cl_2]$[13] in methanol. Purification of these highly colored dinuclear complexes were carried out by careful chromatography on silica with $CH_3CN/H_2O/KNO_3$sat. as eluent.

Table I. Selected spectroscopic data for ligands **2** to **6**

Ligand	Isolated Yield (%)	IR ($\nu_{C=C}$, cm^{-1}) [a)]	UV-Vis λ, nm (ε, $M^{-1}cm^{-1}$) [b)]	Mass spectrum [c)]
2	98	1575	505 (12,300), 483 (12,200), 331 (15,600), 285 (7,200)	623.2
3	71	1584	532 (9,430), 319 (6,500), 287 (4,900)	675.3
4	94	1591	540 (sh, 5,200), 428 (sh, 5,500), 319 (14,000), 285 (15,100)	755.3
5	75	1576	439 (19,400), 324 (18,900), 283 (16,100)	621.3
6	77	1573	483 (20,600), 323 (13,900), 285 (12,600)	673.3

a) $\nu_{C=C}$ stretching vibration measured in KBr pellets; b) π-π* absorption bands measured in CH_2Cl_2/trifluoroacetic acid (0.01 M); c) obtained by FAB^+ using *meta*-nitrobenzylalcohol + 1 % trifluorosulfonic acid as matrix and correspond to *m/z* $[M+H]^+$.

Elimination of excess nitrate and metathesis of the anion for PF_6 afforded the analytically pure red to deep-violet complexes which have also been fully characterized (selected data given in Table II).



Ru₂2, Ru₂3, Ru₂4, Ru₂5, Ru₂6

Table II. Selected data for dinuclear complexes **Ru_2(2-6)**

Complex	R_f [a)]	IR ($\nu_{C=C}$, cm^{-1}) [b)]	UV-Vis λ nm, (ε, $M^{-1}cm^{-1}$) [c)]	Mass spectrum [d)]
$Ru_2$2	0.45	1594	531 (71,100), 430 (39,400)	1727.2, 1582.2, 1437.2
$Ru_2$3	0.49	1595	567 (53,100), 534 (55,100), 453 (31,600)	1779.0, 1634.0, 1489.0, 1344.1
$Ru_2$4	0.60	1596	584 (56,800), 547 (57,300), 471 (33,200)	1859.3, 1714.3, 1569.3, 1424.3
$Ru_2$5	0.40	1603	516 (95,800), 411 (54,700)	1725.4, 1580.4, 1435.2, 1290.3
$Ru_2$6	0.49	1601	525 (117,700), 433 (66,900)	1777.1, 1632.1, 1487.2, 1342.5

a) On silica sheets using $CH_3CN/H_2O/KNO_3$ sat. 50/15/1 as eluent; b) $\nu_{C=C}$ stretching vibration measured in KBr pellets; c) MLCT and π-π*(carotene + terpy) absorption bands measured in acetone; d) obtained by FAB^+ using *meta*-nitrobenzylalcohol as matrix and correspond to *m/z* $[M - PF_6]^+$, $[M - 2PF_6]^+$, $[M - 3PF_6]^+$, $[M - 4PF_6]^+$ respectively from the highest to the lowest mass peak.

The absorption spectra recorded for the bipartite system comprising terminal Ru(terpy) bridged by the *caro-terpy* ligands show that the chromophores of each component are quite well resolved. All complexes feature very intense bands, with shape and position similar to the absorption spectra of the respective protonated ligands, in addition to well defined metal-to-ligand charge transfer (MLCT) transitions in the range of 410 to 470 nm with molar absorption coefficient of *ca* 15,000 $M^{-1}cm^{-1}$ for the only polyenic complexes and *ca* 30,000 $M^{-1}cm^{-1}$ per Ru centre for the hybrid compounds. Small perturbations on position and intensity are expected and indeed observed for the complexes bearing a triple bond due to the presence of π-π^* absorption found in the free ligands. Dinuclear ruthenium(II) complexes also exhibit well-defined redox properties due to the redox activity of the Ru, carotene, bridged terpy and parent terpy moieties.

In summary, we have constructed novel dinuclear ruthenium(II) complexes bearing *caro-terpy* bridging ligands which display a metal-metal separation varying from 22.8 Å (in **$Ru_2$2**) to 32.6 Å (in **$Ru_2$4**). The efficiency of the synthetic method, and the potential utility of starting material **1**, make this methodology an important contribution to the synthesis of 4'-substituted terpyridines. Analysis of the redox and photophysical properties of these complexes especially time-resolved triplet energy emission in the far infra-red, determination of reorganization energies and electronic-coupling matrix elements in the corresponding mixed-valence complexes are currently under study and will be reported in the near future.

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11. ^{1}H-NMR for *caro-terpy* **2** ($CDCl_3$, 25 °C, 200.1 MHz) $\delta = 8.73$ (dd, 4H, $^3J = 4.8$ Hz, $^4J = 1.0$ Hz, $H_{6,6''}$), 8.64 (d, 4H, $^3J = 7.9$ Hz $H_{3,3''}$), 8.50 (s, 4H, $H_{3',5'}$), 7.90 (m, 4H, $H_{4,4''}$), 7.40 (m, 6H, $H_{6,6''} + H_{vinyl}$), 7.07 (AB quartet, 4H, $J_{AB} = 15$ Hz, $\Delta\nu = 120.4$ Hz, H_{vinyl}), 6.76 (m, 2H, H_{vinyl}), 6.50 (m, 2H, H_{vinyl}), 2.10 (s, 6H, CH_3). Elemental analysis calculated for $C_{42}H_{34}N_6$ ($M_r = 622.76$); C, 81.00, H, 5.50, N, 13.49. Found: C, 80.89, H 5.36, N, 13.37.
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