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Synthesis and Coordination Studies of New Mono- and Di-Hydroxy Functionalized 4,4'-dialkenyl-2,2'-Bipyridines.

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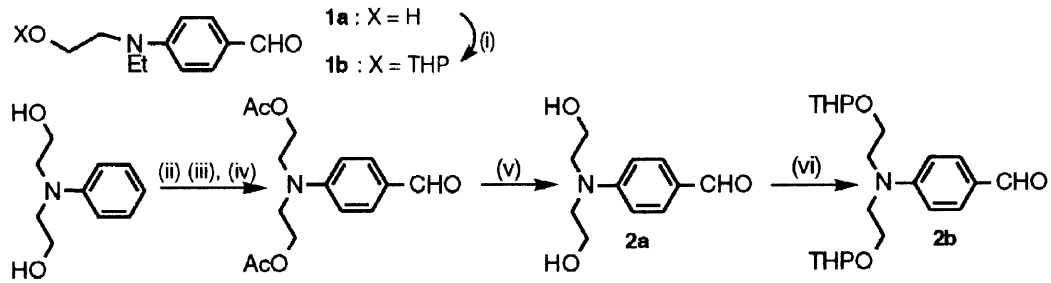
Abstract : A convenient and large scale preparation of new mono- and bis-hydroxy substituted 4,4'-bis(dialkylaminostyryl)-2,2'-bipyridines is reported. Their coordination studies to $[Ru(DEAS\text{-}bpy)_2]^{2+}$ (DEAS-bpy = 4,4'-bis(diethylaminostyryl)-2,2'-bipyridine) are also described. © 1998 Elsevier Science Ltd. All rights reserved.

Second order nonlinear(NLO) materials are particularly promising for electroptic device applications[1]. A current approach for the design of NLO materials is the covalent attachment of NLO-phores onto a polymer backbone[2,3]. This approach generally requires the introduction of appropriate reactive functionalities, such as hydroxy groups, at the electron donating site of the chromophore. Recently, we have shown that large nonlinearities can be achieved by dipolar[4,5] and especially octupolar[6] metal complexes containing bipyridine ligands substituted in 4,4'-positions by dialkylaminostyryl groups[7,8]. Therefore it should be of interest to investigate the incorporation of these chromophores into macromolecular architectures. To this end, we have designed mono- and bis- hydroxy substituted 4,4'-bis(dialkylaminostyryl)-2,2'-bipyridines. Herein we describe a convenient synthesis of these new ligands and we report their coordination studies to ruthenium(II) center.

The 4,4'-dialkenyl-2,2'-bipyridyl ligands **4-6** were typically prepared on a 5g scale from 4,4'-dimethyl-2,2'-bipyridine and the appropriate aldehydes[9-11]. The aldehyde precursor **1a** was obtained in 90 % yield by using the published procedure[12,13], *ie.* in one step from 4-fluorobenzaldehyde and N-ethylaminoethanol. The synthesis of the aldehyde **2a** required a longer but high yield procedure (73 %) starting from bis(2-hydroxyethyl)aniline, *via* acylation of the hydroxy groups, followed by a Vilsmeier formylation and cleavage of the acetate groups (Scheme 1). Aldehydes **1a** and **2a** were then quantitatively protected as their tetrahydropyranyl ethers **1b** and **2b**.



Scheme 1. *Reagents and conditions :* (i) DHP (2.5 equiv.), PTPS (0.2 equiv.),CH_2Cl_2, rt, 24h, 99%. (ii) AcCl (2.2 equiv.), Et_3N (2.2 equiv.), THF, 35°C, 15h, 99%. (iii) $POCl_3$ (1.1 equiv.), DMF, 70°C, 6h. (iv) AcONa (4.0 equiv.), H_2O, rt, 1h, 83%. (v) Na_2CO_3 (2.1 equiv.), MeOH-H_2O, rt, 15h, 99%. (vi) DHP (5.0 equiv.), PTPS (0.4 equiv.),CH_2Cl_2, rt, 24h, 90%.

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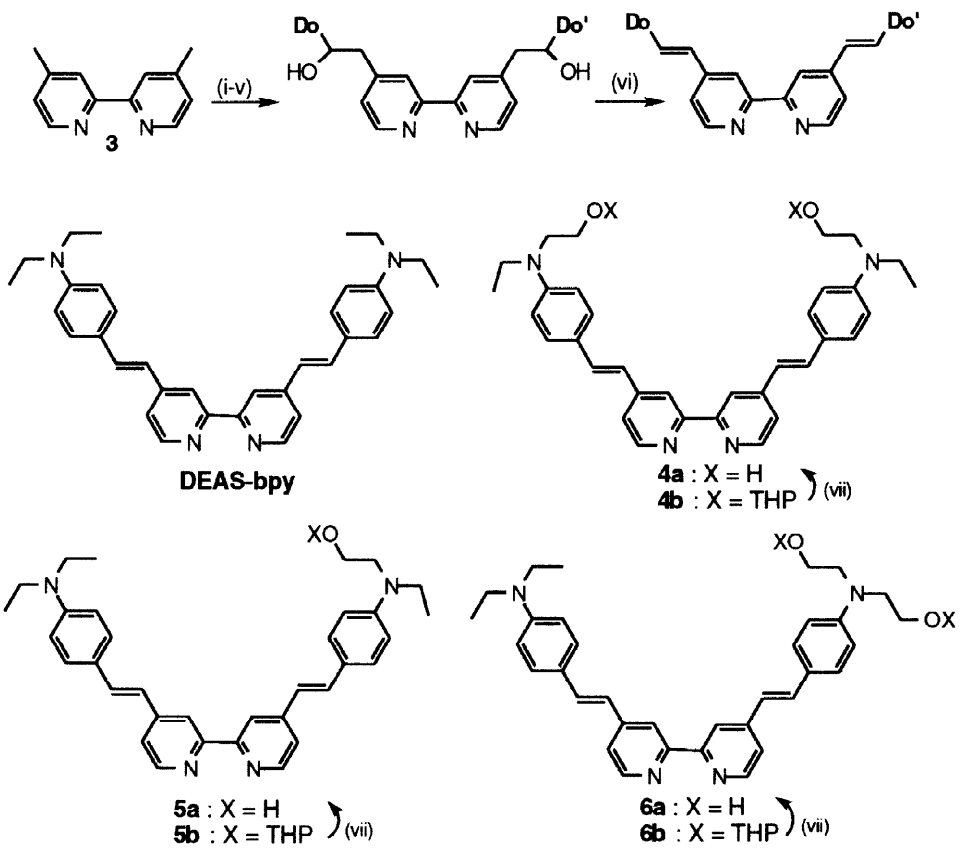
The symmetrical disubstituted bipyridine **4b** was obtained in 70 % yield upon dilithiation of **3**, subsequent addition of **1b** (2 equiv.) and dehydration of the resulting diol using pyridinium toluene-*p*-sulfonate (PTPS). The unsymmetrical disubstituted bipyridine **5b** was conveniently prepared (85 %) from **3**, using a step by step lithiation and the successive addition of *p*-diethylaminobenzaldehyde and **1b** (Scheme 2). Compound **6b** was synthetized by the same procedure in 60 % yield. Finally, THP deprotection with HCl (6N) in refluxing ethanol afforded the desired bipyridines **4a**, **5a** and **6a** in 95 % yield (Scheme 2)[14]. Table 1 summarizes selected data for the new ligands.

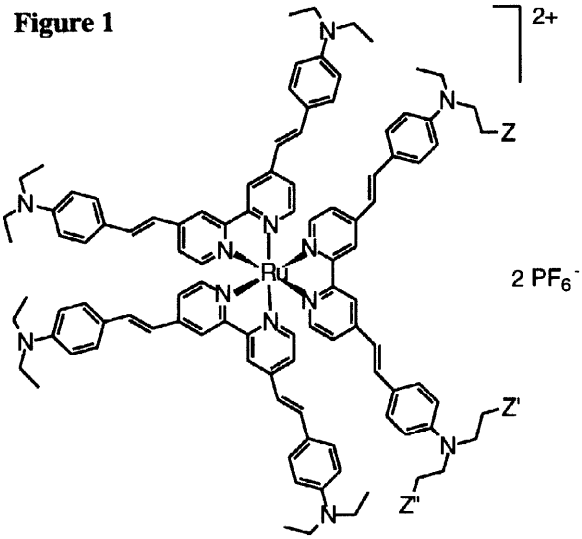


Scheme 2. *Reagents and conditions :* (i) LDA (1.0 equiv.), THF, -78°C, 1h. (ii) **Do**-CHO (1.0 equiv.), THF, -78°C to rt, 15h. (iii) LDA (1.0 equiv.), THF, -78°C, 1h. (iv) **Do'**-CHO (1.0 equiv.), THF, -78°C to rt, 15h. (v) H_2O, rt, 1h. (vi) PTPS (0.1 equiv.), toluene, 110°C, 6h. (vii) HCl (6N) (0.5 equiv.), EtOH-H_2O, 80°C, 15h.

The synthetic methodology for the preparation of tris-bipyridyl ruthenium(II) complexes **8-10** was based on the sequential coordination of the "parent" ligand 4,4'-bis(*p*-diethylaminostyryl)-2,2'-bipyridine (DEAS-bpy)[9] and of the appropriate hydroxy-functionalized bipyridines **4a-6a**. Reaction of $RuCl_3.3H_2O$ with two equivalents of DEAS-bpy and an excess of lithium chloride in refluxing DMF yielded $Ru(DEAS\text{-}bpy)_2Cl_2$ **7** in 90 % yield

6,15. Reaction of **7** with ligands **4a-6a** (1 equiv.) gave the cations **8-10**, which were precipitated as their hexafluorophosphate salts, in 85-90 % yield[16] (Figure 1).

Figure 1



8a : Z = Z' = OH ; Z'' = H
9a : Z = Z' = H ; Z''= OH
10a : Z = H ; Z'= Z''= OH

These complexes were unambiguously identified by ^1H NMR, UV visible and high resolution FAB mass spectrometry (Table 1). The convenient synthesis of these new hydroxy functionalized octupolar complexes opens the way for the construction of polymetallic materials such as metallo-dendrimers and polymers. This work is currently under way in our laboratory.

Table 1. Selected spectral data for ligands and complexes.

Compound	MS[a]	UV-Visible[e] λnm(ε, $M^{-1}cm^{-1}$)
4a	535.3092 (535.3073)[b]	387(55700)
4b	703.4207 (703.4223)[b]	392(58800)
5a	519.3118 (519.3124)[b]	389(43100)
5b	603.3706 (603.3699)[b]	393(55200)
6a	534.2995 (534.2994)	386(47900)
6b	703.4225 (703.4223)[b]	390(61100)
7	1176.4627 (1176(4613)[c]	608(33000), 428(95700)
8a	1785.7908 (1785.7873)[d]	509(151000)
9a	1769.7967 (1769.7924)[d]	517(139000)
10a	1785.7908 (1785.7873)[d]	514(136000)

[a] Observed and (in parenthesis) calculated FAB+ high resolution mass spectrum. [b] $[M + H]^+$. [c] $[M]^+$. [d] $[M - PF_6]^+$. [e] in dichloromethane.

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14. **4a** ^{1}H nmr (200 MHz, $CDCl_3$) δ 8.59 (d, J = 5.2 Hz, 2H), 8.46 (s, 2H), 7.43 (d, J = 8.8 Hz, 4H), 7.38 (d, J = 16.4 Hz, 2H), 7.32 (dd, J = 5.2 and 1.5 Hz, 2H), 6.89 (d, J = 16.4 Hz, 2H), 6.74 (d, J = 8.8 Hz, 4H), 3.82 (t, J = 5.5 Hz, 4H), 3.51 (t, J = 5.5 Hz, 4H), 3.45 (q, J = 7 Hz, 4H), 1.18 (t, J = 7 Hz, 6H). **5a** ^{1}H nmr (200 MHz, $CDCl_3$) δ 8.59 (d, J = 4.8 Hz, 1H), 8.58 (d, J = 5 Hz, 1H), 8.45 (s, 2H), 7.42 (d, J = 8.8 Hz, 4H), 7.37 (d, J = 16.3 Hz, 2H), 7.37 (d, J = 16.3 Hz, 1H), 7.32 (dd, J = 5.3 and 1.5 Hz, 4H), 6.89 (d, J = 16.3 Hz, 1H), 6.87 (d, J = 16.3 Hz, 1H), 6.73 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.81 (t, J = 5.7 Hz, 2H), 3.53-3.32 (m, 8H), 1.60 (s, 1H), 1.17 (t, J = 7 Hz, 9H). **6a** ^{1}H nmr (200 MHz, $CDCl_3$) δ 8.59 (δ, J = 4.8 Hz, 1H), 8.57 (d, J = 4.8 Hz, 1H), 8.45 (s, 2H), 7.41 (d, J = 8 Hz, 4H), 7.37 (d, J = 16.4 Hz, 2H), 7.31 (d, J = 4.6 Hz, 4H), 6.90 (d, J = 16.1 Hz, 1H) 6.87 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 8 Hz, 2H) 6.65 (d, J = 8.5 Hz, 2H), 3.89 (t, J = 4.5 Hz, 4H), 3.63 (t, J = 4.5 Hz, 4H), 3.88 (q, J = 7 Hz, 4H), 1.17 (t, J = 7 Hz, 6H).
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16. **8a** ^{1}H nmr (200 MHz, CD_2Cl_2) δ 8.39 (s, 2H), 8.37 (s, 4H), 7.60-7.23 (m, 30H), 6.97 (d, J = 16.2 Hz, 2H), 6.94 (d, J = 16.2 Hz, 2H), 6.74 (d, J = 9 Hz, 4H), 6.66 (d, J = 8.7 Hz, 8H), 3.77 (t, J = 5 Hz, 4H), 3.51-3.16 (m, 24H), 1.16 (t, J = 6.8 Hz, 30H). **9a** ^{1}H nmr (200 MHz, CD_2Cl_2) δ 8.38 (s, 6H), 7.56-7.29 (m, 30H), 6.97 (d, J = 16 Hz, 1H), 6.94 (d, J = 16 Hz, 5H), 6.74 (d, J = 9 Hz, 2H), 6.66 (d, J = 8.9 Hz, 10 H), 3.77 (t, J = 5.5 Hz, 2H), 3.52-3.24 (m, 24H), 1.16 (t, J = 7 Hz, 33H). **10a** ^{1}H nmr (200 MHz, CD_2Cl_2) δ 8.40 (s, 6H), 7.58-7.32 (m, 30H), 7.00 (d, J = 16 Hz, 1H), 6.94 (d, J = 16 Hz, 5H), 6.73 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.8 Hz, 10H), 3.84 (t, J = 4.6 Hz, 4H), 3.62 (t, J = 4.6 Hz, 4H), 3.44-3.34 (m, 20H), 1.16 (t, J = 7.0 Hz, 30H).