Hydroxy-Functionalized Bipyridine and Tris(bipyridine)metal Chromophores: Synthesis and Optical Properties

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A new family of symmetrically and unsymmetrically-substituted 4,4′-bis[(dialkylamino)styryl]-2,2′-bipyridine ligands, containing 1–4 hydroxy groups on their dialkylamino moieties, have been synthesized. They are readily prepared in good to excellent yields from 4,4′-dimethyl-2,2′-bipyridine and tetrahydropyranyloxy-protected [(hydroxyalkyl)amino]-benzaldehydes. These chromophores display excellent thermal stabilities, with decomposition temperatures of up to 310 °C. The influence of the OH groups on the optical properties (absorption and emission) is discussed. The synthesis of the corresponding heteroleptic and homoleptic tris(bipyridine)-metal(II) complexes (M^{2+} = Ru^{2+}, Zn^{2+}), as building blocks for the elaboration of macromolecular NLO-phores, is also described.

Introduction

Nonlinear optical (NLO) materials, and more recently nanomaterials,[1] have been developed because of their potential applications in integrated photonic devices.[2] Extensive efforts are being concentrated towards the design of macroscopic assemblies such as polymers and dendrimers featuring highly active and thermally stable NLO-phores.[3] Traditionally, NLO-phores are dipolar push-pull chromophores, and the centrosymmetry of the resulting material is broken by use of thermally assisted electrical poling. An alternative approach based on the concept of octupolar nonlinearity emerged in the early 1990s and triggered the advent of a new field of research.[4] In this context, we have recently shown that metal ions act as powerful three-dimensional templates to provide a variety of octupolar arrangements.[5] Moreover, we recently reported the incorporation of octupolar metallochromophores such as tris{[(dibutylamino)styryl]-2,2′-bipyridine}ruthenium(II) complexes[5d] into a polyimide backbone[6] and on a metallodendrimer.[7] To this end, we sought to introduce an appropriate reactive functionality, such as a hydroxy group, at the amino electron-donating site of bis[(dialkylamino)-styryl]-2,2′-bipyridines for the following reasons: (i) among the large variety of recently prepared bipyridine chromophores,[8] bis[(dialkylamino)styryl]-2,2′-bipyridines represent the best balance in terms of NLO efficiency and thermal stability, (ii) the hydroxy group is a versatile function that can be used for the synthesis of multipodal ligands (unsymmetrical ligands) or easily transformed into amino or ester groups for access to polyimides or star polymers by metal-catalyzed atom-transfer radical polymerization (symmetrical ligands).[9]

This article describes a new family of 4,4′-bis[(dialkylamino)styryl]-2,2′-bipyridine ligands bearing 1−4 hydroxy functions at their peripheries.[10] The synthetic procedure allows the preparation of the target ligand on a multigram scale. Furthermore, we show that the introduction of hydroxy function(s) does not significantly affect the intrinsic properties of the ligand [i.e., thermal stability and linear optical behavior (absorption and emission)]. The last part of this article deals with the preparation of hydroxy-functionalized ruthenium and zinc octupolar complexes.

Results and Discussion

Synthesis

The hydroxy function was introduced at an early stage of the synthesis, which consists of a Knoevenagel-type condensation between the appropriate aldehyde and 4,4′-dimethyl-2,2′-bipyridine.[11] By this methodology, one or two hydroxy moieties had to be introduced into (diethylamino)-benzaldehyde (**b**, **c**, Scheme 1). As the preparation of polyimides from these ligands was limited by solubility problems,[6] we decided to develop a more soluble monomer precursor **e**, containing C_4 alkyl substituents. The aldehydes **b**, **c** and **e** were obtained from the corresponding anilines **1b**, **1c** and **1e** by a classical three-step preparation[12] involving (i) the acetylation of the hydroxy function, (ii) a

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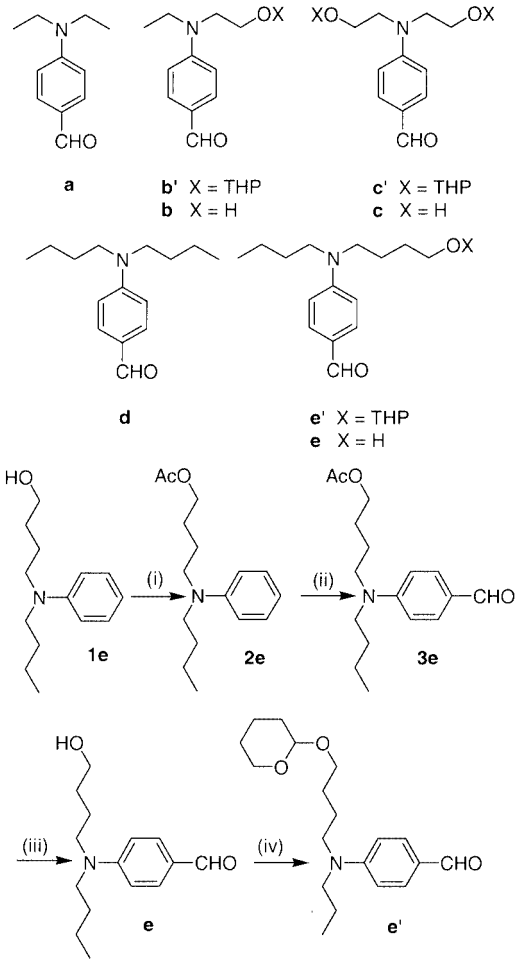


Scheme 1. Preparation of hydroxy-functionalized (dialkylamino)-benzaldehyde; (i) AcCl (2.2 equiv.), NEt_3 (2.2 equiv.), THF, 35 °C, 15 h, 97%; (ii) $POCl_3$ (1.1 equiv.), DMF, 70 °C, 6 h, followed by AcONa (4 equiv.), H_2O, room temp., 1 h, 97%; (iii) Na_2CO_3 (2.1 equiv.), MeOH/H_2O, room temp., 15 h, 97%; (iv) DHP (5 equiv.), PPTS (0.4 equiv.), CH_2Cl_2, room temp., 24 h, 99%

Vilsmeier−Haack formylation and (iii) the cleavage of the acetate group. All reactions were carried out on a large scale (5−20 g) with excellent overall yields (**b**: 84%; **c**: 81%; **e**: 88%). These aldehydes were then quantitatively protected as their tetrahydropyranyl (THP) ethers (**b′**,[13] **c′**, **e′**). The noncommercially available aniline **1e** was prepared by alkylation of *N*-butylaniline with 2-(4-Bromobutyl)tetrahydropyran, followed by removal of the THP moiety (see Exp. Sect.).

The symmetrical bipyridines **6bb**, **6cc** and **6ee** (Figure 1) were classically obtained in 80%, 63% and 74% yields, respectively, also by a three-step preparation (Scheme 2): (i) dilithiation of 4,4′-dimethyl-2,2′-bipyridine (**4**), followed by addition of 2 equiv. of the THP-protected aldehyde **b′**, **c′** or **e′**, (ii) dehydration of the resulting diol in the presence of a catalytic amount of PPTS, and (iii) deprotection of the hydroxy groups with HCl (6 N) in refluxing ethanol. The lower yield (63%) obtained in the case of **6cc**, with four hydroxy moieties, can be explained by its poorer solubility. The unsymmetrical bipyridines **6ab**, **6ac**, **6de** and **6db** (Figure 2) were conveniently prepared by a sequential lithiation/condensation procedure (Scheme 2). Intermediates **5a** and **5d** were obtained by monolithiation of **4** and condensation with **a** and **d**.[14] A second lithiation/condensation reaction with **b′**, **c′** or **e′**, followed by dehydration and deprotection, afforded the expected bipyridine ligands in rather good yields (60−90%). To validate the synthetic methodology, the THP-protected bipyridine ligands **6b′b′**, **6ab′** and **6ac′** were also isolated; in the other cases the deprotection was carried out directly in situ. These new OTHP- and OH-functionalized ligands were fully characterized by ^1H NMR, UV/Vis and emission spectroscopy and mass spectrometry, and gave satisfactorily microanalyses.

Properties

The optical properties and thermal stabilities of these OH/OTHP-functionalized bipyridines are summarized in Table 1; for comparison, those of the parent 4,4′-bis[(dialkylamino)styryl]-2,2′-bipyridines (**6aa**, R = Et; **6dd**, R = Bu) are also reported.

To a first approximation, it appears that introduction of 1−4 hydroxy functions does not significantly modify the

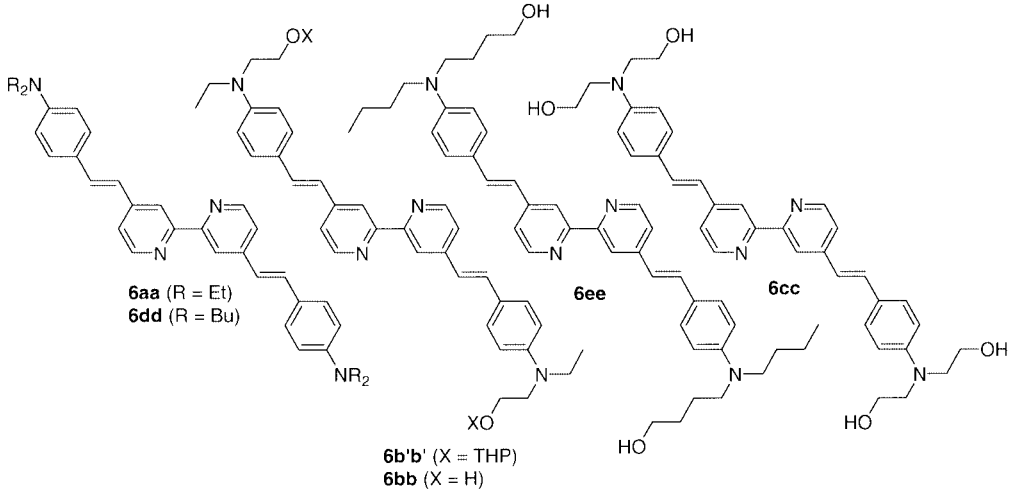


Figure 1. Symmetrical bipyridine ligands

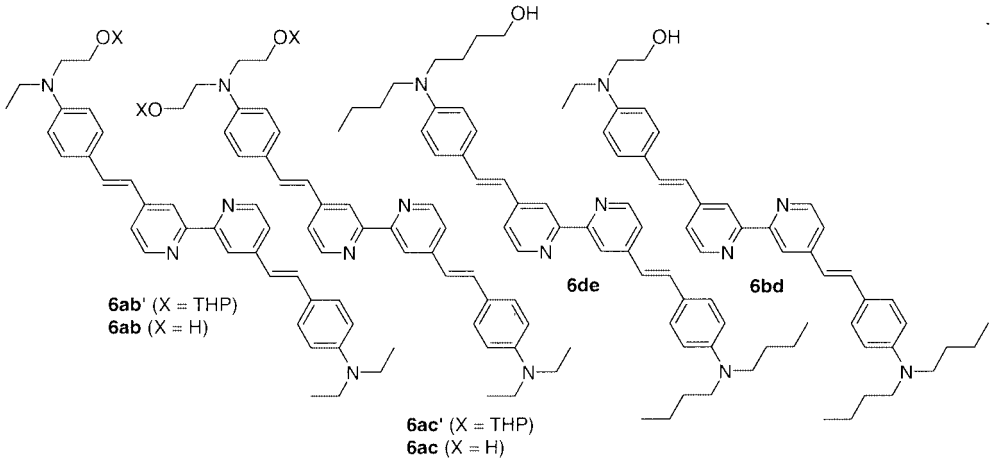
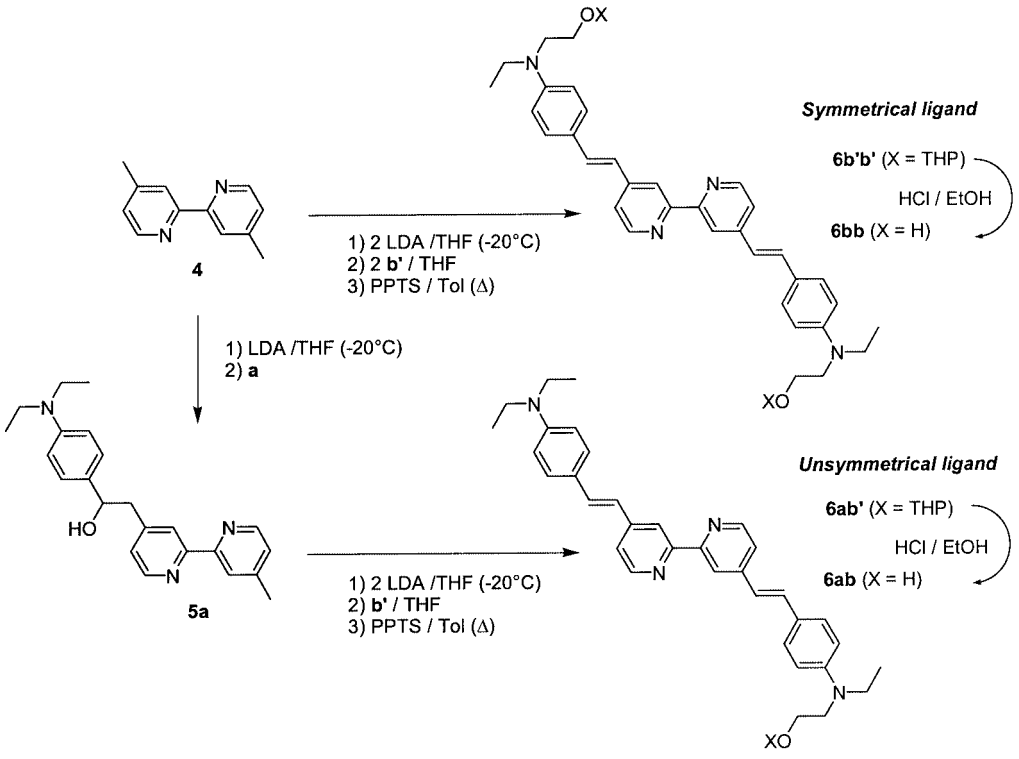


Figure 2. Unsymmetrical bipyridine ligands



Scheme 2. Synthesis of symmetrical (top) and unsymmetrical (bottom) ligands

Table 1. Optical data and thermal stability of bipyridine ligands (Td_5: decomposition temperature at 5% weight loss)

Compound	λ_{max}/nm	ε/L·mol^{-1}·cm^{-1}	λ_{em}/nm	Td_5/°C
6aa	397	57000	495	340
6b′b′	392	59000	–	–
6bb	387	56000	495	335
6cc	382	–	493	310
6ab′	393	55000	–	–
6ab	389	43000	496	325
6ac′	390	61000	–	–
6ac	386	48000	494	335
6dd	401	65000	497	355
6ee	398	54000	497	355

intrinsic properties of the parent chromophore. They show an intense, structureless and broad intra-ligand charge-transfer (ILCT) transition at ca. 390 nm with high molecular extinction coefficients (ε = 50000−60000 L·mol^{-1}·cm^{-1}). They all present very similar emission bands at 495 nm and 500 nm for the C_2 and the C_4 groups, respectively. Moreover, their thermal stabilities, measured by TGA under nitrogen (see Exp. Sect.), remain high (between 310 and 355 °C), similar to the highest thermal stability reported for organic compounds in the literature,[15] and are only slightly affected by the presence of hydroxy functions.

Closer examination of the UV/Vis data (Table 1) reveals interesting differences between the C_2 and C_4 groups.

Whereas the introduction of hydroxy functions at the C_4 group does not significantly affect the λ_{max} value [$\Delta\lambda$(**6dd**/**6ee**) = 3 nm], it promotes a significant blue (hypsochromic) shift of the ILCT transition for the C_2 group ($\Delta\lambda$ = 10−15 nm). Moreover, the hypsochromic shift increases with the number of hydroxy moieties (**6aa** > **6bb** ≈ **6ab** ≈ **6ac** > **6cc**). It is also worth noting that functionalization by an ether (THP) fragment induces a hypsochromic shift [e.g., $\Delta\lambda$(**6aa**/**6b′b′**) = 5 nm] smaller than that induced by a hydroxy group [$\Delta\lambda$(**6aa**/**6bb**) = 10 nm]. All this behavior can be explained by two complementary effects:

(i) The electronegativity of the OH and OTHP series decreases the donor ability of the ethyl chain. Thus, the hydroxy-functionalized diethylamino group displays weaker donor behavior than the parent NEt_2 moieties, resulting in a blue shift of the ILCT transition. In the case of the C_4 group, the alkyl chain is too long to transmit this inductive effect.

(ii) The supplementary hypsochromic shift observed on going from the OTHP to the OH group originates from the potential for formation of an intramolecular hydrogen bond

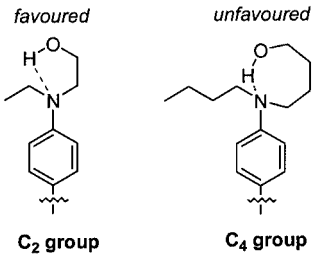


Figure 3. Hydrogen bond formation in hydroxy-functionalized 4,4′-bis[(dialkylamino)styryl]-2,2′-bipyridine

(Figure 3). This effect has already been observed in other chromophores by Dalton et al., by solution FTIR spectroscopy.[16] In the C_2 group, this intramolecular hydrogen bond results in the formation of a stable five-membered ring and contributes to a decrease in the donor ability of the nitrogen atom. No formation of such a hydrogen bond in the C_4 group occurs, since the resulting seven-membered ring is thermodynamically less favored.

This modulation of the donor ability of the NR_2 fragment by OH groups is further confirmed by ^{1}H NMR. Figure 4 shows the aromatic parts of the NMR spectra of unsymmetrical bipyridines **6ab** and **6de**, compared with those of their parent ligands **6aa** and **6dd**, respectively. In the C_4 group, the OH function does not induce any modification, confirming the UV/Vis data. In contrast, a splitting of the signal is observed in the C_2 group; protons 11-H and 7-H of the hydroxy-functionalized branch are deshielded relative to their nonfunctionalized branch counterparts. This deshielding confirms the lower electron donor character of the hydroxy-functionalized diethylamino group and corroborates the blue shift of the ILCT transition observed in UV/Vis spectroscopy.

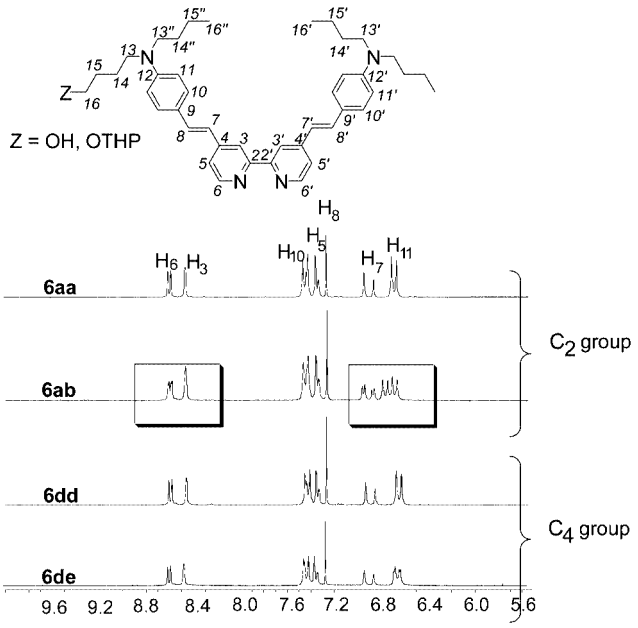
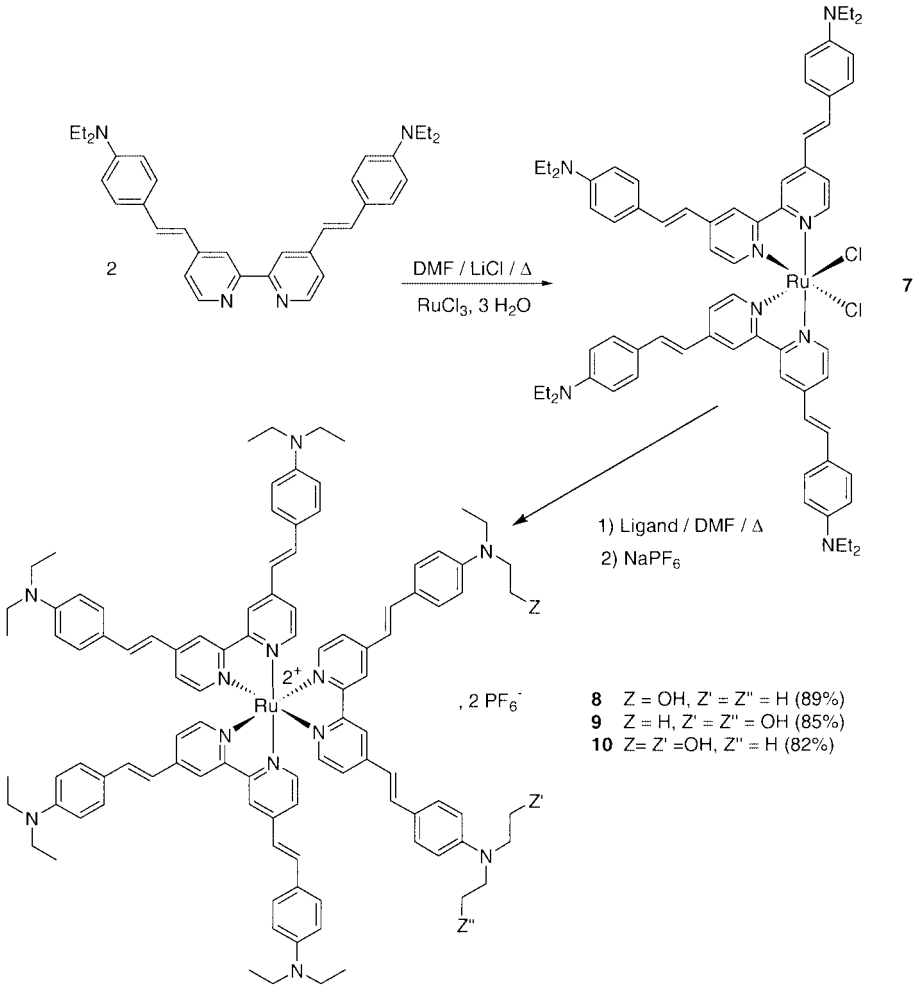


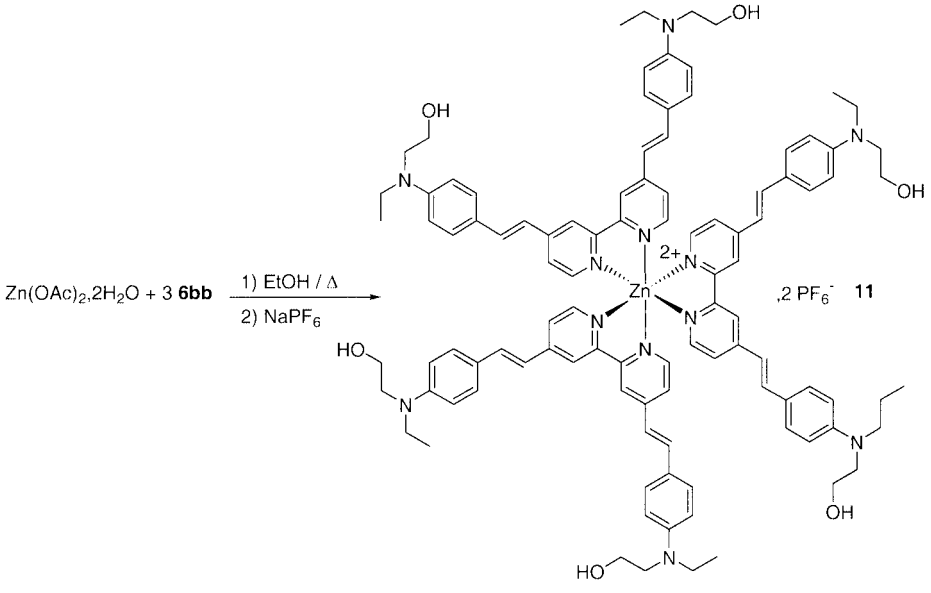
Figure 4. Aromatic part of the ^{1}H NMR spectra

Complexation

These functionalized ligands can be further coordinated to metal centers to give octupolar (in this case D_3-symmetric) building blocks for the design of poly-octupolar architectures. By controlled sequential coordination of bipyridine ligands, heteroleptic ruthenium(II) complexes **8**, **9** and **10**, containing one or two hydroxy functions, were prepared in two-step syntheses (Scheme 3): (i) treatment of ruthenium trichloride trihydrate with 2 equiv. of the parent ligand **6aa** and an excess of lithium chloride resulted in the formation of Ru(**6aa**)$_2$Cl$_2$ (**7**) in 90% yield, and (ii) treatment of **7** with the hydroxy-functionalized bipyridines **6ab**, **6ac** or **6bb**, followed by anion-exchange from chloride to hexafluorophosphate, gave the corresponding deep red complexes [Ru(**6aa**)$_2$(**6ab**)][PF$_6$]$_2$ (**8**), [Ru(**6aa**)$_2$(**6ac**)][PF$_6$]$_2$ (**9**) and [Ru(**6aa**)$_2$(**6bb**)][PF$_6$]$_2$ (**10**) in high yields. The orange homoleptic zinc(II) complex **11**, bearing six hydroxy groups, was prepared in 82% yield by mixing 3 equiv. of bipyridine **6bb** with Zn(OAc)$_2$·2H$_2$O in refluxing ethanol, followed by an anionic metathesis (Scheme 4). All these complexes were characterized by ^{1}H NMR, UV/Vis and high-resolution (FAB) mass spectrometry and/or microanalysis. The UV/Vis spectra of these complexes are very similar to those of the parent complexes with nonfunctionalized ligands. These new tris(bipyridine)ruthenium complexes display two classical broad bands centerd at 510 and 440 nm, with very high extinction coefficients (135000−150000 L·mol^{-1}·cm^{-1}), corresponding to the overlap of the MLCT and ILCT transitions. As would be expected, the zinc(II) complex **11** exhibits only one ILCT transition at 452 nm. Finally, like their parent complexes, compounds **8**−**10** possess excellent thermal stabilities, with 5% weight losses occurring above 325 °C.



Scheme 3. Synthesis of hydroxy-functionalized ruthenium(II) complexes



Scheme 4. Synthesis of hydroxy-functionalized zinc(II) complexes

Conclusion

In this article we have reported the synthesis of new hydroxy-functionalized 4,4′-bis[(dialkylamino)styryl]-2,2′-bipyridines. Such functionalization is a key step for the production of molecular materials for nonlinear optics. The introduction of 1−4 hydroxy groups does not strongly affect the optical properties and thermal stability of the ligand and of the related zinc or ruthenium complexes, when compared to their parent ligands and complexes. These compounds have already allowed the preparation of supramolecular polyoctupolar architectures (polymers[6] and dendrimers[7]), in which a unique octupolar self-ordering effect has been observed. Finally, this approach further opens the way for the design of new star-shaped polymers. Studies in this field, particularly with regard to new NLO materials with intrinsic macroscopic octupolar organization, are in progress.

Experimental Section

General: All reactions were routinely performed under argon by Schlenk techniques. NMR spectra (^{1}H, ^{13}C) were recorded at room temperature with a Bruker DPX 200 spectrometer operating at 200.12 MHz for ^{1}H and 50.33 MHz for ^{13}C NMR. Data are given in ppm relative to tetramethylsilane; residual solvent peaks were used as internal standard. UV/Vis spectra were recorded with a Kontron Uvikon 941 spectrophotometer in dilute dichloromethane solutions (ca. 10^{-5} M). Emission spectra were obtained in dilute dichloromethane solutions with a PTI spectrofluorimeter. Infrared spectra were recorded in KBr pellets with a Nicolet 205 FTIR spectrometer. Thermal stability was measured by use of a TGA 2050 Thermogravimetric Analyzer (TGA) TA instrument. The decomposition temperature at 5% weight loss is termed Td_5. The heating program used is as follows: (i) isothermal at 50 °C for 15 min, (ii) a temperature ramp of 10 °C·min^{-1} up to 600 °C. High-resolution mass spectrometry measurements were performed at the Centre Regional de Mesures Physiques de l'Ouest (Rennes, France) and elemental analyses by the Service Central d'Analyse du CNRS (Solaize, France). Atom-numbering for bipyridine ligands and related complexes is depicted in Figure 4.

Starting Compounds: 4-(Diethylamino)benzaldehyde, *N*-ethyl-, and *N*-(hydroxyethyl)aniline and 4-(dihydroxyethyl)aniline were purchased from Acros and used as received; 4-(dibutylamino)benzaldehyde, 4-[(ethyl)(hydroxyethyl)amino]benzaldehyde and 4-[(dihydroxyethyl)amino]benzaldehyde were synthesized from the corresponding aniline derivatives on 10-g scales by the classical Vilsmeier−Haack formylation, in 90%, 88% and 81% yields, respectively.[8]

2-(4-Bromobutyl)tetrahydropyran: A dichloromethane solution (15 mL) of 4-bromobutan-1-ol (2.4 g, 16 mmol), PPTS (0.8 g, 6.4 mmol) and dihydropyran (3.6 mL, 40 mmol) was stirred for 24 h at room temperature. The reaction mixture was hydrolyzed by addition of water (10 mL), and the product was extracted with dichloromethane (3 × 50 mL). The organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under vacuum. The desired compound was isolated as a brown oil (3.7 g, 99%). ^{1}H NMR ($CDCl_3$): δ = 4.54 (m, 1 H), 3.82−3.69 (m, 2 H), 3.47−3.33 (m, 4 H), 2.05−1.88 (m, 2 H), 1.91−1.47 (m, 8 H) ppm.

***N*-Butyl-*N*-[4-(tetrahydro-2*H*-pyran-2-yloxy)butyl]aniline:** A solution of *N*-butylaniline (5.9 mL, 37 mmol) in THF (30 mL) in a Schlenk tube was cooled to 0 °C, and *n*-butyllithium (1.6 M, 21.7 mL, 37 mmol) was added dropwise. After 1 h of stirring, a THF (15 mL) solution of 2-(4-bromobutyl)tetrahydropyran (6.8 g, 29 mmol) was slowly added and the mixture was stirred for 2 h at room temperature. After hydrolysis with water (30 mL) and evaporation of the THF, the product was extracted with dichloromethane (3 × 30 mL). The organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under vacuum. The resulting brown oil was purified by silica gel chromatography (eluent: dichloromethane/pentane, 1:1). The desired product was isolated as a pale yellow oil (4.1 g, 47%). ^{1}H NMR ($CDCl_3$): δ = 7.17 (m, 2 H), 6.62 (m, 3 H), 4.56 (s, 1 H), 3.90−3.73 (m, 2 H), 3.53−3.37 (m, 2 H), 3.26 (m, 4 H), 1.82−1.51 (m, 12 H), 1.32 (m, 2 H), 0.92 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 148.1, 129.3, 115.2, 111.7, 98.9, 67.4, 62.4, 50.9, 50.8, 30.8, 29.4, 27.4, 25.6, 24.2, 20.5, 19.7, 14.1 ppm. HRMS (EI): calcd. for $C_{19}H_{31}NO_2$ $[M]^+$ 305.2355; found 305.2349.

***N*-Butyl-*N*-(4-hydroxybutyl)aniline (1e):** Hydrochloric acid solution (6 N, 2 mL, 13 mmol) was added to a solution of *N*-butyl-*N*-[4-(tetrahydro-2*H*-pyran-2-yloxy)butyl]aniline (4 g, 13 mmol) in ethanol (50 mL). The mixture was stirred under reflux for 3 h and was then allowed to cool to room temperature. After evaporation of ethanol, the aqueous solution was neutralized by addition of $NaHCO_3$ and then extracted with dichloromethane (3 × 50 mL). The organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under vacuum. The desired product **1e** was isolated as yellow-green oil (2.75 g, 93%). ^{1}H NMR ($CDCl_3$): δ = 7.18 (m, 2 H), 6.65 (m, 3 H), 3.65 (m, 2 H), 3.25 (m, 4 H), 1.60−1.50 (m, 6 H), 1.31 (m, 2 H), 0.92 (t, *J* = 7.2 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ = 148.1, 129.3, 115.8, 112.4, 62.8, 51.2, 51.1, 30.5, 29.4, 23.9, 20.5, 14.1 ppm. HRMS (EI): calcd. for $C_{14}H_{23}NO$ $[M]^+$ 221.1779; found 221.1785.

***N*-(4-Acetoxybutyl)-*N*-butylaniline (2e):** A solution of *N*-butyl-*N*-(4-hydroxybutyl)aniline (2.8 g, 12.7 mmol) and triethylamine (2.7 mL, 19 mmol) in THF (20 mL) in a Schlenk tube was cooled with a cold water bath. Acetyl chloride (0.99 mL, 14 mmol) was then added dropwise and the solution was stirred overnight at 35 °C. After cooling down to room temperature, the mixture was hydrolyzed with water (7 mL). After vigorous stirring for 1 h, the THF was evaporated and the aqueous solution was neutralized by addition of $NaHCO_3$. After extraction of the organic product with dichloromethane (3 × 50 mL), the organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under vacuum. The desired product **2e** was isolated as an orange-yellow oil (3.20 g, 97%). ^{1}H NMR ($CDCl_3$): δ = 7.18 (dd, 2 H), 6.61 (m, 3 H), 4.07 (t, *J* = 6.1 Hz, 2 H), 3.25 (m, 4 H), 2.02 (s, 3 H), 1.63 (m, 4 H), 1.53 (m, 2 H), 1.32 (m, 2 H), 0.92 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 171.2, 148.0, 129.3, 115.5, 111.9, 64.4, 50.9, 50.6, 29.4, 26.3, 23.8, 21.1, 20.4, 14.1 ppm. IR (KBr): $\tilde{\nu}$ = 1731 cm^{-1} ($\nu_{C=O}$). HRMS (EI): calcd. for $C_{16}H_{25}NO_2$ $[M]^+$ 263.1885; found 263.1896.

4-[(4-Acetoxybutyl)(butyl)amino]benzaldehyde (3e): Freshly distilled dimethylformamide (2.4 mL, 30 mmol) in a Schlenk flask was cooled to 0 °C in an ice bath, and $POCl_3$ (1.25 mL, 13 mmol) was added dropwise. After stirring for 1 h at room temperature, the solution became yellow. *N*-(4-Acetoxybutyl)-*N*-butylaniline (3.2 g, 12 mmol) was then added and the crude mixture was stirred at 70 °C for 6 h. The red solution was then cooled to room temperature. Diethyl ether (80 mL) was added and the solution was cooled to 0 °C. An aqueous solution (15 mL) of sodium acetate (4 g, 48 mmol)

was slowly added and the mixture was stirred overnight. The organic layer was separated, washed with water and with a saturated aqueous $NaHCO_3$ solution and dried with $MgSO_4$. The solvent was removed under vacuum and the desired product **3e** was isolated as a brown-orange oil (3.3 g, 94%). ^1H NMR ($CDCl_3$): δ = 9.69 (s, 1 H), 7.68 (d, *J* = 9.0 Hz, 2 H), 6.63 (d, *J* = 9.0 Hz, 2 H), 4.10 (m, 2 H), 3.39−3.29 (m, 4 H), 2.03 (s, 3 H), 1.70−1.53 (m, 6 H), 1.40−1.25 (m, 2 H), 0.95 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 190.0, 171.2, 152.5, 132.2, 124.8, 110.8, 64.0, 50.9, 50.6, 29.3, 26.1, 23.7, 21.0, 20.3, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 1738 cm^{-1} ($\nu_{C=O}$, CO_2Me), 1666 ($\nu_{C=O}$, CHO). HRMS (EI): calcd. for $C_{17}H_{25}NO_3$ $[M]^+$ 291.1834; found 291.1820.

4-[(Butyl)(hydroxybutyl)amino]benzaldehyde (e): 4-[(4-Acetoxybutyl)-(butyl)amino]benzaldehyde (3.30 g, 11.3 mmol) and Na_2CO_3 (1.2 g, 11.3 mmol) were dissolved in a methanol/water mixture (60 mL/20 mL) in a 250-mL round-bottomed flask. After stirring overnight at room temperature, the solution was filtered and neutralized with a hydrochloric acid solution. The aldehyde was extracted with dichloromethane (3 × 50 mL). The organic layers were dried with $MgSO_4$. The solvent was removed under vacuum and the desired product **e** was isolated as a yellow-orange oil (2.75 g, 97%). ^1H NMR ($CDCl_3$): δ = 9.68 (s, 1 H), 7.68 (d, *J* = 9.0 Hz, 2 H), 6.66 (d, *J* = 9.0 Hz, 2 H), 3.68 (t, *J* = 6.0 Hz, 2 H), 3.35 (m, 4 H), 1.74−1.54 (m, 6 H), 1.40−1.32 (m, 2 H), 0.94 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 190.2, 152.7, 132.4, 124.5, 110.8, 62.4, 50.9, 30.0, 29.3, 23.7, 20.3, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 1661 cm^{-1} ($\nu_{C=O}$). HRMS (EI): calcd. for $C_{15}H_{23}NO_2$ $[M]^+$ 249.1728; found 249.1720.

General Procedure for Hydroxy Group Protection

4-{(Ethyl)[(2-tetrahydro-2*H*-pyran-2-yloxy)ethyl]amino}-benzaldehyde (b′): A dichloromethane solution (60 mL) of **b** (10.6 g, 55 mmol), PPTS (2.76 g, **1.1** mmol) and dihydropyran (12.5 mL, 127 mmol) was stirred for 24 h at room temperature. The crude mixture was hydrolyzed by addition of water (45 mL), and the product was extracted with dichloromethane (3 × 50 mL). The organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under vacuum. The desired product was isolated as a brownish-orange oil (15.3 g, 99%). ^1H NMR ($CDCl_3$): δ = 9.68 (s, 1 H), 7.68 (d, *J* = 9.0 Hz, 2 H), 6.70 (d, *J* = 9.0 Hz, 2 H), 4.56 (m, 1 H, 8-H), 3.97−3.72 (m, 2 H), 3.63−3.42 (m, 6 H), 1.79−1.47 (m, 6 H), 1.19 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 190.2, 152.6, 132.2, 124.9, 110.9, 99.2, 64.8, 62.3, 50.2, 45.7, 30.5, 25.4, 19.4, 12.1 ppm. IR (KBr): $\tilde{\nu}$ = 1681 cm^{-1} ($\nu_{C=O}$, CHO). HRMS (FAB): calcd. for $C_{16}H_{23}NO_3$ $[M]^{+\cdot}$ 277.1678; found 277.1685.

4-{Bis[2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl]amino}benzaldehyde (c′): By the same procedure as described for **b′**, compound **c′** was isolated as a brownish-orange oil (7.8 g, 90%). ^1H NMR ($CDCl_3$): δ = 9.66 (s, 1 H), 7.65 (d, *J* = 9.0 Hz, 2 H), 6.74 (d, *J* = 9.0 Hz, 2 H), 4.53 (s, 2 H), 3.91−3.42 (m, 12 H), 1.71−1.46 (m, 12 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 190.2, 152.8, 132.1, 125.3, 111.2, 99.2, 64.6, 62.3, 51.1, 30.5, 25.4, 19.4 ppm. IR (KBr): $\tilde{\nu}$ = 1683 cm^{-1} [$\nu_{C=O}$, CHO). HRMS (FAB): calcd. for $C_{21}H_{31}NO_5$ $[M]^{+\cdot}$ 377.2202; found 377.2226.

4-{[(Butyl)(4-tetrahydro-2*H*-pyran-2-yloxy)butyl]amino}benzaldehyde (e′): By the same procedure as described for **b′**, compound **e′** was isolated from **e** as a brownish-orange oil (2.70 g, 99%). ^1H NMR ($CDCl_3$): δ = 9.68 (s, 1 H), 7.68 (d, *J* = 9.0 Hz, 2 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 4.55 (s, 1 H), 3.79 (m, 2 H), 3.51−3.29 (m, 6 H), 1.77−1.51 (m, 12 H), 1.40−1.25 (m, 2 H), 0.94 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$) = 189.9, 152.6, 132.2, 124.6, 110.8, 99.0, 67.1, 62.5, 50.9, 50.8, 30.8, 29.3, 27.1, 25.5, 24.1, 20.3, 19.8, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 1668 cm^{-1}($\nu_{C=O}$). HRMS (FAB): calcd. for $C_{20}H_{31}NO_3$ 333.2304 $[M]^{+\cdot}$; found 333.2289.

General Procedure for the Synthesis of Symmetrically Hydroxy-Functionalized Bipyridines

4,4′-Bis(4-{(ethyl)[(2-tetrahydro-2*H*-pyran-2-yloxy)ethyl]amino}-styryl)-2,2′-bipyridine (6b′b′): *n*BuLi (1.6 m in hexane, 13.8 mL, 22 mmol) was added by syringe at −20 °C to a THF solution (10 mL) of diisopropylamine (2.9 mL, 22 mmol). The solution was then stirred for 15 min and a solution of 4,4′-dimethyl-2,2′-bipyridine (1.84 g, 10 mmol) in THF (30 mL) was added dropwise at −20 °C. The brown-red mixture was stirred for 2 h at −20 °C. A solution of **b′** (5.55 g, 20 mmol) in THF (20 mL) was slowly added at −20 °C. The resulting yellow-green solution was stirred for 2 h at −20 °C and then allowed to warm to room temperature overnight. After hydrolysis with water (20 mL) and extraction with dichloromethane (3 × 50 mL), the organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under vacuum. The resulting yellow oil was dissolved in toluene (150 mL). After addition of a catalytic amount of PPTS (0.25 g, 0.1 mmol), the red mixture was stirred under reflux for 4 h in a Dean−Stark apparatus. After evaporation of the toluene in vacuo, the residue was dissolved in dichloromethane (150 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (3 × 25 mL). The organic layer was dried with $MgSO_4$ and filtered, and the solvent was removed. After recrystallization from ethyl acetate, the desired compound **6b′b′** was obtained as a yellow microcrystalline powder (5.06 g, 85%). ^1H NMR ($CDCl_3$): δ = 8.58 (d, *J* = 5.1 Hz, 2 H, 6-H), 8.45 (s, 2 H, 3-H), 7.41 (d, *J* = 8.8 Hz, 4 H, 10-H), 7.37 (d, *J* = 16.2 Hz, 2 H, 8-H), 7.31 (dd, *J* = 5.1, *J* = 1.5 Hz, 2 H, 5-H), 6.87 (d, *J* = 16.2 Hz, 2 H, 7-H), 6.69 (d, *J* = 8.8 Hz, 4 H, 11-H), 4.58 (s, 2 H, 15-H), 3.95−3.77 (m, 4 H, 14-H), 3.61−3.40 (m, 12 H, 13,13′,19-H), 1.78−1.51 (m, 12 H, 16,17,18-H), 1.18 (t, *J* = 7.0 Hz, 6 H, 14′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon_{max.}$ [L·mol^{-1}cm^{-1}]) = 392 (59000) nm. HRMS (FAB): calcd. for $C_{44}H_{55}N_4O_4$ $[M + H]^+$ 703.4223; found 703.4207. $C_{44}H_{54}N_4O_4$ (702.94): calcd. C 75.16, H 7.74, N 7.97; found C 74.69, H 7.64, N 8.23.

4,4′-Bis{4-[(ethyl)(2-hydroxyethyl)amino]styryl}-2,2′-bipyridine (6bb): Hydrochloric acid solution (6 N) was added to a solution of **6b′b′** (1.5 g, 2 mmol) in ethanol (60 mL) in a Schlenk tube and the resulting mixture was heated under reflux for 3 h. After cooling to room temperature, the red solution was concentrated and the desired product was precipitated by addition of a saturated aqueous $NaHCO_3$ solution. The yellow solid was then filtered, washed with water and diethyl ether and finally dried under vacuum (1 g, 95%). ^1H NMR ($CDCl_3$): δ = 8.59 (d, *J* = 5.2 Hz, 2 H, 6-H, 6′-H), 8.46 (s, 2 H, 3-H, 3′-H), 7.43 (d, *J* = 8.8 Hz, 4 H, 11-H, 11′-H), 7.38 (d, *J* = 16.4 Hz, 2 H, 8-H, 8′-H), 7.32 (dd, *J* = 5.2, 1.5 Hz, 2 H, 5-H, 5′-H), 6.89/6.87 (2 d, *J* = 16.4 Hz, 1 H + 1 H, 7-H, 7′-H), 6.71/6.67 (2 d, *J* = 8.8 Hz, 2 H + 2 H, 10-H, 10′-H), 3.82 (t, *J* = 5.5 Hz, 2 H, 14-H), 3.51 (t, *J* = 5.5 Hz, 2 H, 13-H), 3.45 (q, *J* = 7.0 Hz, 6 H, 13′-H), 1.18 (t, *J* = 7.0 Hz, 9 H, 14′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}) = 389 (43100) nm. $C_{34}H_{38}N_4O_2 \cdot 1/2H_2O$ (543.71): calcd. C 75.11, H 7.23, N 10.30; found C 75.19, H 7.11, N 10.29. HRMS (FAB): calcd. for $C_{34}H_{39}N_4O_2$ $[M + H]^+$ 535.3073; found 535.3092.

4,4′-Bis{4-[bis(2-dihydroxyethyl)amino]styryl}-2,2′-bipyridine (6cc): This compound was obtained as a yellow microcrystalline powder (1.73 g, 63%) after recrystallization from ethyl acetate, according to the previously described procedure. ^1H NMR (DMSO): δ = 8.59 (d, *J* = 5.0 Hz, 2 H, 6-H), 8.46 (s, 2 H, 3-H), 7.55 (d, *J* = 5.0 Hz, 2 H, 5-H), 7.51 (d, *J* = 9.1 Hz, 4 H, 10-H), 7.48 (d, *J* = 16.3 Hz,

2 H, 8-H), 7.06 (d, J = 16.3 Hz, 2 H, 7-H), 6.73 (d, J = 9.1 Hz, 4 H, 11-H), 3.60−3.51 (m, 8 H, 14-H), 3.49−3.47 (m, 8 H, 13-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} = 382 nm. $C_{34}H_{38}N_4O_4{\cdot}H_2O$ (584.72): calcd. C 68.77, H 6.80, N 9.50; found C 69.84, H 6.90, N 9.58. HRMS (FAB): calcd. for $C_{34}H_{39}N_4O_4$ $[M + H]^+$ 567.2971; found 567.2972).

4,4′-Bis{4-[(butyl)(4-hydroxybutyl)amino]styryl}-2,2′-bipyridine (6ee): This compound was obtained as a yellow microcrystalline powder (1.3 g, 74%) after recrystallization from ethyl acetate according to the previously described procedure. ^{1}H NMR ($CDCl_3$): δ = 8.58 (d, J = 5.0 Hz, 2 H, 6-H), 8.44 (s, 2 H, H^3), 7.40 (d, J = 9.0 Hz, 4 H, 10-H), 7.36 (d, J = 16.3 Hz, 2 H, 8-H), 7.31 (dd, J = 5, J = 1.3 Hz, 2 H, 5-H), 6.86 (d, J = 16.3 Hz, 2 H, 7-H), 6.62 (d, J = 9.0 Hz, 4 H, 11-H), 3.67 (t, J = 6.0 Hz, 4 H, 16-H), 3.31 (m, 8 H, 13,13′-H), 1.81−1.48 (m, 12 H, 14,14′,15-H), 1.45−1.24 (m, 4 H, 15′-H), 0.94 (t, J = 7.0 Hz, 6 H, 16′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 398 (54 000) nm. HRMS (FAB): calcd. for $C_{42}H_{55}N_4O_2$ $[M + H]^+$ 647.4325; found 647.4324. $C_{42}H_{54}N_4O_2{\cdot}H_2O$ (664.935): calcd. C 75.87, H 8.49, N 8.43; found C 75.44, H 8.26, N 8.54.

General Procedure for the Synthesis of Unsymmetrically Hydroxy-Functionalized Bipyridines

4-{2-[4-(Diethylamino)phenyl]-2-hydroxyethyl}-4′-methyl-2,2′-bipyridine (5a): nBuLi (1.6 M in hexane, 6.2 mL) was added by syringe at −20 °C to a THF solution (8 mL) of diisopropylamine (1.3 mL, 10 mmol). The solution was then stirred for 15 min and a solution of 4,4′-dimethyl-2,2′-bipyridine (1.84 g, 10 mmol) in THF (60 mL) was added dropwise at −20 °C. The red mixture was stirred for 2 h. A solution of **a** (1.77 g, 10 mmol) in THF (20 mL) was slowly added at −20 °C. The resulting yellow-green solution was stirred for 2 h at −20 °C and then at room temperature overnight. After hydrolysis with water (20 mL) and extraction with dichloromethane (3 × 50 mL), the organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under vacuum. The product was recovered as a orange-yellow oil. (3.8 g, 99%). ^{1}H NMR ($CDCl_3$): δ = 8.52 (d, J = 5.0 Hz, 1 H, 6-H), 8.50 (d, J = 5.0 Hz, 1 H, 6′-H), 8.28 (s, 1 H, 3-H), 8.19 (s, 1 H, 3′-H), 7.19 (d, J = 9.0 Hz, 2 H, 10-H), 7.13 (dd, J = 5.0, J = 1.7, 1 H, 5-H), 7.10 (dd, J = 5.0, J = 1.0, 1 H, 5′-H), 6.23 (d, J = 9.0 Hz, 2 H, 11-H), 4.92−4.85 (m, 2 H, 8-H), 3.32 (q, J = 7.1 Hz, 4 H, 13-H), 3.11−3.04 (m, 2 H, 7-H), 2.41 (s, 3 H, 7′-H), 1.13 (t, J = 7.1 Hz, 6 H, 14-H) ppm.

4-{2-[4-(Dibutylamino)phenyl]-2-hydroxyethyl}-4′-methyl-2,2′-bipyridine (5d): By the same procedure as for **5a**, compound **5d** was obtained as a orange-yellow oil (4.1 g, 99%). ^{1}H NMR ($CDCl_3$): δ = 8.53 (d, J = 5.0 Hz, 1 H, 6-H), 8.51 (d, J = 5.0 Hz, 1 H, 6′-H), 8.28 (s, 1 H, 3-H), 8.20 (s, 1 H, 3′-H), 7.18 (d, J = 8.8 Hz, 2 H, 10-H), 7.13 (dd, J = 5.0, J = 1.6, 1 H, 5-H), 7.10 (dd, J = 5.0, J = 1.6, 1 H, 5′-H), 6.58 (d, J = 8.8 Hz, 2 H, 11-H), 4.92−4.85 (m, 1 H, 8-H), 3.23 (t, J = 7.2 Hz, 4 H, 13-H), 3.11−3.04 (m, 2 H, 7-H), 2.41 (s, 3 H, 7′-H), 1.60−1.46 (m, 4 H, 14-H), 1.41−1.22 (m, 4 H, 15-H), 0.92 (t, J = 7.2 Hz, 6 H, 16-H) ppm.

4′-[4-(Diethylamino)styryl]-4-(4-{[(ethyl)[(2-tetrahydro-2*H*-pyran-2-yloxy)ethyl]amino}styryl)-2,2′-bipyridine (6ab′): This product was synthesized by the same procedure as used for **5a**, from **5a** (3.80 g, 10 mmol) and **b′** (2.78 g, 10 mmol). The resulting diol was then dehydrated by PPTS (0.25 g, 1 mmol) in toluene (140 mL). After evaporation of the toluene in vacuo, the residue was dissolved in dichloromethane and washed with a saturated aqueous solution of $NaHCO_3$. The organic layer was dried with $MgSO_4$ and filtered, and the solvent was removed. Bipyridine **6ab′** was obtained as a yellow microcrystalline powder (5.10 g, 85%) after recrystallization from ethyl acetate. ^{1}H NMR ($CDCl_3$): δ = 8.58 (d, J = 5.2 Hz, 2 H, 6,6′-H), 8.45 (s, 2 H, 3,3′-H), 7.41 (d, J = 8.6 Hz, 4 H, 10,10′-H), 7.37 (d, J = 16.3 Hz, 2 H, 8,8′-H), 7.30 (dd, J = 5.2, J = 1.6, 2 H, 5,5′-H), 6.87 (d, J = 16.3 Hz, 2 H, 7,7′-H), 6.69 (d, J = 8.6 Hz, 2 H, 11-H), 6.65 (d, J = 8.6 Hz, 2 H, 11′-H) 4.58 (s, 1 H, 15-H), 3.88−3.77 (m, 2 H, 14-H), 3.61−3.32 (m, 10 H, 13,13′,13′′,19-H), 1.75−1.47 (m, 6 H, 16,17,18-H), 1.17 (t, J = 7.0 Hz, 9 H, 14′,14′′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 393 (55000) nm. HRMS (FAB): calcd. for $C_{39}H_{47}N_4O_2$ $[M + H]^+$ 603.3699; found 603.3706. $C_{39}H_{46}N_4O_2$ (602.82): calcd. C 77.71, H 7.69, N 9.29; found C 77.34, H 7.51, N 9.33.

4′-[4-(Diethylamino)styryl]-4-{4-[(ethyl)(2-hydroxyethyl)amino]-styryl}-2,2′-bipyridine (6ab): Removal of the THP moieties was carried out as previously described for **6bb**, and the resulting product **6ab** was obtained as a yellow microcrystalline powder (2.4 g, 92%). ^{1}H NMR ($CDCl_3$): δ = 8.59/8.58 (2 d, J = 5.0 Hz, 1 H +1 H, 6,6′-H), 8.45 (s, 2 H, 3,3′-H), 7.42 (d, J = 8.9 Hz, 4 H, 10,1′-H), 7.37 (d, J = 16.4 Hz, 2 H, 8,8′-H), 7.32 (dd, J = 5.0, J = 1.5, 2 H, 5,5′-H), 6.89 (d, J = 16.4 Hz, 1 H, 7-H), 6.87 (d, J = 16.4 Hz, 1 H, 7′-H), 6.73 (d, J = 8.9 Hz, 2 H, 11-H), 6.65 (d, J = 8.9 Hz, 2 H, 11′-H), 3.81 (t, J = 6.5 Hz, 2 H, 14-H), 3.50 (t, J = 7.0 Hz, 2 H, 13-H), 3.38 (q, J = 6.5 Hz, 6 H, 13′,13′′-H), 1.17 (t, J = 7.0 Hz, 9 H, 14,14′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 389 (43000) nm; emission (CH_2Cl_2): λ_{em} = 496 nm. Td_5 = 325 °C. HRMS (FAB): calcd. for $C_{34}H_{39}N_4O$ $[M + H]^+$ 519.3124; found 519.3118. $C_{34}H_{38}N_4O{\cdot}1/2H_2O$ (527.71): calcd. C 77.39, H 7.45, N 10.62; found C 76.96, H 7.29, N 10.55.

4-(4-{Bis[2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl]amino}styryl)-4′-[4-(diethylamino)styryl]-2,2′-bipyridine (6ac′): This product was synthesized by the same procedure as used for **6ab′**, from **5a** (1.90 g, 5 mmol) and **c′** (1.90 g, 5 mmol). After recrystallization from ethyl acetate, the desired product **6ac′** was obtained as an orange powder (2.25 g, 64%). ^{1}H NMR ($CDCl_3$): δ = 8.58 (d, J = 5.0 Hz, 2 H, 6,6′-H), 8.45 (s, 2 H, 3,3′-H), 7.41 (d, J = 8.8 Hz, 4 H, 10,10′-H), 7.37 (d, J = 16.2 Hz, 2 H, 8,8′-H), 7.31 (dd, J = 5.0, J = 1.5, 2 H, 5,5′-H), 6.87 (d, J = 16.2 Hz, 2 H, 7,7′-H), 6.70/6.65 (2 d, J = 8.8 Hz, 2 H + 2 H, 11,11′-H), 4.57 (s, 2 H, 15-H), 3.91−3.76 (m, 4 H, 14-H), 3.67−3.56 (m, 4 H, 19-H), 3.47 (t, J = 6.5 Hz, 4 H, 13-H), 3.38 (q, J = 7.0 Hz, 4 H, 13′-H), 1.80−1.51 (m, 12 H, 16,17,18-H), 1.17 (t, J = 7.0 Hz, 14′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 390 (61000) nm. HRMS (FAB): calcd. for $C_{44}H_{55}N_4O_4$ $[M + H]^+$ 703.4223; found 703.4225. $C_{44}H_{54}N_4O_4$ (702.94): calcd. C 75.16, H 7.74, N 7.97; found C 74.95, H 7.51, N 7.97.

4′-[4-(Diethylamino)styryl]-4-{4-[bis(2-hydroxyethyl)amino]styryl}-2,2′-bipyridine (6ac): Removal of the THP moieties was carried out as previously described for **6bb**, and the resulting product **6ac** was obtained as a yellow microcrystalline powder (1 g, 95%). ^{1}H NMR ($CDCl_3$): δ = 8.58/8.57 (2 d, J = 5.0 Hz, 1 H + 1 H, 6,6′-H), 8.44 (s, 2 H, 3,3′-H), 7.42 (d, J = 9.0 Hz, 4 H, 10,10′-H), 7.37 (d, J = 16.2 Hz, 2 H, 8,8′-H), 7.31 (dd, J = 5.0, J = 1.6, 2 H, 5,5′-H), 6.90 (d, J = 16.2 Hz, 1 H, 7-H), 6.86 (d, J = 16.2 Hz, 1 H, 7′-H), 6.69 (d, J = 9.0 Hz, 2 H, 11-H), 6.65 (d, J = 9.0 Hz, 2 H, 11′-H), 3.89 (t, J = 4.6 Hz, 4 H, 14-H), 3.63 (t, J = 4.6 Hz, 4 H, 13-H), 3.37 (q, J = 7.0 Hz, 4 H, 13′-H), 1.17 (t, J = 7.0 Hz, 6 H, 14′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 386 (48000) nm; emission: (CH_2Cl_2): λ_{em} = 494 nm. Td_5 = 334 °C. HRMS (FAB): calcd. for $C_{34}H_{38}N_4O_2$ $[M]^{+\cdot}$ 534.2994; found 534.2995. $C_{34}H_{38}N_4O_2{\cdot}1/2H_2O$: calcd. C 75.11, H 7.23, N 10.30; found C 74.73, H 7.32, N 10.38.

4′-[4-(Dibutylamino)styryl]-4-{4-[(ethyl)(2-hydroxyethyl)amino]-styryl}-2,2′-bipyridine (6db): This product was synthesized by the same three-step procedure as used for **6ab**, but from **5d** (1.8 g, 4.33 mmol) and **b′** (1.2 g, 4.33 mmol), and was isolated as a yellow powder (1.6 g, 64%) after recrystallization from ethyl acetate. ^{1}H NMR ($CDCl_3$): δ = 8.59/8.58 (2 d, *J* = 5.3 Hz, 1 H + 1 H, 6,6′-H), 8.48 (s, 2 H, 3,3′-H), 7.41 (d, *J* = 9.0 Hz, 4 H, 11,11′-H), 7.37 (d, *J* = 16.2 Hz, 2 H, 8,8′-H), 7.33 (d, *J* = 5.3 Hz, 2 H, 5,5′-H), 6.88/6.86 (2 d, *J* = 16.2 Hz, 1 H + 1 H, 7,7′-H), 6.73/6.62 (2 d, *J* = 9.0 Hz, 2 H + 2 H, 10,10′-H), 3.80 (t, *J* = 5.8 Hz, 2 H, 14-H), 3.52−3.39 (m, 4 H, 13,13′′-H), 3.28 (t, *J* = 7.0 Hz, 4 H, 13′-H), 1.67−1.45 (m, 4 H, 14′-H), 1.40−1.27 (m, 4 H, 15′-H), 1.17 (t, *J* = 7.0 Hz, 3 H, 14′′-H), 0.94 (t, *J* = 7.0 Hz, 6 H, 16′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 381 (43000) nm. HRMS (FAB): calcd. for $C_{38}H_{47}N_4O$ [M + H]$^+$ 575.3750; found 575.3750. $C_{38}H_{46}N_4O·3/2H_2O$ (593.84): calcd. C 75.84, H 8.21, N 9.31; found C 76.05, H 7.86, N 9.25.

4′-[4-(Dibutylamino)styryl]-4-{4-[(butyl)(4-hydroxybutyl)amino]-styryl}-2,2′-bipyridine (6de): This product was synthesized by the same three-step procedure as used for **6ab**, but from **5d** (0.75 g, 1.96 mmol) and **e′** (0.65 g, 1.96 mmol), and was isolated as a yellow powder (0.89 g, 72%) after recrystallization from ethyl acetate. ^{1}H NMR ($CDCl_3$): δ = 8.58 (d, *J* = 5.2 Hz, 2 H, 6,6′-H), 8.46 (s, 2 H, 3,3′-H), 7.41 (d, *J* = 8.8 Hz, 4 H, 10,10′-H), 7.38 (d, *J* = 16.1 Hz, 2 H, 8,8′-H), 7.32 (dd, *J* = 5.2, *J* = 1.6, 2 H, 5,5′-H), 6.86 (d, *J* = 16.1 Hz, 2 H, 7,7′-H), 6.62 (2d, *J* = 8.8 Hz, 2 H + 2 H, 11,11′-H), 3.67 (m, 2 H, 16-H), 3.29 (m, 8 H, 13,13′,13′′-H), 1.65−1.49 (m, 10 H, 14,14′,14′′,15-H), 1.40−1.27 (m, 6 H, 15′,15′′-H), 0.94 (t, *J* = 7.1 Hz, 9 H, 16′,16′′-H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 400 (54000) nm; emission (CH_2Cl_2): λ_{em} = 499 nm. *T*d$_5$ = 356 °C.

Synthesis of (Bipyridine)metal Complexes

Ru(6aa)$_2$Cl$_2$ (7): $RuCl_3·3(H_2O)$ (524 mg, 2.10^{-3} mol, 1 equiv.), LiCl (848 mg, 20.10^{-3} mol, 10 equiv.) and 4,4′-bis[4-(diethylamino)-styryl]-2,2′-bipyridine (2 g, 4.10^{-3} mol, 2 equiv.), were dissolved in dimethylformamide (10 mL) in a Schlenk vessel and then stirred under reflux for 5 h. After the mixture had cooled to room temperature, acetone (120 mL) was added to the resulting brown-green solution, and reduction of the temperature to −20 °C resulted in the precipitation of the desired complex, which was filtered off, washed with water (3 × 50 mL) and diethyl ether (3 × 30 mL), dissolved in dichloromethane (50 mL) and dried with $MgSO_4$. The solvents were removed under vacuum, and a microcrystalline power was recovered (520 mg, 92% yield). ^{1}H NMR gave only broad signals. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 607 (33000), 428 (96000) nm. HRMS (FAB): calcd. for $C_{68}H_{76}N_8Cl_2Ru$ [Ru(**6aa**)$_2$Cl$_2$]$^{+·}$ 1176.4626; found 1176.4627. $C_{68}H_{76}Cl_2N_8Ru·2CH_2Cl_2$ (1276.345): calcd. C 62.41 H 5.99, N 8.32; found C 62.28, H 6.31, N 8.67.

[Ru(6aa)$_2$(6bb)][PF$_6$]$_2$ (10): Complex **7** (200 mg, 0.17 mmol) and **6bb** (91 mg, 0.17 mmol) were dissolved in DMF (6 mL) in a Schlenk tube, and the resulting green mixture became red upon heating under reflux for 5 h. After the mixture had been cooled to room temperature, an aqueous solution (40 mL) of NH_4PF_6 (110 mg, 0.68 mmol) was slowly added, resulting in the immediate precipitation of the desired complex **10**. The red powder was filtered off, washed with water and diethyl ether, precipitated again twice from dichloromethane/pentane and dried under vacuum (230 mg, 82%). ^{1}H NMR (CD_2Cl_2): δ = 8.39 (s, 2 H), 8.37 (s, 4 H), 7.60−7.23 (m, 30 H), 6.97 (d, *J* = 16.2 Hz, 2 H), 6.94 (d, *J* = 16.2 Hz, 4 H), 6.74 (d, *J* = 9.0 Hz, 4 H), 6.66 (d, *J* = 8.7 Hz, 8 H), 3.77 (t, *J* = 5.0 Hz, 4 H), 3.51−3.16 (m, 24 H), 1.16 (t, *J* = 6.8 Hz, 30 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 509 (151000), 448 (144000) nm. *T*d$_5$ = 325 °C. HRMS (FAB): calcd. for $C_{102}H_{114}F_6N_{12}O_2PRu$ [M − PF$_6$]$^+$ 1785.7873; found 1785.7908.

[Ru(6aa)$_2$(6ab)][PF$_6$]$_2$ (8): By the same procedure as used for **10**, the desired complex **8** was obtained from complex **7** (200 mg, 0.17 mmol) and **6ab** (90 mg, 0.17 mmol), as a red powder (250 mg, 89%). ^{1}H NMR (CD_2Cl_2): δ = 8.38 (s, 6 H), 7.60−7.23 (m, 30 H), 6.97 (d, *J* = 16.1 Hz, 1 H), 6.95 (d, *J* = 16.1 Hz, 5 H), 6.74 (d, *J* = 9.0 Hz), 6.66 (d, *J* = 8.9 Hz, 10 H), 3.77 (t, *J* = 5.5 Hz, 2 H), 3.51−3.16 (m, 24 H), 1.16 (t, *J* = 7.0 Hz, 33 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 517 (139000), 442 (134000) nm. *T*d$_5$ = 331 °C. HRMS (FAB): calcd. for $C_{102}H_{114}F_6N_{12}OPRu$ [M − PF$_6$]$^+$ 1769.7924; found 1769.7967. $C_{102}H_{114}F_{12}N_{12}OP_2Ru·CH_2Cl_2$ (2000.05): calcd. C 61.86, H 5.85, N 8.40; found C 61.48, H 5.86, N 8.31.

[Ru(6aa)$_2$(6ac)][PF$_6$]$_2$ (9): By the same procedure as used for **10**, the desired complex **9** was obtained from complex **7** (200 mg, 0.17 mmol) and **6ac** (90 mg, 0.17 mmol), as a red powder (238 mg, 85%). ^{1}H NMR (CD_2Cl_2): δ = 8.40 (s, 6 H), 7.58−7.32 (m, 30 H), 7.00 (d, *J* = 1 6.0 Hz, 1 H), 6.94 (d, *J* = 1 6.0 Hz, 5 H), 6.73 (d, *J* = 8.8 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 10 H), 3.84 (t, *J* = 4.6 Hz, 4 H), 3.62 (t, *J* = 4.6 Hz, 4 H), 3.44−3.34 (m, 20 H), 1.16 (t, *J* = 7.0 Hz, 30 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max} [L·mol^{-1}·cm^{-1}]) = 514 (136000), 440 (139000) nm. *T*d$_5$ = 328 °C. HRMS (FAB): calcd. for $C_{102}H_{114}F_6N_{12}O_2PRu$ [M − PF$_6$]$^{+·}$ 1785.7873; found 1785.7891.

[Zn(6bb)$_3$][PF$_6$]$_2$ (11): Zinc acetate dihydrate (56 mg, 0.26 mmol) and 3 equiv. of **6bb** (413 mg, 0.77 mmol) were dissolved in dry ethanol (30 mL). The mixture was heated under reflux for 16 h. After cooling to room temperature, the solution was poured into an aqueous solution (50 mL) of $NaPF_6$ (215 mg). After addition of toluene (100 mL), the solvent was evaporated. The product was purified by precipitation in ether to afford an orange solid (410 mg, 82%). ^{1}H NMR: δ = 8.63 (s, 2 H), 7.88 (d, *J* = 5.5 Hz, 2 H), 7.72 (d, *J* = 1 6.0 Hz, 2 H), 7.57−7.53 (m, 4 H), 7.08 (d, *J* = 1 6.0 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 3.69−3.65 (m, 4 H), 3.54 (m, 8 H), 1.24 (t, *J* = 6.8 Hz, 6 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} = 452 nm. $C_{102}H_{114}F_{12}N_{12}O_6P_2Zn·2CH_2Cl_2$ (2129.3): calcd. C 58.66, H 5.59, N 7.89; found C 58.54, H 5.55, N 7.91.

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