Synthesis and characterization of 4-alkenyl and 4,4′-dialkenyl-2,2′-bipyridyl ligands bearing π-donor substituents

Manuel Bourgault, Thierry Renouard, Barbara Lognoné, Chakour Mountassir, and Hubert Le Bozec

Abstract: The synthesis of a new series of π-donor mono- and disubstituted vinyl bipyridines (donor = 4-R_2N-C_6H_4-; 4-RO-C_6H_4-; (C_5H_5)Fe(C_5H_4-); (C_5H_5)Ru(C_5H_4-)) has been achieved by reaction of the mono- and dilithio species of 4,4′-dimethyl-2,2′-bipyridine and the monolithio species of 4-nonyl-4′-methyl-2,2′-bipyridine with the appropriate aldehydes. Their ^{1}H NMR and UV–visible characterizations are reported.

Key words: 2,2′-bipyridines, π-donor substituents, UV–visible, ^{1}H NMR, nonlinear optics.

Résumé : La synthèse d'une nouvelle série de ligands mono- et di-alcényles 2,2′-bipyridines substitués par des groupements conjugués π-donneurs (donneur = 4-R_2N-C_6H_4-; 4-RO-C_6H_4-; (C_5H_5)Fe(C_5H_4-); (C_5H_5)Ru(C_5H_4-)) a été réalisée par réaction des espèces mono- et di-lithiées de la 4,4′-diméthyl-2,2′-bipyridine et mono-lithiée de la 4-nonyl-4′-méthyl-2,2′-bipyridine avec les aldéhydes appropriés. Leurs caractérisations RMN ^{1}H et UV–visible sont également décrites.

Mots clés : 2,2′-bipyridines, substituants π-donneurs, UV–visible, RMN ^{1}H, optique non lineaire.

Introduction

Recent work in our laboratory has focused on the design, synthesis, and second-order nonlinear optical (NLO) properties of new bipyridyl metal complexes. We have previously reported the synthesis of a series of 4-alkenyl-4′-methyl-2,2′-bipyridine complexes of rhenium, zinc, and mercury, in which the alkenyl fragment bears a π-donor group such as di-*n*-butylaminophenyl (1). The molecular hyperpolarizabilities of these new dipolar organometallic compounds were examined using the EFISH technique and large β values were found, especially for the bipyridyl zinc complex (**I**). In addition, we have recently discovered a giant octupolar nonlinearity, among the highest β values ever reported, for the octahedral trisubstituted ruthenium complexes (**II**) containing the bis-4,4′-di-*n*-butylaminostyryl-2,2′-bipyridine ligand (2). To gain insight into the potential scope of dipolar and octupolar bipyridyl metal complexes as NLO materials, we have carried out the preparation of a series of donor-substituted bipyridines. In this paper we report the synthesis and spectroscopic and electronic characterizations of 4-alkenyl- and 4,4′-dialkenyl-2,2′-bipyridyl ligands containing π-donor dialkylaminophenyl, alkoxyphenyl, or metallocenyl groups.

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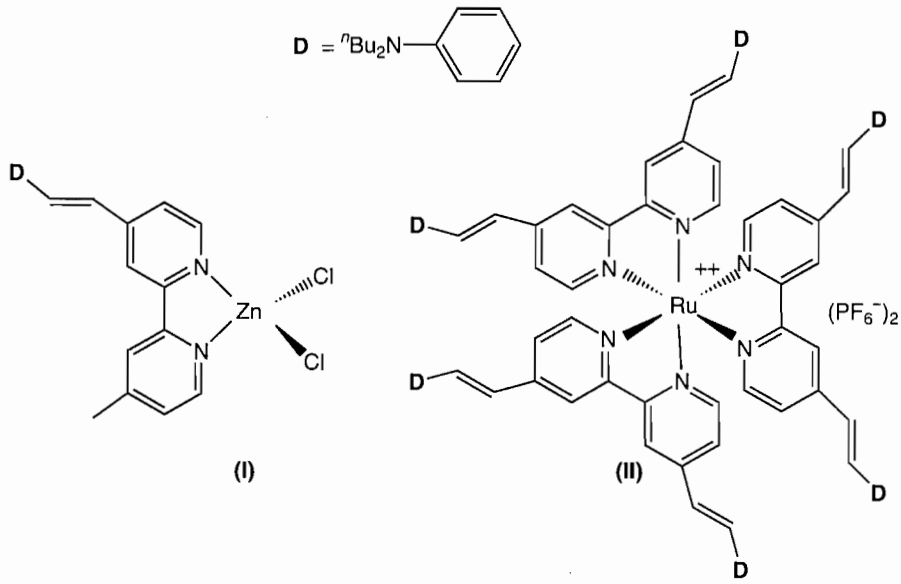
Results and discussion

The 4-alkenyl-2,2′-bipyridyl ligands were prepared from 4,4′-dimethyl-2,2′-bipyridine **1** by an approach analogous to that used by Beer et al. in the preparation of 4-methyl-4′-ferrocenylvinyl-2,2′-bipyridine **6** (3). Reaction of **1** with one equivalent of lithium diisopropylamide (LDA) is known to generate the mono-lithio species (4). The reaction of this anion with the appropriate aldehydes gave the corresponding alcohols, and subsequent treatment with *p*-toluenesulfonic acid yielded the respective 4-methyl-4′-alkenyl-2,2′-bipyridines **3***a–d*, **4**, **6**, and **7** in 49–96% yield (Scheme 2). The dialkylaminobenzaldehyde precursors were obtained by formylation (Vilsmeier reaction) of the aniline derivatives (5) whereas the 4-alkoxybenzaldehydes were synthesized from 4-hydroxybenzaldehyde and the appropriate alkyl bromide or mesylate reagents (see experimental section) (6). To enhance the solubility of the resultant complexes in common organic solvents, which is the prerequisite condition to measure the dipole moments μ and the molecular hyperpolarizabilities β, the synthesis of 4-nonyl-4′-alkenyl-2,2′-bipyridines **5** and **8** was attempted. Compound **5** was synthesized in 37% yield from 4-nonyl-4′-methyl-2,2′-bipyridine **2** (7, 8) by using the same previous procedure, whereas **8** was conveniently prepared (68% yield) in a one-pot reaction from **1** using a step by step lithiation and the successive addition of ferrocene carbaldehyde and octyl bromide (Scheme 2).

The symmetrical 4,4′-disubstituted 2,2′-bipyridines compounds were obtained from **1** upon treatment with two equivalents of LDA followed by addition of the appropriate aldehydes (Scheme 3) (6, 9, 10). Dehydration of the dialdehydes was accomplished either with *p*-toluenesulfonic acid or with pyridium *p*-toluenesulfonate and afforded the new bis-4,4′-alkenyl-2,2′-bipyridines **9**, **10**, and **12** in moderate to

Scheme 1.



good yield (Table 1). Ligands **11** and **13** were also synthesized from the chiral (S)-(+)-4-[*N*-methyl-*N*-(2-methylbutyl)amino]benzaldehyde and (*S*)-(+)-4-(2-methylbutoxy)benzaldehyde, respectively, in order to promote the noncentrosymmetric crystallization of the corresponding organometallic materials (Scheme 3).

These compounds were easily characterized by means of their analytical data (see experimental section) and ^{1}H NMR and UV–visible data (Table 1). The configuration of the double bond formed after dehydration was in every case established as *E* on the basis of the proton-proton coupling constant, $J_{H^7H^8} \approx 16$ Hz. The aromatic region of **3–8** shows six different signals ($H^{3,3'}$, $H^{5,5'}$, $H^{6,6'}$) characteristic of disymmetric substituted bipyridines. In all cases the lowest field resonances are H^6 and $H^{6'}$ as expected from the deshielding by the adjacent nitrogen. The protons H^3 and $H^{3'}$ are also found at lower field than H^5 and $H^{5'}$, which is known to be due to the *transoid* conformation of the bipyridines (11). In the case of symmetric ligands **9–13** the aromatic region gives rise, as expected, to only three signals. The optical absorption spectra for the mono- and bis-dialkylaminostyryl bipyridines are all characterized by intense broad transitions in the region 350–400 nm (**3***a–c*: $\varepsilon \approx 22\,000$; **9–11**: $\varepsilon \approx 50\,000$), which are assigned to intramolecular charge transfer transitions (ICT). In addition, this absorption band exhibits a solvatochromic shift characteristic of a large dipole moment change between the ground and the excited states and suggestive of appreciable microscopic nonlinearities. A less intense ICT band is observed at higher energy for compounds **3***c*, **4**, **5**, **12**, and **13** ($\lambda \approx 330$–350 nm), which is consistent with the following relative ordering of donor strength: $N(^nBu)_2 > N(Me)_2 > N(Et)(Ar) > O(Alk)$. The visible absorption spectra of the ferrocenylvinyl bipyridines **6** and **8** exhibit two broad bands at ca. 475 and 375 nm that can be assigned to metal-to-ligand charge transfer and π–π^* transitions, respectively (12). These two bands are hypsochromically shifted ($\lambda = 310$ and 345 nm) for the ruthenium analog **7**, as expected for the replacement of ferrocene by the less electron-rich ruthenocene (12). An extensive investigation regarding the coordination studies of these ligands to form mono- and tris-bipyridine metal complexes, along with studies of their optical nonlinearities, will be described in the future.

Experimental

All reactions were conducted under argon or nitrogen atmosphere. The solvents were dried by standard methods. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. Electronic absorption spectra were recorded on a Uvikon 941+ spectrophotometer. Proton (300.13 MHz) NMR spectra were recorded on a Bruker AM 300 spectrometer at 297 K using $CDCl_3$ as solvent and referenced to TMS. High-resolution mass spectra were obtained on a Varian MAT 311 at CRMPO, University of Rennes. Elemental analyses were performed by the Service Central de Microanalyses du CNRS at Lyon, France. Melting points, uncorrected, were taken on a Kofler apparatus.

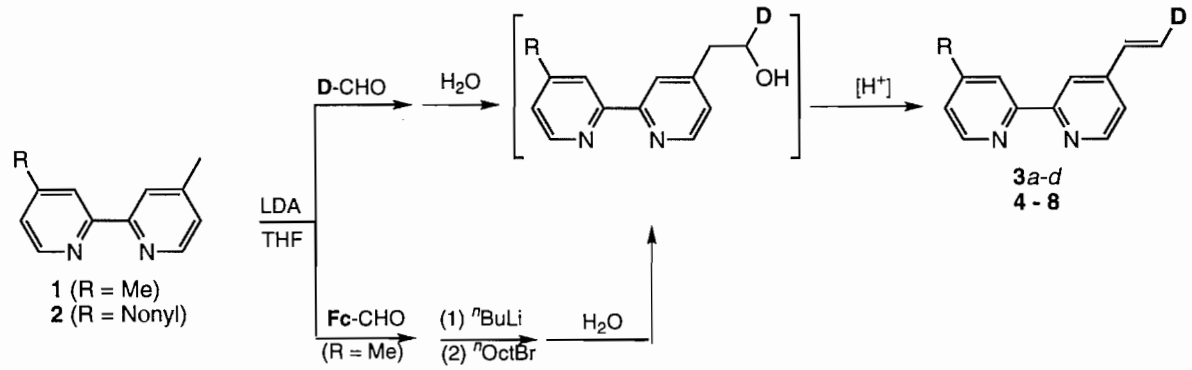
Materials

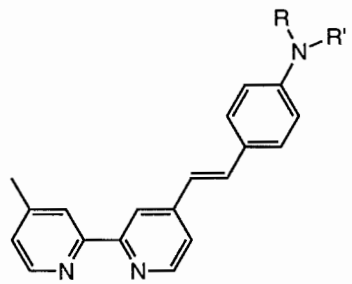
4,4′-Dimethyl-2,2′-bipyridine (13) and ruthenocenecarbaldehyde (14) were prepared by described procedures. 4-(*N,N*-Dimethylamino)benzaldehyde, 9-ethyl-3-carbazole carboxaldehyde, 4-methoxybenzaldehyde, and ferrocenecarbaldehyde were commercial products (Aldrich or Acros).

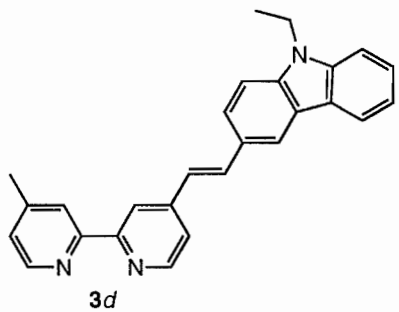
4-(*N,N*-Di-*n*-butylamino)benzaldehyde (ref. 5)

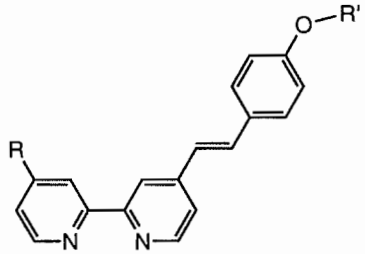
Dimethylformamide (10 mL) was cooled to 0°C and treated dropwise with phosphorus oxychloride (2.1 mL, 22.5 mmol). The solution was stirred at 0°C for 1 h and then at room temperature for 1 h. To the red solution was added dropwise *N,N*-di-*n*-butylaniline (4.53 mL, 20 mmol). The mixture was heated at 60°C for 10 h and then cooled to 0°C. A solution of 2 g of sodium acetate in 20 mL of cold water was added slowly with stirring. The reaction mixture was then stirred for an additional 1 h, and the resulting solution was extracted with

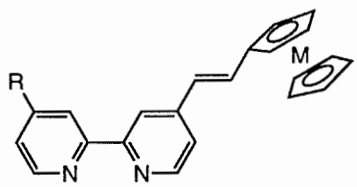
Scheme 2.











ether. The combined extract was washed with saturated aqueous sodium bicarbonate and then with water, and the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was distilled in vacuum at 147–150°C/1 Torr (= 133.3 Pa) to yield 4-(*N*,*N*-di-*n*-butylamino)benzaldehyde as a yellow liquid (4.37 g, 90%); IR, ν_{max}(cm^{-1}): 1686 (C=O); ^{1}H NMR, δ: 9.67 (s, 1H, CHO), 7.66 (dd, 2H, *J* = 9.0 and 2.7 Hz, C_6H_4-), 6.62 (dd, 2H, *J* = 9.0 and 2.7 Hz, C_6H_4-), 3.32 (t, 4H, *J* = 7.7 Hz, N-CH_2-), 1.58 (m, 4H, CH_2-), 1.35 (m, 4H, CH_2-), 0.35 (t, 6H, *J* = 7.3 Hz, CH_3).

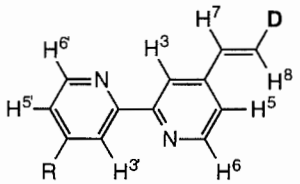
(*N*-Methyl-*N*-octyl)aniline

To an ice-cooled solution of *N*-methylaniline (6.5 g, 60 mmol) in 20 mL of freshly distilled THF was added 1.6 M *n*-butyllithium (40 mL, 66 mmol) dropwise. The resulting mixture was stirred for 0.5 h and octylbromide (11.5 mL, 66 mmol) was added slowly. The solution was allowed to warm to room temperature. The orange solution was cooled in an ice-water bath and hydrolysed with 10 mL of water. The organic layer was separated, dried over $MgSO_4$, and filtered, and the solvent was evaporated to dryness. The title compound was obtained as an orange oil (11.8 g; 90%); ^{1}H NMR, δ: 7.33 (dd, 2H, *J* = 7 and 8.8 Hz, C_6H_5-), 6.80 (m, 3H, C_6H_5-), 3.40 (t, 2H, *J* = 7.5 Hz, N-CH_2-), 3.02 (s, 3H, N-CH_3), 1.68 (m, 2H, N-CH_2-CH_2-), 1.41 (m, 10H, $(CH_2)_5$-), 1.01 (t, 3H, *J* = 7.5 Hz, CH_2-CH_3).

4-(*N*-Methyl-*N*-octylamino)benzaldehyde

The title compound was obtained as an orange oil (12.5 g, 74%) from (*N*-methyl-*N*-octyl)aniline (15 g, 73 mmol), phosphorus oxychloride (7 mL, 75 mmol) and dimethylformamide (30 mL); bp 110°C at 0.03 Torr; IR, ν_{max}(cm^{-1}): 1682 (C=O);

Table 1. Yield, selected ^{1}H NMR, and UV–visible data for bipyridines **1**–**13**.



Compound	% Yield	^{1}H NMR (δ_{ppm} ; J_{Hz})[a]						UV–visible[b]
		$H^{6,6'}$	$H^{3,3'}$	$H^{5,5'}$	H^8	H^7	J_{7-8}	λ_{max} (nm)
1	—	8.47	8.16	7.05				—
2	75	8.47	8.23	7.11				—
3*a*	96	8.53, 8.50	8.48, 8.27	7.30, 7.11	7.35	6.88	16.2	388
3*b*	74	8.59, 8.58	8.48, 8.30	7.36, 7.16	7.42	6.92	16.3	374
3*c*	61	8.51, 8.50	8.46, 8.25	7.31, 7.13	7.36	6.89	16.3	389
3*d*	51	8.62, 8.59	8.55, 8.27	7.49, 7.16	7.66	7.15	16.3	351
4	70	8.61, 8.57	8.48, 8.25	7.33, 7.15	7.40	6.97	16.3	329
5	37	8.56, 8.52	8.51, 8.26	7.34, 7.14	7.40	7.00	16.4	325
6	69	8.53, 8.52	8.45, 8.27	7.29, 7.15	7.28	6.73	16.1	375, 472
7	49	8.50, 8.49	8.39, 8.25	7.20, 7.12	7.14	6.65	16.2	310, 345
8	68	8.58, 8.58	8.43, 8.25	7.27, 7.15	7.27	6.70	16.1	378, 469
9	83	8.60	8.46	7.33	7.38	6.88	16.2	401
10	80	8.60	8.46	7.33	7.39	6.90	16.2	394
11	51	8.60	8.47	7.33	7.39	6.90	16.2	394
12	20	8.64	8.51	7.36	7.41	6.98	16.3	337
13	23	8.64	8.51	7.36	7.41	6.98	16.3	336

[a]Data in $CDCl_3$.
[b]Data in CH_2Cl_2.

^{1}H NMR, δ: 9.62 (s, 1H, CHO), 7.62 (dd, 2H, J = 9.0 Hz, C_6H_4-), 6.59 (dd, 2H, J = 9.0 Hz, C_6H_4-), 3.31 (t, 2H, J = 7.6 Hz, N-CH_2-), 2.95 (s, 3H, N-CH_3), 1.52 (t, 2H, J = 6.9 Hz, N-CH_2-CH_2-), 1.22 (m, 10H, $(CH_2)_5$-), 0.80 (t, 3H, J = 6.7 Hz, CH_2-CH_3).

(*N*-Methyl-*N*-2-methylbutyl)aniline

The title compound was obtained as a yellow oil (3.54 g, 66%) from *N*-methylaniline (3.2 g, 30 mmol), (*S*)-(+)-2-methylbutylmesylate (5.5 g, 33 mmol), and 1.6 M *n*-butyllithium (20 mL, 32 mmol) in 20 mL of freshly distilled THF; ^{1}H NMR, δ: 7.30 (m, 2H, C_6H_5-), 6.76 (m, 3H, C_6H_5-), 3.21(2 × q, 2H, J = 6.8 and 14.5 Hz, N-CH_2-), 3.03 (s, 3H, N-CH_3), 1.92 (m, 1H, CH-CH_3), 1.56 (m, 1H, CH_2-CH_3), 1.20 (m, 1H, CH_2-CH_3), 1.02 (t, 3H, J = 7.3 Hz, CH_2-CH_3), 0.99 (d, 3H, J = 6.7 Hz, CH-CH_3).

(*S*)-(+)-4-(*N*-Methyl-*N*-(2-methylbutyl)amino)-benzaldehyde

The title compound was obtained as an orange oil (3.5 g, 85%) from (*N*-methyl-*N*-2-methylbutyl)aniline (3.54 g, 20 mmol), $POCl_3$ (2 mL, 20 mmol), and DMF (10 mL); $[\alpha]_D$ +26 (c = 1.0, CH_2Cl_2); IR, ν_{max}(cm^{-1}): 1684 (C═O); ^{1}H NMR, δ: 9.64 (s, 1H, CHO), 7.63 (d, 2H, J = 9.0 Hz, C_6H_4-), 6.60 (d, 2H, J = 9 Hz, C_6H_4-), 3.17 (2 × q, 2H, J = 6.8 and 14.6 Hz, N-CH_2-), 2.97 (s, 3H, N-CH_3), 1.77 (m, 1H, CH-CH_3), 1.37 (m, 1H, CH_2-CH_3), 1.07 (m, 1H, CH_2-CH_3), 0.86 (t, 3H, J = 7.4 Hz, CH_2-CH_3), 0.82 (d, 3H, J = 6.6 Hz, CH-CH_3).

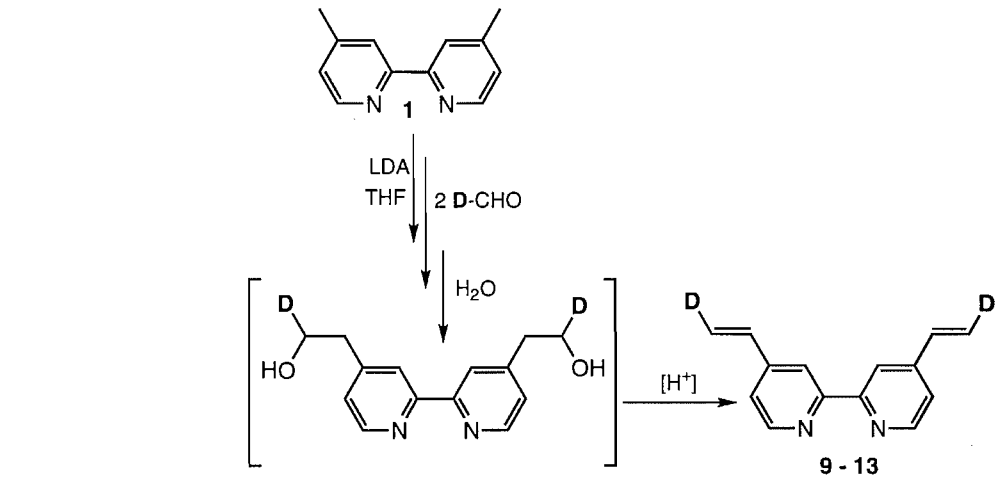
4-Octyloxybenzaldehyde (ref. 6)

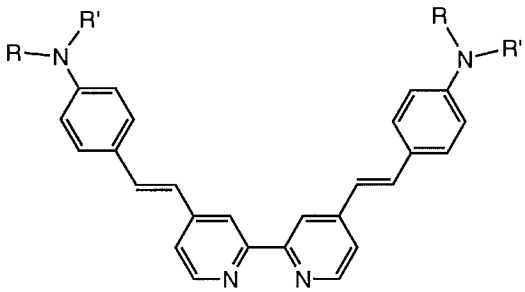
To a solution of 4-hydroxybenzaldehyde (6.11 g, 50 mmol) in 300 mL of ethanol was added potassium carbonate (17 g, 123 mmol). The resulting mixture was stirred for 0.5 h at room temperature and octylbromide (8.6 mL, 50 mmol) was added slowly. The yellow solution was refluxed for 70 h and then cooled to room temperature. The mixture was filtered and the solvent evaporated. The yellow residue was dissolved in ether and washed with water (until the washings were neutral). The solution was dried over $MgSO_4$, and the solvent evaporated to dryness. The title compound was obtained as a yellow oil (9.6 g, 82%); IR, ν_{max}(cm^{-1}): 1696 (C═O); ^{1}H NMR, δ: 9.84 (s, 1H, CHO), 7.79 (dd, 2H, J = 8.8 and 2.6 Hz, C_6H_4-), 6.95 (dd, 2H, J = 8.8 and 2.6 Hz, C_6H_4-), 4.0 (t, 2H, J = 6.5 Hz, O-CH_2), 1.78 (m, 2H, CH_2-), 1.5–1.1 (m, 10H, $(CH_2)_5$-), 0.86 (t, 3H, J = 6.6 Hz, CH_3).

(*S*)-(+)-4-(2-Methylbutoxy)benzaldehyde

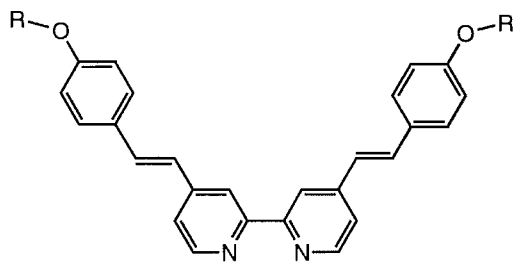
The title compound was obtained as a yellow oil (3.3 g, 57%) from 4-hydroxybenzaldehyde (3.66 g, 30 mmol), potassium carbonate (17 g, 123 mmol), and 4.98 g of (*S*)-(+)-2-methylbutylmesylate; $[\alpha]_D$ +7 (c = 1.6, CH_2Cl_2); IR, ν_{max}(cm^{-1}): 1694 (C═O); ^{1}H NMR, δ: 9.72 (s, 1H, CHO), 7.67 (dd, 2H, J = 8.8 and 2.6 Hz, C_6H_4-), 6.84 (dd, 2H, J = 8.8 and 2.6 Hz, C_6H_4-), 3.74 (dd, 1H, J = 9.1 and 6.0 Hz, O-CH_2-), 3.66 (dd, 1H, J = 9.1 and 6.0 Hz, O-CH_2-), 1.74 (m, 1H, CH-CH_3), 1.42 (m, 1H, CH_2-), 1.12 (m, 1H, CH_2-), 0.88 (d, 3H, J = 6.7 Hz, CH_3), 0.80 (t, 3H, J = 7.4 Hz, CH_3).

Scheme 2.





9 : R , R' = ^{n}Bu , ^{n}Bu
10 : R , R' =Me , ^{n}Oct
11 : R , R' = Me ,$CH_2CH(Me)(Et)$



12 : R = ^{n}Oct
13 : R = $CH_2CH(Me)(Et)$

4-Nonyl-4′-methyl-2,2′-bipyridine 2

A solution of 4,4′-dimethyl-2,2′-bipyridine **1** (1.84 g, 10 mmol) in 30 mL THF was added dropwise to a stirred solution of freshly prepared LDA (12.9 mmol) in 40 mL THF at 0°C. The resulting red mixture was stirred 1 h at 0°C. Octylbromide (2 mL, 10 mmol) was added and the mixture was stirred for an additional 1 h at 0°C, treated with water, and evaporated in vacuo. The yellow oil was dissolved in 100 mL CH_2Cl_2, washed with water (2 × 75 mL), dried over $MgSO_4$, and evaporated. Recrystallization from hexane (15 mL) yielded **2** as white crystals (2.21 g); mp 42–45°C; ^{1}H NMR, δ: 8.47 (d, 2H, $H^{6,6'}$), 8.23 (m, 2H, $H^{3,3'}$), 7.11 (m, 2H, $H^{5,5'}$), 2,66 (t, 2H, J = 8.0 Hz, CH_2-), 2.40 (s, 3H, CH_3), 1.65 (m, 2H, CH_2-), 1.40–1.15 (m, 12H, $(CH_2)_6$-), 0.85 (t, 3H, J = 8.0 Hz, CH_3). Anal. calcd. for $C_{20}H_{28}N_2$: C 81.03; H 9.52; found: C 80.96, H 10.39.

4-[*p*-(*N*,*N*-Dibutylamino)styryl]-4′-methyl-2,2′-bipyridine *3a*

To a stirred solution of freshly prepared LDA (51.6 mmol) in 60 mL of THF at −78°C was added dropwise a solution of **1** (7.9 g, 43 mmol) in 120 mL of THF. The red solution was stirred for 15 min at −78°C and 1 h at 0°C. A solution of 4-(*N*,*N*-dibutylamino)benzaldehyde (10 g, 43 mmol) in 40 mL of THF was then added dropwise and the yellow-green solution was stirred for 2 h at 0°C and overnight at room temperature. The mixture was quenched with 50 mL of water and extracted with CH_2Cl_2 (3 × 100 mL). The combined extract was dried over $MgSO_4$ and evaporated in vacuo. The crude product was chromatographed on silica gel with dichloromethane–methanol – ammonium hydroxide (100/5/1) as the eluant. The resulting alcohol was then dissolved in 250 mL of toluene and treated with *p*-toluenesulfonic acid monohydrate (500 mg, 2.6 mmol). The mixture was refluxed for 4 h, then cooled to room temperature, washed with saturated aqueous sodium bicarbonate, dried over $MgSO_4$, and evaporated in vacuo to give **3***a* as an orange oil (16.4 g); UV, λ_{max} (nm): 382 (toluene), 388 (CH_2Cl_2), 397 (DMF); ^{1}H NMR, δ: 8.53 (d, 1H, J = 5.1 Hz, H^6), 8.50 (d, 1H, J = 5.0 Hz, $H^{6'}$), 8.48 (d, 1H, J = 1.6 Hz, H^3), 8.27 (s, 1H, $H^{3'}$), 7.40 (d, 2H, J = 9.0 Hz, C_6H_4-), 7.35 (d, 1H, J = 16.2 Hz, CH=), 7.30 (dd, 1H, J = 5.1 and 1.6 Hz, H^5), 7.11 (dd, 1H, J = 5.0 and 0.9 Hz, $H^{5'}$), 6.88 (d, 1H, J = 16.2 Hz, CH=), 6.63 (d, 2H, J = 9.0 Hz, C_6H_4-), 3.29 (t, 4H, J = 7.8 Hz, N-CH_2-), 2.42 (s, 3H, CH_3), 1.57 (m, 4H, CH_2-), 1.35 (m, 4H, CH_2-), 0.95 (t, 6H, J = 7.3 Hz, CH_3). Anal. calcd. for $C_{27}H_{33}N_3$: C 81.16, H 8.32, N 10.52; found: C 81.32, H 8.59, N 10.21.

4-[*p*-(*N*,*N*-Dimethylamino)styryl]-4′-methyl-2,2′-bipyridine *3b*

The title compound was prepared analogously as described for

3*a*, using **1** (2.76 g, 15 mmol) and 4-(*N*,*N*-dimethylamino)benzaldehyde (2.4 g, 15 mmol) as starting materials, and was isolated as yellow-orange microcrystals after recrystallization from dichloromethane–ether (3.54 g); mp 140°C; ^{1}H NMR, δ: 8.59 (d, 1H, J = 5.2 Hz, H^6), 8.58 (d, 1H, J = 4.9 Hz, $H^{6'}$), 8.48 (d, 1H, J = 1.2 Hz, H^3), 8.30 (s, 1H, $H^{3'}$), 7.47 (d, 2H, J = 8.9 Hz, C_6H_4-), 7.42 (d, 1H, J = 16.3 Hz, CH═), 7.36 (dd, 1H, J = 5.2 and 1.7 Hz, H^5), 7.16 (dd, 1H, J = 4.9 and 1.7 Hz, $H^{5'}$), 6.92 (d, 1H, J = 16.3 Hz, CH═), 6.73 (d, 2H, J = 8.9 Hz, C_6H_4-), 3.02 (s, 6H, N-CH_3), 2.46 (s, 3H, CH_3). Anal. calcd. for $C_{21}H_{21}N_3$: C 79.97, H 6.71, N 13.32; found: C 79.23, H 6.76, N 13.00. HRMS *m/z*, calcd.: 315.1735; found: 315.1733.

4-[*p*-(*N*-Methyl-*N*-octyl)aminostyryl]-4′-methyl-2,2′-bipyridine 3*c*

The title compound was prepared analogously as described for **3***a*, using **1** (0.92 g, 5 mmol) and 4-(*N*-methyl-*N*-octyl)aminobenzaldehyde (1.25 g, 5.1 mmol) as starting materials, and was isolated as an orange oil after flash chromatography on silica gel with dichloromethane–methanol (90:10) as the eluant (1.26 g); ^{1}H NMR, δ: 8.51 (d, 1H, J = 5.2 Hz, H^6), 8.50 (d, 1H, J = 4.0 Hz, $H^{6'}$), 8.46 (d, 1H, J = 1.2 Hz, H^3), 8.25 (s, 1H, $H^{3'}$), 7.42 (d, 2H, J = 8.9 Hz, C_6H_4), 7.36 (d, 1H, J = 16.3 Hz, CH═), 7.31 (dd, 1H, J = 5.2 and 1.7 Hz, H^5), 7.13 (dd, 1H, J = 4.8 and 0.9 Hz, $H^{5'}$), 6.89 (d, 1H, J = 16.3 Hz, CH═), 6.66 (d, 2H, J = 8.9 Hz, C_6H_4-), 3.32 (t, 2H, J = 7.7 Hz, N-CH_2-), 2.94 (s, 3H, N-CH_3), 2.41 (s, 3H, CH_3), 1.56 (m, 2H, CH_2-), 1.28 (m, 10H, $(CH_2)_5$-), 0.86 (t, 3H, J = 6.9 Hz, CH_3); HRMS *m/z* calcd. for $C_{28}H_{35}N_3$: 413.2831; found: 413.2847.

4-[(9-Ethyl-3-carbazolyl)vinyl]-4′-methyl-2,2′-bipyridine 3*d*

The title compound was prepared analogously as described for **3***a*, using **1** (2.76 g, 15 mmol) and 9-ethyl-3-carbazole carboxaldehyde (3.33 g, 15 mmol) as starting materials, and was isolated as a yellow solid after flash chromatography on alumina with dichloromethane–acetonitrile (90:10) as the eluant (3.0 g); mp 174°C; ^{1}H NMR, δ: 8.62 (d, 1H, J = 5.1 Hz, H^6), 8.59 (d, 1H, J = 5.0 Hz, $H^{6'}$), 8.55 (d, 1H, J = 1.5 Hz, H^3), 8.27 (s, 2H, $H^{3'}$ and H arom), 8.13 (d, 1H, J = 7.7 Hz, H arom), 7.71 (dd, 1H, J = 8.5 and 1.5 Hz, H arom), 7.66 (d, 1H, J = 16.3 Hz, CH═), 7.49 (m, 1H, H arom), 7.49 (m, 3H, H^5 and H arom), 7.26 (m, 1H, H arom), 7.16 (dd, 1H, J = 5.0 and 0.9 Hz, $H^{5'}$), 7.15 (d, 1H, J = 16.3 Hz, CH═), 4.36 (q, 2H, J = 7.2 Hz, CH_2-), 2.45 (s, 3H, CH_3), 1.44 (t, 3H, J = 7.2 Hz, CH_3). Anal. calcd. for $C_{27}H_{23}N_3$: C 83.26, H 5.95, N 10.79; found: C 82.35, H 5.99, N 10.55. HRMS *m/z*, calcd.: 389.1892; found: 389.1892.

4-[*p*-(Octyloxy)styryl]-4′-methyl-2,2′-bipyridine 4

The title compound was prepared analogously as described for **3***a*, using **1** (1 g, 5.4 mmol) and 4-octyloxybenzaldehyde (1.27 g, 5.4 mmol) as starting materials, and was isolated as a white solid after recrystallization from ethyl acetate (1.51 g); mp 60–62°C; ^{1}H NMR, δ: 8.61 (d, 1H, J = 5.1 Hz, H^6), 8.57 (d, 1H, J = 5.0 Hz, $H^{6'}$), 8.48 (s, 1H, H^3), 8.25 (s, 1H, $H^{3'}$), 7.48 (d, 2H, J = 8.7 Hz, C_6H_4-), 7.40 (d, 1H, J = 16.3 Hz, CH═), 7.33 (dd, 1H, J = 5.1 and 1.6 Hz, H^5), 7.15 (dd, 1H, J = 5.0 and 0.9 Hz, $H^{5'}$), 6.97 (d, 1H, J = 16.3 Hz, CH═), 6.91 (d, 2H, J = 8.7 Hz, C_6H_4-), 3.98 (t, 2H, J = 6.5 Hz, O-CH_2-), 2.44 (s, 3H, CH_3), 1.78 (m, 2H, CH_2-), 1.50–1.20 (m, 10H, $(CH_2)_5$-), 0.89 (t, 3H, J = 6.9 Hz, CH_3). Anal. calcd. for $C_{27}H_{32}N_2O{\cdot}0.5\ H_2O$: C 79.22, H 8.31, N 6.85; found: C 79.08, H 7.87, N 7.07.

4-[*p*-(Methoxy)styryl]-4′-nonyl-2,2′-bipyridine 5

The title compound was prepared analogously as described for **3***a*, using **2** (1.73 g, 5.8 mmol) and 4-methoxybenzaldehyde (1.12 g, 7 mmol), and was isolated as a white solid after flash chromatography on silica gel with dichloromethane–ethanol as the eluant (0.88 g); mp 62–64°C; ^{1}H NMR, δ: 8.56 (d, 1H, J = 5.1 Hz, H^6), 8.52 (d, 1H, J = 5.0 Hz, $H^{6'}$), 8.51 (s, 1H, H^3), 8.26 (s, 1H, $H^{3'}$), 7.51 (d, 2H, J = 8.7 Hz, C_6H_4-), 7.40 (d, 1H, J = 16.4 Hz, CH═), 7.34 (dd, 1H, J = 5.1 and 1.7 Hz, H^5), 7.14 (dd, 1H, J = 5.0 and 1.6 Hz, $H^{5'}$), 7.0 (d, 1H, J = 16.4 Hz, CH═), 6.91 (d, 2H, J = 8.7 Hz, C_6H_4-), 3.81 (s, 3H, CH_3), 2.68 (t, 2H, J = 7.4 Hz), 1.67 (m, 2H, CH_2-), 1.35–1.20 (m, 12H, $(CH_2)_6$-), 0.85 (t, 3H, J = 6.9 Hz, CH_3); HRMS *m/z* calcd. for $C_{28}H_{34}N_2O$: 414.2671; found: 414.2670.

4-Ferrocenylvinyl-4′-methyl-2,2′-bipyridine 6 (ref. 4)

The title compound was prepared analogously as described for **3***a*, using **1** (2.76 g, 15 mmol) and ferrocenecarbaldehyde (3.21 g, 15 mmol) as starting materials, and was isolated as a red solid after flash chromatography on alumina with dichloromethane–methanol as the eluant (3.97 g); mp 156°C (dec.); ^{1}H NMR, δ: 8.53 (d, 1H, J = 5.2 Hz, H^6), 8.52 (d, 1H, J = 5.4 Hz, $H^{6'}$), 8.45 (d, 1H, J = 1.6 Hz, H^3), 8.27 (d, 1H, $H^{3'}$), 7.29 (dd, 1H, J = 5.2 and 1.7 Hz, H^5), 7.28 (d, 1H, J = 16.1 Hz, CH═), 7.15 (d, 1H, J = 4.9 Hz, $H^{5'}$), 6.73 (d, 1H, J = 16.1 Hz, CH═), 4.51 (t, 2H, J = 1.8 Hz, C_5H_4-), 4.33 (t, 2H, J = 1.8 Hz, C_5H_4-), 4.13 (s, 5H, C_5H_5), 2.42 (s, 3H, CH_3). Anal. calcd. for $C_{23}H_{20}N_2Fe$: C 72.65, H 5.30, N 7.37; found: C 72.22, H 5.17, N 7.45. HRMS *m/z*, calcd.: 380.0976; found: 380.0980.

4-Ruthenocenylvinyl-4′-methyl-2,2′-bipyridine 7

The title compound was prepared analogously as described for **3***a*, using **1** (1.5 g, 8.15 mmol) and ruthenocenecarbaldehyde (2.1 g, 8.15 mmol), and was isolated as a pale yellow solid after recrystallization from ethyl acetate–pentane (1.7 g); mp 120°C (dec.); ^{1}H NMR, δ: 8.50 (d, 1H, J = 4.8 Hz, H^6), 8.49 (d, 1H, J = 4.6 Hz, $H^{6'}$), 8.39 (d, 1H, J = 1.5 Hz, H^3), 8.25 (s, 1H, $H^{3'}$), 7.20 (dd, 1H, J = 5.1 and 1.7 Hz, H^5), 7.14 (d, 1H, J = 16.2 Hz, CH═), 7.12 (dd, 1H, J = 4.6 and 0.9 Hz, $H^{5'}$), 6.65 (d, 1H, J = 16.2 Hz, CH═), 4.90 (t, 2H, J = 1.7 Hz, C_5H_4-), 4.64 (t, 2H, J = 1.7 Hz, C_5H_4-), 4.52 (s, 5H, C_5H_5), 2.40 (s, 3H, CH_3). Anal. calcd. for $C_{23}H_{20}N_2Ru$: C 64.94, H 4.71, N 6.59; found: C 64.85, H 4.89, N 6.90.

4-Ferrocenylvinyl-4′-nonyl-2,2-bipyridine 8

To a stirred solution of freshly prepared LDA (6.0 mmol) in 10 mL THF at −78°C was added dropwise a solution of **1** (1.0 g, 5.4 mmol) in 50 mL THF. The red solution was stirred for 15 min at −78°C and 1 h at 0°C. A solution of ferrocenecarbaldehyde (1.16 g, 5.4 mmol) in 40 mL THF was added dropwise and the yellow-green solution was stirred for 2 h at 0°C. The reaction mixture was then cooled to −78°C and treated with 1.6 M butyllithium solution in hexane (3.8 mL, 6.1 mmol). After being stirred for 1 h at 0°C, octylbromide (1.05 g, 5.4 mmol) was slowly added and the solution was stirred for 2 h at 0°C and then overnight at 25°C. The mixture was quenched with 50 mL water, extracted with ethyl acetate (3 × 75 mL), dried over $MgSO_4$, and evaporated. The crude product was

purified by chromatography on alumina using ether–ethanol as the eluant. The resulting red oil was dissolved in 125 mL dry toluene, *p*-toluenesulfonic acid monohydrate (500 mg, 2.6 mmol) was added, and the mixture was refluxed for 4 h and then cooled to room temperature. The solution was washed with 100 mL saturated water solution of $NaHCO_3$, dried, and evaporated in vacuo. Recrystallization from ethyl acetate yielded **8** as red crystals (1.8 g); ^{1}H NMR, δ: 8.58 (d, 2H, J = 5.0 Hz, H^6 and $H^{6'}$), 8.43 (d, 1H, J = 1.5 Hz, H^3), 8.25 (d, 1H, J = 1.0 Hz, $H^{3'}$), 7.27 (d, 1H, J = 16.1 Hz, CH═), 7.27 (dd, 1H, J = 5.0 and 1.5 Hz, H^5), 7.15 (dd, 1H, J = 5.0 and 1.5 Hz, $H^{5'}$), 6.70 (d, 1H, J = 16.1 Hz, CH═), 4.50 (t, 2H, J = 1.8 Hz, C_5H_4-), 4.36 (t, 2H, J = 1.8 Hz, C_5H_4-), 4.14 (s, 5H, C_5H_5), 2.69 (t, 2H, J = 7.7 Hz, CH_2-), 1.69 (m, 2H, CH_2-), 1.40–1.10 (m, 12H, $(CH_2)_6$-), 0.86 (t, 3H, J = 7.0 Hz, CH_3). Anal. calcd. for $C_{31}H_{36}N_2Fe$: C 75.63, H 7.32, N 5.69; found: C 75.82, H 7.32, N 5.73.

4,4′-Bis[*p*-(*N*,*N*-dibutylamino)styryl]-2,2′-bipyridine 9

To a stirred solution of freshly prepared LDA (21 mmol) in 30 mL THF at −78°C was added slowly a solution of **1** (1.84 g, 10 mmol) in 75 mL THF. The red-brown solution was stirred for 1.5 h at −78°C. A solution of 4-(*N*,*N*-dibutylamino)benzaldehyde (4.66 g, 20 mmol) in 20 mL THF was then added dropwise and the yellow-green solution was stirred for 2 h at −78°C and then overnight at 25°C. The mixture was quenched with 100 mL water and extracted with CH_2Cl_2 (2 × 100 mL). The combined extract was dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by chromatography on silica gel with dichloromethane–methanol – ammonium hydroxide (100/5/1) as the eluant. The resulting diol was then dissolved in 250 mL toluene and treated with pyridinium *p*-toluene sulfonate (0.1 g, 0.4 mmol). The mixture was refluxed for 4 h, then cooled to room temperature, washed with saturated aqueous sodium bicarbonate, dried over $MgSO_4$, and evaporated in vacuo. Recrystallization from ethyl acetate yielded **9** as orange microcrystals (5.2 g); mp 140°C; ^{1}H NMR, δ: 8.60 (d, 2H, J = 5.1 Hz, $H^{6,6'}$), 8.46 (d, 2H, J = 1.1 Hz , $H^{3,3'}$), 7.42 (d, 4H, J = 8.8 Hz, C_6H_4-), 7.38 (d, 2H, J = 16.2 Hz, CH═), 7.33 (dd, 2H, J = 5.1 and 1.1 Hz, $H^{5,5'}$), 6.88 (d, 2H, J = 16.2 Hz, CH═), 6.63 (d, 4H, J = 8.8 Hz, C_6H_4-), 3.30 (t, 8H, J = 7.6 Hz, N-CH_2-), 1.59 (m, 8H, CH_2-), 1.36 (m, 8H, CH_2-), 0.96 (t, 12H, J = 7.3 Hz, CH_3). Anal. calcd. for $C_{42}H_{54}N_4$: C 82.04, H 8.85, N 9.11; found: C 81.96, H 8.73, N 8.94.

4,4′-Bis[p-[(*N*-methyl-*N*-octyl)amino]styryl]-2,2′-bipyridine 10

The title compound was prepared analogously as described for **9**, using **1** (1.84 g, 10 mmol) and 4-(*N*-methyl-*N*-octylamino)benzaldehyde (5.0 g, 20 mmol) as starting materials, and was isolated as orange microcrystals after recrystallization from ethyl acetate (5.0 g); mp 136°C; ^{1}H NMR, δ: 8.60 (d, 2H, J = 5.2 Hz, $H^{6,6'}$), 8.46 (s, 2H, $H^{3,3'}$), 7.44 (d, 4H, J = 8.8 Hz, C_6H_4-), 7.39 (d, 2H, J = 16.2 Hz, CH═), 7.33 (dd, 2H, J = 5.2 and 1.5 Hz, $H^{5,5'}$), 6.90 (d, 2H, J = 16.2 Hz, CH═), 6.67 (d, 4H, J = 8.8 Hz, C_6H_4-), 3.33 (t, 4H, J = 7.5 Hz, N-CH_2-), 2.97 (s, 6H, N-CH_3), 1.59 (m, 4H, CH_2-), 1.29 (m, 20H, $(CH_2)_5$-), 0.88 (t, 6H, J = 6.6 Hz, CH_3); HRMS *m/z*, calcd. for $C_{44}H_{58}N_4$: 642.4661; found: 642.470.

(*S*)-(+)-4,4′-Bis[*p*-[*N*-methyl-*N*-(2-methylbutyl)amino]-styryl]-2,2′-bipyridine 11

The title compound was prepared analogously as described for **9**, using **1** (1.48 g, 8 mmol) and 4-[*N*-methyl-*N*-(2-methylbutyl)amino]benzaldehyde (3.4 g, 16 mmol) as starting materials, and was isolated as yellow-orange microcrystals after recrystallization from ethanol (2.3 g); mp 184°C; $[\alpha]_D$ = +12 (c = 1.0, CH_2Cl_2); ^{1}H NMR, δ: 8.60 (d, 2H, J = 5.2 Hz, $H^{6,6'}$), 8.47 (s, 2H, $H^{3,3'}$), 7.44 (d, 4H, J = 8.9 Hz, C_6H_4-), 7.39 (d, 2H, J = 16.2 Hz, CH═), 7.33 (dd, 2H, J = 5.2 and 1.5 Hz, $H^{5,5'}$), 6.90 (d, 2H, J = 16.2 Hz, CH═), 6.67 (d, 4H, J = 8.9 Hz, C_6H_4-), 3.28 (dd, 2H, J = 14.6 and 6.8 Hz, N-CH_2-), 3.10 (dd, 2H, J = 14.6 and 7.9 Hz, N-CH_2-), 3.00 (s, 6H, N-CH_3), 1.86 (m, 2H, CH-), 1.46 (dq, 2H, CH_2-), 1.13 (dq, 2H, CH_2-), 0.91 (m, 2 × 6H, CH-CH_3 and CH_2-CH_3). Anal. calcd. for $C_{38}H_{46}N_4$: C 81.68, H 8.30, N 10.03; found: C 80.53, H 8.26, N 9.76. HRMS *m/z*, calcd: 558.3722; found: 558.368.

4,4′-Bis[*p*-(octyloxy)styryl]-2,2′-bipyridine 12

The title compound was prepared analogously as described for **9**, using **1** (1.50 g, 8.14 mmol) and 4-octyloxybenzaldehyde (3.81 g, 16.28 mmol) as starting materials, and was isolated as white microcrystals after recrystallization from ethyl acetate (1.0 g); mp 146°C; ^{1}H NMR, δ: 8.64 (d, 2H, J = 5.2 Hz, $H^{6,6'}$), 8.51 (d, 2H, J = 1.6 Hz, $H^{3,3'}$), 7.49 (d, 4H, J = 8.7 Hz, C_6H_4-), 7.41 (d, 2H, J = 16.3 Hz, CH═), 7.36 (dd, 2H, J = 5.2 and 1.6 Hz, $H^{5,5'}$), 6.98 (d, 2H, J = 16.3 Hz, CH═), 6.91 (d, 4H, J = 8.7 Hz, C_6H_4-), 3.98 (t, 4H, J = 6.6 Hz, O-CH_2-), 1.79 (m, 4H, CH_2-), 1.60–1.20 (m, 20H, $(CH_2)_5$-), 0.88 (t, 6H, J = 6.6 Hz, CH_3). Anal. calcd. for $C_{42}H_{52}N_2O_2$: C 81.78, H 8.50, N 4.54; found: C 81.20, H 8.54, N 4.27.

(*S*)-(+)-4,4′-Bis[*p*-[(2-methyl)butoxy]styryl]-2,2′-bipyridine 13

The title compound was prepared analogously as described for **9**, using **1** (1.19 g, 6.45 mmol) and 4-(2-methylbutoxy)benzaldehyde (2.48 g, 12.90 mmol) as starting materials, and was isolated as pale yellow microcrystals after recrystallization from ethyl acetate (0.8 g); mp > 200°C; ^{1}H NMR, δ: 8.64 (d, 2H, J = 5.2 Hz, $H^{6,6'}$), 8.51 (d, 2H, J = 1.7 Hz, $H^{3,3'}$), 7.49 (d, 4H, J = 8.7 Hz, C_6H_4-), 7.41 (d, 2H, J = 16.3 Hz, CH═), 7.36 (dd, 2H, J = 5.2 and 1.7 Hz, $H^{5,5'}$), 6.98 (d, 2H, J = 16.3 Hz, CH═), 6.91 (d, 4H, J = 8.7 Hz, C_6H_4-), 3.85 (dd, 4H, J = 9.0 and 6.0 Hz, O-CH_2-), 1.86 (m, 2H, CH-), 1.56 (m, 2H, CH_2-), 1.25 (m, 2H, CH_2-), 0.95 (t, 6H, J = 6.7 Hz, CH_3), 0.95 (t, 6H, J = 7.4 Hz, CH_3). Anal. calcd. for $C_{36}H_{40}N_2O_2$: C 81.16, H 7.47, N 5.26; found: C 80.33, H 7.58, N 5.23.

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