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Dendritic polyallyl and polyferrocenyl bipyridine ligands: Synthesis, MALDI-TOF characterization and ruthenium(II) complexation studies

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ABSTRACT

A series of 6- and 18-armed dendritic polyallyl- and polyferrocenyl-containing bipyridine ligands were synthesized through the coupling reaction of 4,4′-bis(bromomethyl)-2,2′-bipyridine with AB_3 and AB_9 dendrons. All these bipyridine ligands were successfully characterized using standard physico-chemical techniques as well as MALDI-TOF mass spectrometric analysis. The complexation studies of these ligands toward $RuCl_2(bpy)_2$ indicated that, in contrast to the bulky 18-ferrocenyl bipyridine ligand **7**, the 6-allyl **4** and the 18-allyl **5** bipyridine ligands react with $Ru(bpy)_2Cl_2$ to give the corresponding ruthenium(II) complexes **9** and **10**. In the case of ligand **7**, the steric bulk of the two nonaferrocenyl wedges at the 4,4′-position of the bipyridine moiety prevents the conversion of the transoid structure of the ligand to the cisiod structure needed for chelation to the metal. Thus, the 18-ferrocenyl ruthenium(II) dendrimer was not obtained. Metallodendrimers **9** and **10** have been characterized by a combination of analytical methods, especially MALDI-TOF mass spectrometric techniques. The hydrogenation of the 6-allyl ruthenium(II) dendrimer **9** in the presence of Pd/C catalyst gave the expected *n*-propyl complex **11**. This reaction constitutes a new way for the direct synthesis of alkyl bipyridine metallodendrimers. The coordination of the alkene dendritic bipyridine ligand to the metal before the catalytic hydrogenation is absolutely necessary, because of their poisoning effect for the catalyst.

1. Introduction

Construction of organic, inorganic and organometallic dendrimers is now a well-established field of research [1]. However, publications from the last few years demonstrate a continuing interest in the development of new and ever more efficient synthetic methodologies [2], and a considerable number of dendritic compounds have been prepared for industrial applications [3] as well as academic studies [4]. Because of their controlled molecular architectures, dendrimers have found use in various areas such as catalysis [5], supramolecular chemistry [6], biomimetics [7], surface chemistry [8], light-harvesting materials [9], and medicine [10]. Among metallodendrimers, ruthenium bipyridine complexes have been widely studied because of their versatile photo [11] - and/or electrochemical [12] properties. It has been demonstrated that the modification of dendritic ligands around the ruthenium(II) affects the photochemical and electrochemical properties of the metal [11,12]. Furthermore, chelating bidentate N-donor ligands such as 2,2′-bipyridine to ruthenium(II) have also proven effectiveness in catalysis [13]. For example, Bruneau et al. have reported the efficiency of ruthenium mono(bipyridine) complexes such as $[Cp^*(\eta^2\text{-bipy})(CH_3CN)Ru(II)][PF_6]$, for the catalytic regioselective nucleophilic substitution of unsymmetrical allylic carbonate [11a]. In their investigations, they found that the catalytic properties in this reaction was dependent on the 2,2′-bipyridine structure. Thus, introducing dendritic bipyridine ligands in such systems should improve the stability, solubility, efficiency and recyclability of the catalyst [14]. For the above mentioned reasons and a variety of dendrimers and metallodendrimers application domains, the design of new organic, inorganic and organometallic dendritic structures [14,15] is highly desired. In this context, we have synthesized and characterized new 2,2′-bipyridine ligands carrying AB_3 or AB_9 polyallyl- and polyferrocenyl dendritic wedge in their 4,4′-positions. We also describe the synthesis of two ruthenium(II)-cored metallodendrimers bearing, respectively, 6- and 18-allyl groups at their periphery, as well as their MALDI-TOF mass spectrometric analysis. Furthermore, we have shown that in contrast to free allyl bipyridine ligands that are poison for the Pd/C catalyst, the corresponding ruthenium(II) complexes were hydrogenated in similar conditions, leading quantitatively to the *n*-propyl counterparts.

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2. Results and discussion

2.1. Synthesis and spectroscopic characterization of the 6- and 18-armed dendritic bipyridine ligands

2.1.1. Synthesis of 6- and 18-allyl dendritic bipyridine compounds *4* and *5*

Dendritic polyallyl bipyridine ligands **4** and **5** were synthesized as summarized in Scheme 1, following the literature procedure [11a].

The excess of 3-allyl phenol dendron **2** [15b,16] and the 9-allyl phenol dendrons **3** [16] react with 4,4′-bis(bromomethyl)-2,2′-bipyridine **1** [17] to give the corresponding dendritic 6-allyl and 18-allyl bipyridine ligands **4** and **5** in 96% and 95% yield, respectively. In this step, the number of peripheral functions is doubled. The reaction was followed by the complete disappearance of the ^{1}H NMR signal at 4.50 ppm, assigned to the CH_2Br group, and the appearance of a singlet at 5.17 ppm indicative of the CH_2O bond formation. Dendritic bipyridine ligands **4** and **5** were successfully characterized by standard NMR and mass spectrometric analysis. Prominent molecular peaks at *m*/*z*: 637.48 $[M]^+$ for **4** and *m*/*z*: 2006.38 $[M]^+$ for **5** are present in their mass spectrum. The aromatic region of **4** and **5** in their ^{1}H NMR spectra exhibits three sets of signals (a doublet at 8.69 ppm, a singlet at 8.46 ppm and a doublet at 7.45 ppm for **4**, and a doublet at 8.69 ppm, a singlet at 8.48 ppm and a doublet at 7.46 ppm for **5**) assigned to the three different aromatic protons of bipyridine moieties. Attempts to prepare the *n*-propyl counterparts of **4** and **5** by catalytic hydrogenation of allyl groups, using Pd/C catalyst were unsuccessful. Indeed, free bipyridine ligands are poison for the Pd/C catalyst, they inhibit its activity. Thus, the access to *n*-propyl bipyridine derivatives is not possible using these reaction conditions.

2.1.2. Synthesis of 18-ferrocenyl dendritic bipyridine ligand *7*

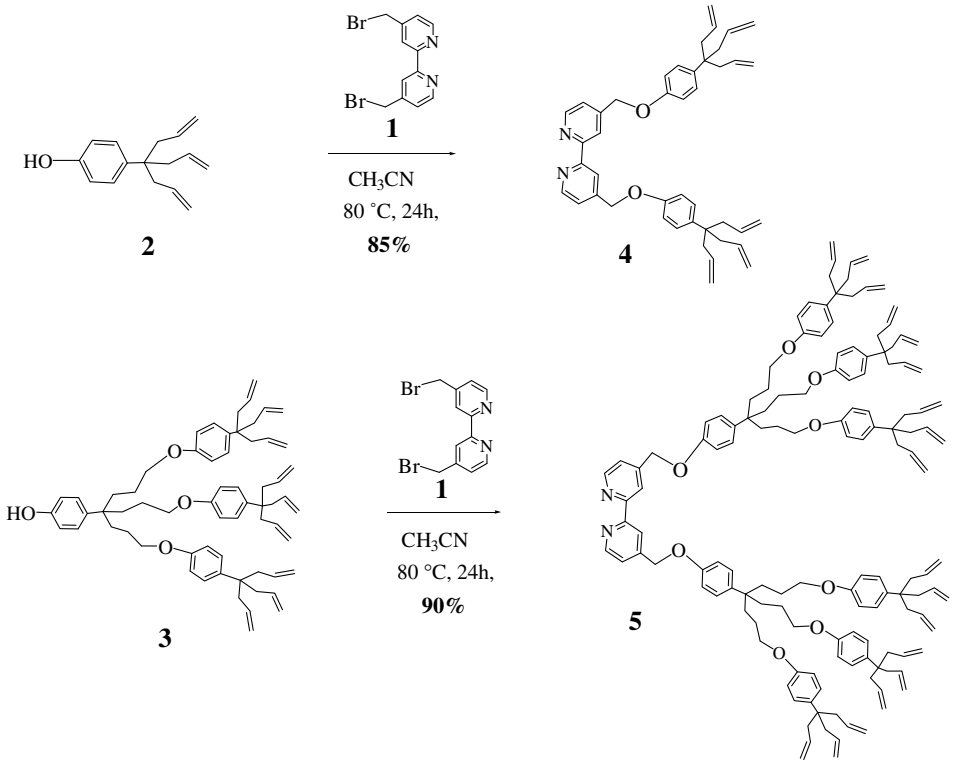
The synthetic procedure to the 18-ferrocenyl bipyridine ligand **7** is summarized in Scheme 2.

The coupling reaction of 4,4′-bis(bromomethyl)-2,2′-bipyridine **1** [17] with excess of nonaferrocenyl dendron **6** [18] in a mixture of CH_3CN and THF (1/1) gave, after purification on a silica gel column, the 18-ferrocenyl bipyridine ligand **7** as an orange solid in a 89% yield. The characterization of compound **7** was carried out using standard NMR and MALDI-TOF mass spectrometric techniques, as well as elemental analysis. Their MALDI-TOF mass spectrum contains a dominant molecular peak at *m*/*z*: 6846.32 $[M]^+$, and small amount of extra peaks probably due to fragmentation in the mass spectrometer and traces of impurities left after the silica gel column. The proton NMR spectra of **7** exhibits three sets of signals in the aromatic part at 8.68, 8.51 and 7.46 ppm, assigned to the three protons of the bipyridine moiety. The 18-ferrocenyl bipyridine **7** represent an interesting polymetallic ligand for the direct synthesis of hetero polymetallodendrimers having new photo-, electrochemical and catalytic properties.

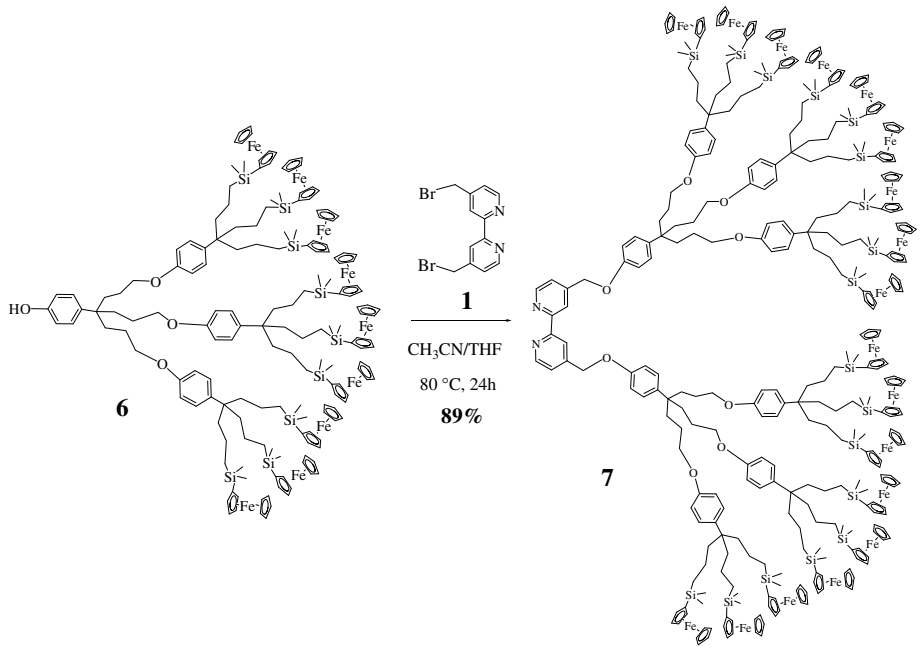
2.2. Synthesis and characterization of 6- and 18-allyl dendritic bipyridine ruthenium(II) complexes *9* and *10*

The complexation of dendritic bipyridine ligands **4** and **5** with $RuCl_2(bpy)_2$ complex **8** [17] gave the 6-allyl and 18-allyl dendritic bipyridine ruthenium(II) complexes **9** and **10**, respectively (Scheme 3).

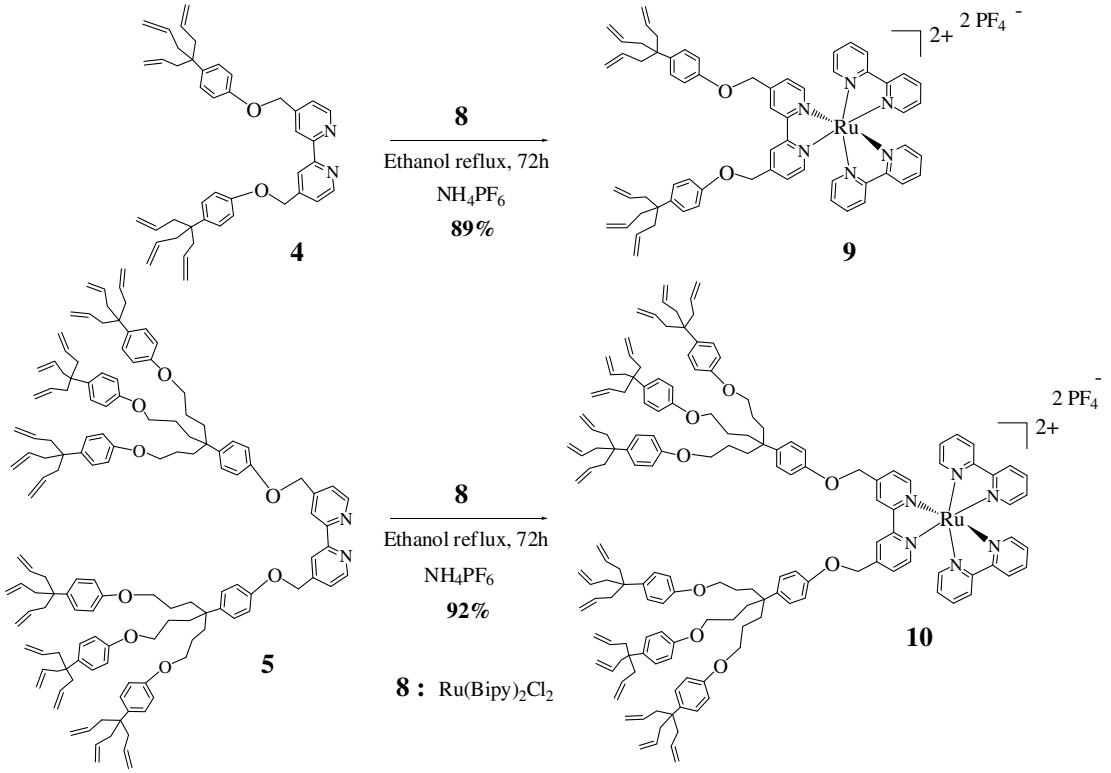
The reaction of the readily obtained $RuCl_2(bpy)_2$ complex **8** [17] with, respectively, one equivalent of 6-allyl-2,2′-bipyridine ligand **4** or 18-allyl-2,2′-bipyridine ligand **5** in boiling ethanol for three days, gave the hexafluorophosphate salts of 6-allyl-2,2′-bipyridine ruthenium complex **9** and 18-allyl-2,2′-bipyridine ruthenium complex **10** in 89 and 92% yield. Compounds **9** and **10** were obtained as



Scheme 1. Synthesis of the 6- and 18-allyl dendritic bipyridine ligands **4** and **5**.

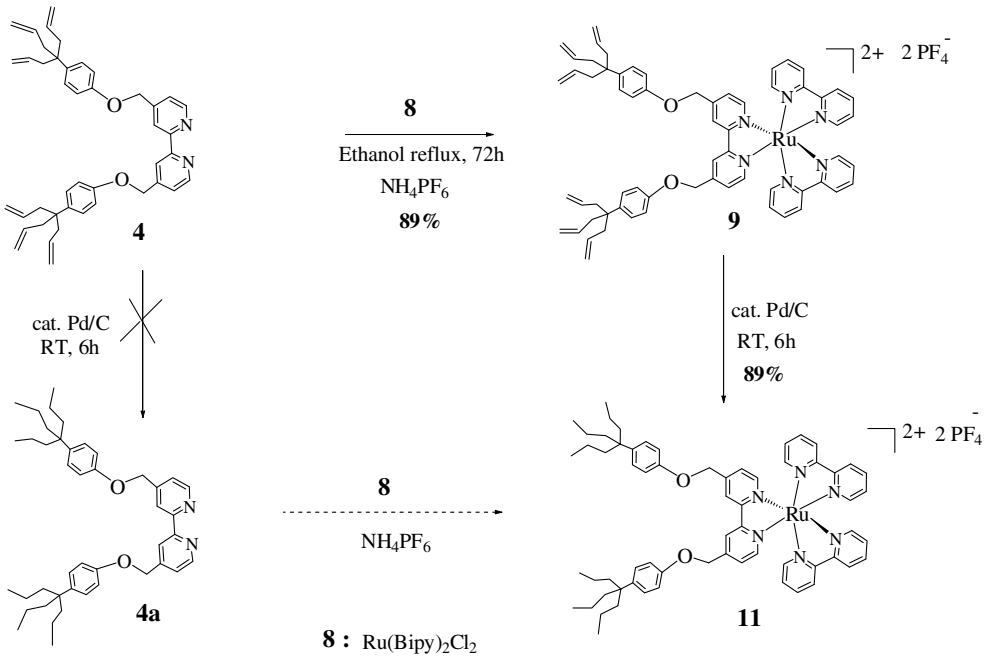


Scheme 2. Synthesis of the 18-ferrocenyl dendritic bipyridine ligand **7**.



Scheme 3. Synthesis of dendritic allyl bipyridine ruthenium(II) complexes **9** and **10**.

yellow-orange solids. Due to the presence of allyl dendritic wedge in their structures, they are soluble in common halogenated hydrocarbons solvent such as $CDCl_3$ or CD_2Cl_2. The structure of the dendritic complexes **9** and **10** were readily identified by their NMR spectra and MALDI-TOF mass spectrometry. The MALDI-TOF mass spectrum of each complex shows two prominent peaks at *m*/*z*: 1195.15 (calcd.: 1195.28) and 1050.21 (calcd.: 1050.32) for **9** and 2565.88 (calcd.: 2565.29) and 2418.49 (calcd.: 2420.32) for **10**, assigned, respectively, to $[M-PF_6]^+$ and $[M-2PF_6]^+$. The investigations of photo- and electrochemical behaviors of these metallodendrimers as well as the use of the above mentioned dendritic ligands in catalysis are currently underway. In contrast to allyl bipyridine ligands **4** and **5**, the complexation of $RuCl_2(bpy)_2$ with the 18-ferrocenyl bipyridine ligand **7** did not proceed



Scheme 4. Synthesis of the 6-*n*-propyl dendritic bipyridine ruthenium(II) complex **11**.

smoothly under the same experimental conditions. The expected ruthenium(II) complex was not obtained and the bipyridine nonaferrocenyl ligand **7** was quantitatively recovered. Lengthening the reaction time under hard reaction conditions (reflux of DMF) was also unsuccessful. This result is probably due to the conversion of the transoid structure of the free ligand to the cisoid conformation (needed for metal chelation), prevented from the steric bulk of the two nonaferrocenyl wedges at the 4,4′-positions of the bipyridine moiety.

*2.3. Synthesis of 6-n-propyl dendritic bipyridine ruthenium(II) complexex **11***

Pursuing our investigation in the preparation of new organic and organometallic dendrimers, we have successfully synthesized the 6-*n*-propyl dendritic bipyridine ruthenium(II) complex **11** from their 6-allyl counterpart **9**, by hydrogenation using Pd/C catalyst (10% Pd) as summarized in Scheme 4.

Whereas allyl bipyridine ligands **4** and **5** are inert towards hydrogen in the presence of Pd/C catalyst, their complexation to the ruthenium(II) before the hydrogenation of allyl groups represents a direct and quantitative procedure for the synthesis of *n*-polypropyl ruthenium(II) complexes. Thus the complexation of 6-propyl bipyridine ligand **4** to $RuCl_2(bpy)_2$ **8** followed by the hydrogenation of allyl groups led to the 6-*n*-propyl complex **11**. The NMR data of **11** as well as their MALDI-TOF mass spectrum are consistent with the proposed structure. The MALDI-TOF mass spectrum shows a prominent peak at *m*/*z*: 1209.49 (calcd.: 1209.39) assigned to $[M-PF_6]^+$. The complexation of the bipyridine moiety to ruthenium(II) is an essential step for the preparation of **11**, because its avoids the free ligands poisoning of the Pd/C catalyst, that inhibits the hydrogenation reaction in these conditions.

3. Conclusion

In this paper, we are reporting the synthesis and characterization of dendritic 2,2′-bipyridine ligands bearing bearing 3-allyl and 9-allyl as well as 9-ferrocenyl dendritic wedge at their 4,4′-positions. The obtained 6-allyl, 18-allyl and 18-ferrocenyl bipyridine ligands were successfully characterized by their molecular peak in MALDI-TOF mass spectrometric analysis. Except for the 18-ferrocenyl compound, the complexation of these ligands to $Ru(bpy)_2Cl_2$ was also successful. The corresponding metallodendrimers were obtained and identified by their molecular peak in MALDI-TOF mass spectrometry. In the case of the 18-ferrocenyl ligand, the steric bulk of the two dendritic wedge at the 4,4′-positions of the bipyridine moiety prevents the transoid free ligand to isomerize to the cisoid form, an essential feature for their chelation to the metal. Furthermore, we have also shown that the complexation of allyl bipyridine ligands to the metal follow by hydrogenation of allyl groups is a valuable procedure for the synthesis of various polyalkyl bipyridine-based complexes. We are currently investigating the photochemical and electrochemical properties of these ligands and metallodendrimers. We are also studied their complexation behavior as well as their influences on the properties of catalytically active species.

4. Experimental

4.1. General remarks

Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were pre-dried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. Acetonitrile (CH_3CN) was stirred under argon overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride just before use. All other chemicals were used as received. The ^1H, ^{13}C, ^{31}P NMR spectra were recorded at 25 °C with a Brucker AC 250 FT spectrometer (^1H: 250.13, ^{13}C: 62.91 MHz) and a Brucker AC 200 FT spectrometer (^1H: 200.16, ^{13}C: 50.33, ^{31}P: 81.02, 19F: 188.33 MHz) at the CESAMO. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS). Elemental analyses were carried out at the Vernaison CNRS center. The matrix-assisted laser-desorption (MALDI) mass spectra were recorded using a Perceptive Biosystems Voyager Elite (Framingham, MA) time-of-flight (TOF) mass spectrometer.

4.2. General procedure for the synthesis of dendritic bipyridine ligands

4.2.1. Dendritic 6- and 18-allyl bipyridine ligands (**4**) and (**5**)

One equivalent of 4,4′-bis(bromomethyl)-2,2′-bipyridine (**1**) was treated with two equivalents of dendron in the presence of three equivalents of K_2CO_3 in CH_3CN. The mixture was stirred at reflux for 24 h. After removal of the solvent under vacuum, the product was extracted with Et_2O and dried over Na_2SO_4. The solvent was evaporated and the product was purified by chromatography (silica gel, pentane/diethyl ether 8:2; then diethyl ether).

*4.2.1.1. Dendritic 6-allyl bipyridine ligand (**4**).* This compound was obtained as a white solid in 85% yield. ^{1}H NMR ($CDCl_3$, 250 MHz) δ_{ppm}: 8.69 (d, $^3J_{H,H}$ = 5 Hz, 2H, pyridine-H), 8.46 (s, 2H, pyridine-H), 7.45 (d, $^3J_{H,H}$ = 5 Hz, 2H, pyridine-H), 7.23 (d, $^3J_{H,H}$ = 8.3 Hz, 4H, Ar), 6.94 (d, $^3J_{H,H}$ = 8.7 Hz, 4H, Ar), 5.57 (m, 6H, $CH_2CH{=}CH_2$), 5.16 (s, 4H, CH_2O), 4.96 (m, 12H, $CH_2CH{=}CH_2$), 2.42 (d, $^3J_{H,H}$ = 7.1 Hz, 12H, $CH_2CH{=}CH_2$). ^{13}C NMR ($CDCl_3$, 63 MHz) δ_{ppm}: 156.2 (C_q, Ar–O), 156.1 (C_q, Ar–O), 156.0 (C, Ar-pyridine), 153.2 (C_q, Ar), 149.5 (C, Ar-pyridine), 147.6 (C_q, Ar), 139.1 (C, Ar-pyridine), 134.6 ($CH_2CH{=}CH_2$), 127.8 (CH, Ar), 121.8 (C, Ar-pyridine), 119.1 (C, Ar-pyridine), 117.6 ($CH_2CH{=}CH_2$), 114.3 (CH, Ar), 68.4 (CH_2-O), 42.5 (C-CH_2), 42.8 (C-CH_2), 41.9 (CH_2). MS (EI, 70 eV) *m/z*: 637.43 $[M]^+$ (calcd. 638.87). Elemental Anal. Calc. for $C_{44}H_{48}O_2N_2$ (638.87): C, 82.98; H, 7.60. Found: C, 83.62; H, 7.62%.

*4.2.1.2. Dendritic 18-allyl bipyridine ligand (**5**).* This compound was obtained as a white solid in 90% yield. ^{1}H NMR ($CDCl_3$, 250 MHz) δ_{ppm}: 8.70 (d, $^3J_{H,H}$ = 5 Hz, 2H, pyridine-H), 8.47 (s, 2H, pyridine-H), 8.46 (d, $^3J_{H,H}$ = 5 Hz, 2H, pyridine-H), 7.31 (d, $^3J_{H,H}$ = 8.3 Hz, 4H, Ar), 7.19 (d, $^3J_{H,H}$ = 8.5 Hz, 12H, Ar), 6.95 (d, $^3J_{H,H}$ = 8.3 Hz, 4H, Ar), 6.81 (d, $^3J_{H,H}$ = 8.5 Hz, 12H, Ar), 5.57 (m, 18H, $CH_2CH{=}CH_2$), 5.17 (s, 4H, CH_2O), 4.96 (m, 36H, $CH_2CH{=}CH_2$), 3.89 (broad, 12H, CH_2O), 2.41 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, $CH_2CH{=}CH_2$), 1.99 (broad, 12H, CH_2), 1.60 (broad, 12H, CH_2). ^{13}C NMR ($CDCl_3$, 63 MHz) δ_{ppm}: 156.7 (C_q, Ar–O), 156.1 (C_q, Ar–O), 156.0 (C, Ar-pyridine), 153.2 (C_q, Ar), 149.4 (C, Ar-pyridine), 147.5 (C_q, Ar), 139.1 (C, Ar-pyridine), 138.3 (C_q, Ar), 137.4 (CH, Ar), 134.5 ($CH_2CH{=}CH_2$), 127.6 (CH, Ar), 127.5 (CH, Ar), 121.6 (C, Ar-pyridine), 118.8 (C, Ar-pyridine), 117.4 ($CH_2CH{=}CH_2$), 113.7 (CH, Ar), 68.3 (CH_2-O), 68.0 (CH_2-O), 42.5 (C-CH_2), 42.0 (C-CH_2), 41.9 (CH_2), 33.6 (CH_2), 23.6 (CH_2). MALDI-TOF mass spectrum, *m/z*: 2006.4 $[M]^+$ (calcd. 2006.8). Elemental Anal. Calc. for $C_{140}H_{168}O_8N_2$: C, 83.78; H, 8.43. Found: C, 83.62; H, 8.47%.

4.2.2. Dendritic 18-ferrocenyl bipyridine ligand (**7**)

This compound was obtained as an orange solid in 89% yield, according to the procedure described above for **4** and **5**, but using a mixture of CH_3CN and THF (*v*/*v* 1:1) as solvent, instead of CH_3CN. ^{1}H NMR ($CDCl_3$, 250 MHz) δ_{ppm}: 8.67 (broad, 2H, pyridine-H), 8.48 (broad, 2H, pyridine-H), 7.46 (broad, 2H, pyridine-H), 7.32 (broad, 4H, Ar), 7.15 (d, $^3J_{H,H}$ = 8.5 Hz, 12H, Ar), 6.92 (broad, 4H, Ar), 6.85 (d, $^3J_{H,H}$ = 7.5 Hz, 12H, Ar), 5.15 (s, 4H, CH_2O), 4.29 (s, 36H, Cp), 4.08 (s, 90H, Cp), 4.01 (s, 36H, Cp), 3.51 (s, 12H, CH_2O), 1.60 (broad, 12H, CH_2), 1.21 (broad, 12H, CH_2), 0.62 (broad, 24H, CH_2Si), 0.16 (broad, 108H, CH_3Si), 0.08 (broad, 36H, CH_3Si). ^{13}C NMR ($CDCl_3$, 63 MHz) δ_{ppm}: 159.01 (C_q, Ar–O), 156.1 (C_q, Ar–O), 156.0 (C, Ar-pyridine), 153.2 (C_q, Ar), 149.4 (C, Ar-pyridine), 139.7 (C_q, Ar), 139.1 (C, Ar-pyridine), 138.3 (C_q, Ar), 127.6 (CH, Ar), 127.2 (CH, Ar), 121.6 (C, Ar-pyridine), 118.8 (C, Ar-pyridine), 113.7 (CH, Ar), 73.0 (C_5H_4), 71.4 (CH_2-O), 70.6 (CH, C_5H_4), 68.1 (C_5H_5), 60.2 (CH_2-O), 43.2 (C-CH_2), 42.2 (C-CH_2), 18.2 (CH_2), 17.6 (CH_2Si), 14.5 (CH_2), −1.8 ($SiCH_3$), −4.5 ($SiCH_3$). MALDI-TOF mass spectrum, *m/z*: 6846.2 $[M]^+$ (calcd. 6841.4). Elemental Anal. Calc. for $C_{374}H_{510}O_8N_2Si_{24}Fe_{18}$: C, 65.66; H, 7.51. Found: C, 65.67; H, 7.54%.

4.3. General procedure for the synthesis of dendritic bipyridine ruthenium(II) (**9**) and (**10**)

One equivalent of $Ru(bpy)_2Cl_2$ was added to a solution of one equivalent of dendritic 2,2′-bipyridine ligand in ethanol. The mixture was stirred at reflux for 3 days. After removal of the solvent under vacuum, the residue was dissolved in CH_2Cl_2 and the solution washed with water several times. The solvent was removed under vacuum and the residue dissolved in a mixture of acetone and water (*v*/*v* 2:1). After addition of NH_4PF_6, an orange-yellow solid was formed. The later was dissolved in CH_2Cl_2, the organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under vacuum to yield the bipyridine complexes as orange-yellow solids.

4.3.1. Dendritic 6-allyl bipyridine complex (**9**)

This compound was obtained in 89% yield. ^{1}H NMR ($CDCl_3$, 250 MHz) δ_{ppm}: 8.55 (s, 2H, pyridine-H), 8.40 (d_{broad}, 4H, pyridine-H), 7.95 (t, 4H, pyridine-H), 7.77 (t, 4H, pyridine-H), 7.71 (d, 2H, pyridine-H), 7.54 (d_{broad}, 2H, pyridine-H), 7.42 (t_{broad}, 4H, pyridine-H), 7.24 (d, $^3J_{H,H}$ = 8.3 Hz, 4H, Ar), 6.96 (d, $^3J_{H,H}$ = 8.7 Hz, 4H, Ar), 5.53 (m, 6H, $CH_2CH{=}CH_2$), 5.24 (s, 4H, CH_2O), 4.98 (m, 12H, $CH_2CH{=}CH_2$), 2.42 (d, $^3J_{H,H}$ = 7.1 Hz, 12H, $CH_2CH{=}CH_2$). ^{13}C NMR ($CDCl_3$, 63 MHz) δ_{ppm}: 156.4 (C_q, Ar–O), 155.4 (C, Ar-pyridine), 151.4 (C_q, Ar), (C, Ar-pyridine), 151.0 (C, Ar-pyridine), 149.7 (C, Ar-pyridine), 149.6 (C_q, Ar), 139.3 (C, Ar-pyridine), 137.9 (C, Ar-pyridine), 134.4 ($CH_2CH{=}CH_2$), 128.0 (CH, Ar), 126.0 (C, Ar-pyridine), 124.2 (C, Ar-pyridine), 122.1 (C, Ar-pyridine), 119.1 (C, Ar-pyridine), 117.6 ($CH_2CH{=}CH_2$), 114.3 (CH, Ar), 67.4 (CH_2-O), 43.0 (C-CH_2), 41.8 (CH_2). ^{31}P NMR ($CDCl_3$, 50.33 MHz) δ_{ppm}: 59.8 (PF_6). ^{19}F NMR ($CDCl_3$, 188.33 MHz) δ_{ppm}: −72.2 (PF_6). MALDI-TOF mass spectrum, *m/z*: 1195.15 $[M-PF_6]^+$ (calcd.: 1195.28) and 1050.21 $[M-2PF_6]^+$ (calcd.: 1050.32). Elemental Anal. Calc. for $C_{64}H_{64}O_2N_6F_{12}P_2Ru$ (1340.35): C, 57.35; H, 4.81. Found: C, 57.63; H, 4.66%.

4.3.2. Dendritic 18-allyl dendritic bipyridine complex (**10**)

This compound was obtained as a white solid in 92% yield. ^{1}H NMR ($CDCl_3$, 250 MHz) δ_{ppm}: 8.59 (s, 2H, pyridine-H), 8.36 (d, $^3J_{H,H}$ = 8.3 Hz, 4H, pyridine-H), 7.97 (t, $^3J_{H,H}$ = 8 Hz, 4H, pyridine-H), 7.74 (m, 4+2H, pyridine-H), 7.50 (m, 4+2H, pyridine-H), 7.32 (d, $^3J_{H,H}$ = 8.8 Hz, 4H, Ar), 7.19 (d, $^3J_{H,H}$ = 8.5 Hz, 12H, Ar), 6.95 (d, $^3J_{H,H}$ = 8.3 Hz, 4H, Ar), 6.79 (d, $^3J_{H,H}$ = 8.5 Hz, 12H, Ar), 5.55 (m, 18H, $CH_2CH{=}CH_2$), 5.3 (s, 4H, CH_2O), 4.99 (m, 36H, $CH_2CH{=}CH_2$), 3.90 (broad, 12H, CH_2O), 2.41 (d, 12H, $CH_2CH{=}CH_2$), 1.86 (broad, 12H, CH_2), 1.58 (broad, 12H, CH_2). ^{13}C NMR ($CDCl_3$, 63 MHz) δ_{ppm}: 157.1 (C_q, Ar–O), 156.3 (C_q, Ar–O), 155.9 (C, Ar-pyridine), 149.1 (C, Ar-pyridine), 147.5 (C_q, Ar), 139.3 (C, Ar-pyridine), 137.2 (C_q, Ar), 137.4 (CH, Ar), 134.6 (C, $CH_2CH{=}CH_2$), 127.6 (CH, Ar), 127.4 (CH, Ar), 121.7 (C, Ar-pyridine), 118.5 (C, Ar-pyridine), 116.8 ($CH_2CH{=}CH_2$), 113.7 (CH, Ar), 67.9 (CH_2-O), 67.8 (CH_2-O), 42.3 (C-CH_2), 41.8 (C-CH_2), 41.6 (CH_2), 33.4 (CH_2), 23.5 (CH_2); ^{31}P NMR ($CDCl_3$, 50.33 MHz): δ = 59.8 (PF_6). ^{19}F NMR ($CDCl_3$, 188.33 MHz) δ_{ppm}: −72.2 (PF_6). MALDI-TOF mass spectrum, *m/z*: 2565.49 $[M-PF_6]^+$ (calcd. 2565.29), 2418.49 $[M-2PF_6]^+$ (calcd. 2420.32). Elemental Anal. Calc. for $C_{160}H_{184}F_{12}N_6O_8P_2Ru$: C, 70.91; H, 6.84. Found: C, 71.01; H, 6.80%.

4.3.3. 6-*n*-propyl dendritic bipyridine complex (**11**)

This compound was obtained as an orange-red oil in 89% yield. ^{1}H NMR ($CDCl_3$, 250 MHz) δ_{ppm}: 8.52 (s, 2H, pyridine-H), 8.40 (d, 4H, pyridine-H), 7.97 (t, 4H, pyridine-H), 7.74 (t, 4H, pyridine-H), 7.68 (d, 2H, pyridine-H), 7.56 (d, 2H, pyridine-H), 7.46 (m, 4H, pyridine-H), 7.24 (d, $^3J_{H,H}$ = 8.3 Hz, 4H, Ar), 6.92 (d, $^3J_{H,H}$ = 8.7 Hz, 4H, Ar), 5.24 (s, 4H, CH_2O), 1.56 (m, 12H, CH_2), 1.03 (m, 12H, CH_2), 0.84 (t, 18H, CH_3). ^{13}C NMR ($CDCl_3$, 63 MHz) δ_{ppm}: 156.5 (C_q, Ar–O), 156.4 C, Ar-pyridine), 155.1 (C, Ar-pyridine), 151.5 (C_q, Ar),

151.4 (C, Ar-pyridine), 151.0 (C, Ar-pyridine), 149.6 (C, Ar-pyridine), 141.7 (C, Ar-pyridine), 137.9 (C, Ar-pyridine), 128.2 (C, Ar-pyridine), 127.7 (CH, Ar), 126.1 (C, Ar-pyridine), 124.0 (C, Ar-pyridine), 114.0 (CH, Ar), 104.4 (C, Ar-pyridine), 67.4 (CH_2-O), 42.7 (C-CH_2), 40.2 (CH_2), 16.7 (CH_2), 14.8 (CH_3). ^{31}P NMR ($CDCl_3$, 50.33 MHz) δ_{ppm}: 59.8 (PF_6). ^{19}F NMR ($CDCl_3$, 188.33 MHz) δ_{ppm}: −72.3 (d, PF_6). MALDI-TOF mass spectrum, *m/z*: 1209.49 $[M-PF_6]^+$, (calcd. 1209.39). Elemental Anal. Calc. for $C_{64}H_{78}O_2N_6F_{12}P_2Ru$ (1354.36): C, 56.76; H, 5.80. Found: C, 56.84; H, 5.70%.

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