Synthesis and Photophysical Properties of New 2,2′-Bipyridine-Bridged Bis[ruthenium(II)tris-2,2′-bipyridine] Complexes

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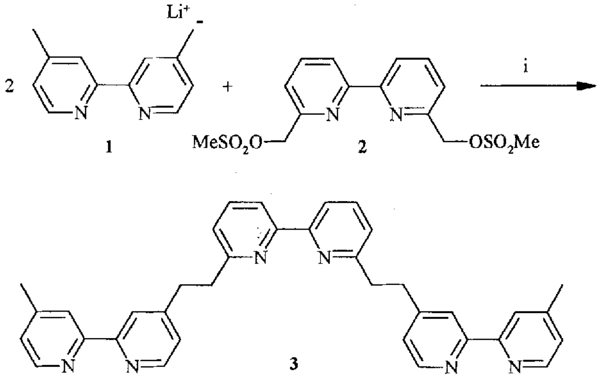
We have synthesized a new type of tris-2,2′-bipyridine ligand with 4,4′- and 6,6′-disubstituted 2,2′-bipyridine (bpy) units. The terminal 4,4′-disubstituted 2,2′-bipyridine moieties are selectively coordinated by $Ru(bpy)_2$ (bpy = 2,2′-bipyridine), whereas the central 2,2′-bipyridine ligand does not participate in any metal ion coordination. The two $Ru(bpy)_3$ units of **7** and **8** do not interact appreciably, as is evident from their electrochemical and photophysical data. The lifetime of the excited state of compound **7** at 77 K is similar to that of $Ru(bpy)_2$(4,4′-dimethyl-2,2′-bipyridine), whereas that of compound **8** under the same conditions is comparatively long.

Multimetallic assemblies of defined structure are key design targets for the study of energy- and electron transfer[1]. Ruthenium complexes of polypyridine ligands play a central role in these systems due to their chemical stability, redox properties, and favorable photophysical characteristics[2]. Most di- and oligonuclear ruthenium complexes have been synthesized by metal complexation of a multitopic ligand[3]. This procedure does not always provide full control over the final composition of the oligonuclear complex[4]. The selective synthesis of assemblies with free binding sites is especially difficult. We report here on the preparation of new tris-2,2′-bipyridine ligands with different binding sites and their selective twofold coordination by $Ru(bpy)_2$[5] moieties. The redox, absorption, and luminescence properties of the 2,2′-bipyridine-bridged bis(ruthenium) complexes thus obtained have been investigated.

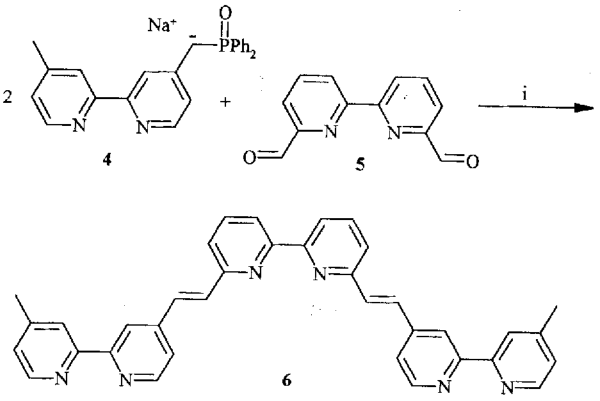
Results and Discussion

A twofold substitution of **2**[6] by lithiated 2,2′-bipyridine **1**[7] gave compound **3** in 41% isolated yield. The resonance of all eight ethano bridge protons in the ^{1}H-NMR spectrum of **3** collapse into a singlet, whereas the 6,6′- and 4,4′-aromatic substitution patterns are clearly distinguishable. A Wittig-Horner-Emmons-Wadsworth procedure was used for the synthesis of **6** from 2,2′-bipyridine phosphane oxide **4**[8] and 6,6′-diformyl-2,2′-bipyridine[9]. The exclusively *trans* geometry of the newly formed double bonds of **6** was confirmed by the coupling constants of the proton NMR spectrum.

Scheme 1. Reagents and reaction conditions: i) THF, 0 °C, 2 h



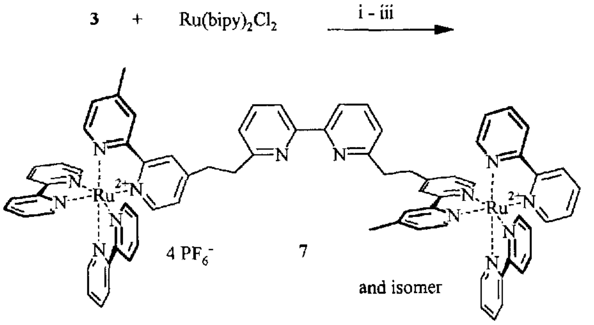
Scheme 2. Reagents and conditions: i) THF, 60 °C, 1 h, then 15 min at reflux temperature



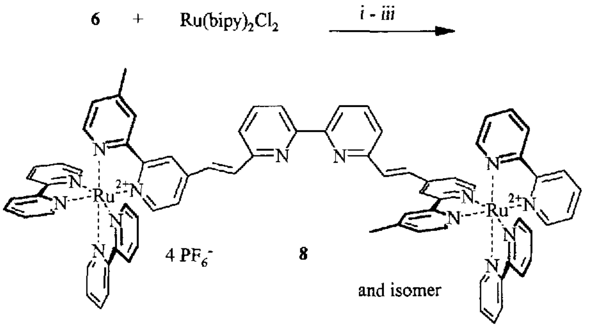
The coordination of the new ligands **3** and **6** with $Ru(bpy)_2$ groups shows a remarkable selectivity: only the terminal 2,2′-bipyridine units were coordinated under standard conditions[10] for $Ru(bpy)_3$ complex formation. A rationale for this observation is the different steric hindrance of the terminal and central 2,2′-bipyridine moieties.

The 6,6'-substitution of the central 2,2'-bipyridine ligand prevents the formation of an octahedral Ru(bpy)$_3$ complex[11]. All attempts to further functionalize the central 2,2'-bipyridine unit of **7** and **8** were unsuccessful. Neither quaternization with MeI[12] nor complexation with metal ions, such as PdCl$_2$[13], ZnBr$_2$[14], or Hg(CF$_3$CO$_2$)$_2$[15] gave any products.

Scheme 3. Reagents and conditions: i) THF, 20 °C, 2 h

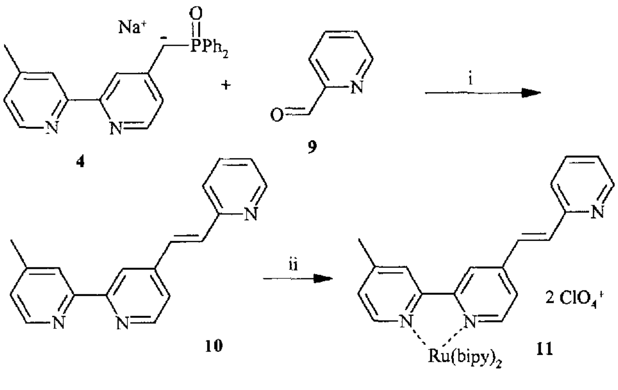


Scheme 4. Reagents and conditions: i) EtOH/H$_2$O, reflux, Ru(bipy)$_2$Cl$_2$; ii) **6**; iii) NaPF$_6$

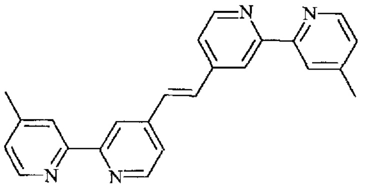


Compound **11** was prepared to compare the physical properties of a vinylpyridine-substituted ruthenium complex with those of the extended system **8**. The compound, which corresponds to one half of **8**, was obtained via coupling of **4** with 2-formylpyridine (**9**) and ruthenium complexation of the 2,2'-bipyridine moiety.

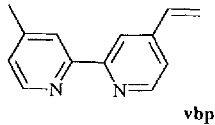
Scheme 5. Reagents and conditions: i) AgClO$_4$, acetone, Ru(bipy)$_2$Cl$_2$; ii) **6**; iii) NaPF$_6$



In Table 1, the redox potentials of compounds **7**, **8**, and **11** are summarized. The [Ru(bpy)$_3$]$^{2+}$ moieties in **7** and **8** act as independent redox centers. The measured potentials for the Ru^{II}/Ru^{III} processes of **7**, **8**, and **11** are identical to the reported values for complexes with a similar substructure, such as [(4,4'-dmb)$_2$Ru(bbpe)]$^{2+}$[16] and [Ru(4,4'-dmb)$_2$(vbpy)]$^{2+}$[17].



bbpe



vbpy

Table 1. Redox potentials[a] of compounds **7**, **8**, and **11**

Compound	E^f [V][a]	ΔE_p [mV]
7	0.84	70
8	0.85	70
11	0.85	70

[a] Values quoted were at 50 mV/s in 3 × 10^{-3} M solutions of the compounds in 0.1 M Bu$_4$N · PF$_6$–CH$_3$CN at 25 °C vs ferrocene/ferrocenium; formal potential $E^f = 1/2(E_{p,c} + E_{p,a})$ · $E_{p,c}$ = cathodic peak potential; $E_{p,a}$ = anodic peak potential; $\Delta E_p = E_{p,a} - E_{p,c}$.

Figure 1 shows the absorption and emission spectra of compounds **7**, **8**, and **11** in acetonitrile solution (1 · 10^{-5} M) at 298 K. A summary of the photophysical data is given in Table 2. In the same table, data relating to Ru(bpy)$_2$(4,4'-dmb)$^{2+}$ are also shown for comparison purposes. Each compound exhibits ligand-centered bands in the near UV region and metal-to-ligand charge-transfer (MLCT) bands in the visible region.

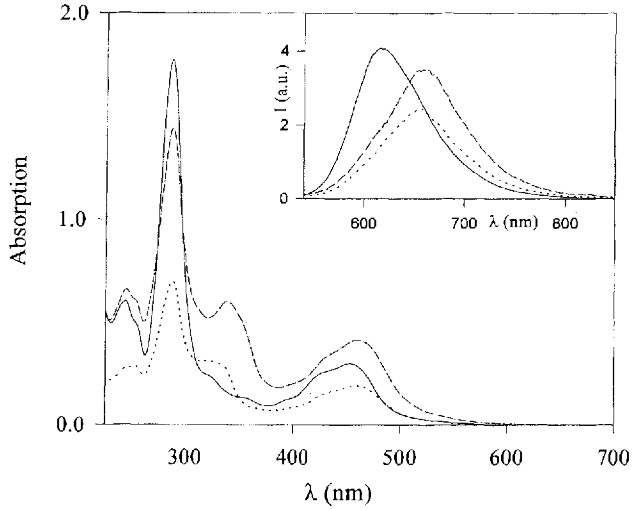
It is well-known that in Ru^{II}(polypyridine) complexes emission originates from the lowest, formally spin-forbidden, ^{3}MLCT level. The luminescence behavior of compound **7** is, as expected, very similar to that of Ru(bpy)$_2$(4,4'-dmb)$^{2+}$[1,18], which is in fact its chromophoric unit. The two Ru-based moieties do not interact appreciably (see also electrochemical results), other than in the case of analogous dinuclear complexes in which two Ru(bpy)$_3^{2+}$-type moieties are linked by aliphatic[19] or aliphatic-aromatic[20] chains[2]. Emission of the mononuclear compound **11** occurs at lower energy, as would be expected since the substituted 2,2'-bipyridine ligand is a better electron-acceptor than bipyridine. The emission band of the structurally similar compound Ru(4,4'-dmb)$_2$(bbpe)$^{2+}$, studied by Meyer et al.[17] is found at much lower energy (λ_{max} = 732 nm). The different behavior of Meyer's compound can be ascribed to the presence of the electron-donating methyl substituents in the ancillary 2,2'-bipyridine ligands, the different substitution position (4 vs. 2) on the pyridine ring in compound **11**, and perhaps also to the more extended conjugation of the ligand involved in the lowest energy CT transition. In compound **8**, the emission

Table 2. Photophysical data of compounds **7**, **8**, and **11**

Compound	**Absorption**		**Emission at 298 K**			**Emission at 77 K**	
	λ_{max} [nm]	ε $[M^{-1}cm^{-1}]$	λ_{max} [nm]	τ [ns]	φ	λ_{max} [nm]	τ [ms]
7	453 287	29400 177500	618	157	0.015	589	5.5
8	461 287	41020 144200	661	190	0.0016	647	15.6
11	459 288	18500 69300	657	160	0.0011	640	16.3
$Ru(bpy)_2(4,4'\text{-dmb})^{2+}$	445[a]	16000[a]	615[a]			586[b]	5.2[b]

[a] Acetonitrile solution, ref.[18] – [b] MeOH/EtOH, ref.[18]

Figure 1. Absorption (left) and emission (upper right) spectra of compounds **7** (–), **8** (– – –) and **11** (···) in acetonitrile solution (1×10^{-5} M) at 298 K



band is slightly bathochromically shifted compared to the mononuclear compound, **11**, although this shift is smaller than in the case of $Ru(4,4'\text{-dmb})_2(bbpe)Ru(4,4'\text{-dmb})_2^{4+}$ or $Ru(4,4'\text{-dmb})_2(bbpe)^{2+}$[17].

A remarkable characteristic of **8** and **11** is the very long excited state lifetime at 77 K. As discussed by Meyer et al.[17,21] the extended lifetime is a delocalization effect. Delocalization decreases changes in local bond displacements due to electronic excitation. This reduces vibrational overlap between excited state and ground state, with a consequent decrease in the rate of radiationless deactivation. At room temperature, this effect is not observable because under such conditions the dominant pathway for radiationless deactivation of the luminescent ^{3}MLCT level is conversion to an upper-lying, distorted ligand-field level rather than direct deactivation to the ground state[1].

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Experimental Section

Melting points were taken on a hot-plate microscope apparatus and are not corrected. – NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C) In [D]chloroform solution unless otherwise stated. The multiplicities of the ^{13}C signals were determined with the DEPT technique and are quoted as: (+) for CH_3 or CH, (–) for CH_2 and (C_{quat}) for quaternary carbons. – Column chromatography (CC) was performed on silica gel. – Redox potentials were measured under nitrogen in 0.1 M Bu_4NPF_6 acetonitrile solution at 20 °C using a glassy carbon working electrode and a platinum wire counter electrode. Reference electrode: $Ag^+/AgCl^+$ in LiCl satd. ethanol; potentiostat: Autolab PGSTAT20, Eco Chemie; program GPES V3.0. – Absorption spectra were measured in acetonitrile solution at room temperature with a Perkin-Elmer Lambda 6 spectrophotometer. – Luminescence experiments were performed in air-equilibrated acetonitrile solution at room temperature and in freshly distilled butyronitrile at 77 K. Uncorrected luminescence spectra were obtained with a Perkin-Elmer LS 50 spectrofluorimeter. Luminescence decay measurements in the nanosecond range were performed with an Edinburgh single-photon counting apparatus. Luminescence quantum yields were measured by the method described by Demas and Crosby[22], using $[Ru(bpy)_3]^{2+}$ ($F = 2.8 \cdot 10^{-2}$ in aerated water[23]) as a standard.

Ligand **3**: A solution of 4,4′-dimethyl-2,2′-bipyridine (**1**) (920 mg, 5 mmol) and 6 mmol of LDA in 50 ml of dry THF was stirred for 3.5 h at 0 °C. After addition of 6,6′-bis(hydroxymethyl)-2,2′-bipyridine methylsulfonate (**2**) (750 mg, 2.2 mmol), the mixture was allowed to react for 2 h at 0 °C. The reaction was quenched by the addition of satd. aqueous NH_4Cl solution and the mixture was diluted with CH_2Cl_2. The organic phase was washed four times with satd. NH_4Cl solution and water, dried over $MgSO_4$ and the solvent was completely removed in vacuo. Recrystallization from *n*-heptane yielded **3** (490 mg, 41%) as a white solid ($R_f = 0.3$, SiO_2; $CH_2Cl_2/MeOH/NH_3$, 100:5:0.5), m.p. 162 °C. – IR (KBr): $\tilde{\nu} = 1594$ cm^{-1}, 1573, 1536, 1459, 1439, 1374, 992, 824, 807. – UV (CH_3CN): λ_{max} (ε) = 202 nm (110660), 242 (31630), 284 (41530). – ^{1}H NMR: δ = 2.43 (s, 6H), 3.25 (s, 8H), 7.13 (m, 6H), 7.69 (dd, J = 7.8 Hz, J = 7.8 Hz, 2H), 8.22 (s, 2H), 8.28 (d, J = 7.8 Hz, 2H), 8.35 (s, 2H), 8.53 (m, 4H). – ^{13}C NMR: δ = 21.1 (+), 34.9 (–), 38.5 (–), 118.7 (+), 121.3 (+), 121.9 (+), 122.7 (+), 123.9 (+), 124.6 (+), 137.0 (+), 148.0 (C_{quat}), 148.8 (+), 148.9 (+), 151.8 (C_{quat}), 155.8 (C_{quat}), 155.9 (C_{quat}), 156.1 (C_{quat}), 159.5 (C_{quat}). – MS (70 eV); *m/z* (%): 548 (100) [M^+]. – $C_{36}H_{32}N_6$: calcd. 548.268; found 548.268 (MS).

4-[(Diphenylphosphinoyl)methyl]-4′-methyl-2,2′-bipyridine (**4**; H^+ instead of Na^+): To a solution of 4,4′-dimethyl-2,2′-bipyridine (920 mg, 5 mmol) in 30 ml of THF, 6 mmol of LDA was added at 0 °C. The solution was stirred for 2 h, cooled to –78 °C, chlorodiphenylphosphane (0.9 ml, 6 mmol) was added and the yellow reaction mixture was stirred for 3 h at this temperature. The reaction was then quenched with satd. aqueous NH_4Cl solution and 80 ml of CH_2Cl_2 was added. The organic phase was washed with satd. NH_4Cl solution and water, dried over $MgSO_4$, and the solvent was evaporated in vacuo. CC of the crude product [CH_2Cl_2/MeOH/NH_3 (25% in water), 100:5:0.5] gave **4** (1100 mg, 57%, $R_f = 0.26$) as a white solid, m.p. 184 °C. – IR (KBr): $\tilde{\nu} = 3057\ cm^{-1}$, 2951, 1594, 1437, 1184, 1119, 832, 693, 463. – UV (CH_3CN): λ_{max} (ε) = 196 nm (80910), 222 (29790), 248 (10840), 284 (14720). – ^1H NMR: δ = 2.38 (s, 3H), 3.70 (d, $^3J_{H,P}$ = 13.9 Hz, 2H), 7.07 (d, ^3J = 4.9 Hz, 1H), 7.19 (m, 1H), 7.45 (m, 6H), 7.69 (m, 4H), 8.07 (s, 1H), 8.10 (s, 1H), 8.45 (m, 2H). – ^{13}C NMR: δ = 21.1 (+), 37.9 (–, d, $^1J_{C,P}$ = 64.2 Hz), 121.9 (+), 122.8 (+, d, $^3J_{C,P}$ = 5.7 Hz), 124.6 (+), 124.9 (+, d, $^3J_{C,P}$ = 4.4 Hz), 128.6 (+), 128.7 (+), 130.9 (+), 131.0 (+), 131.2 (C_{quat}), 132.0 (+), 132.1 (+), 132.2 (C_{quat}), 141.7 (C_{quat}), 141.7 (C_{quat}), 148.0 (C_{quat}), 148.8 (+), 148.9 (C_{quat}), 149.0 (C_{quat}), 155.5 (C_{quat}), 156.2 (C_{quat}). – ^{31}P NMR (81 MHz): δ = 29.5. – MS (70 eV); *m/z* (%): 384 (100) [M^+]. – $C_{24}H_{21}N_2OP$ (384.4): calcd. C 74.99, H 5.51, N 7.29); found C 75.03, H 5.60, N 7.27. – Mol. mass 384 (MS).

Ligand **6**: 4-[(Diphenylphosphinoyl)methyl]-4′-methyl-2,2′-bipyridine (**4**; H^+ instead of Na^+) (830 mg, 2.3 mmol) and sodium hydride (110 mg, 4.6 mmol) were heated in 50 ml of dry THF to 60 °C for 30 min. After addition of 180 mg (0.85 mmol) of 6,6′-diformyl-2,2′-bipyridine (**5**), the mixture was heated to 60 °C for 60 min and then refluxed for a further 15 min. The suspension was diluted with 5 ml of satd. aqueous NH_4Cl solution and 100 ml CH_2Cl_2. The precipitated solid was filtered off, washed with dil. aqueous NaOH solution and with dichloromethane, and then recrystallized from toluene to yield **6** (200 mg, 43%) as a white solid (R_f = 0.47, SiO_2; CH_2Cl_2/MeOH/NH_3, 100:5:0.5), m.p. 303 °C. – IR (KBr): $\tilde{\nu} = 152\ cm^{-1}$, 1563, 1433, 970, 553. – UV ($CHCl_3$): λ_{max} (ε) = 248 nm (40740), 288 (51290), 326 (426570), 332 (44160), 348 (28840). – ^1H NMR: δ = 2.47 (s, 6H), 7.18 (d, J = 4.9 Hz, 2H), 7.47 (d, J = 7.4 Hz, 2H), 7.50 (dd, J = 5.1 and 1.7 Hz, 2H), 7.57 (d, J = 15.9 Hz, 2H), 7.90 (m, 4H), 8.29 (s, 2H), 8.55 (d, J = 7.9 Hz), 8.60 (d, J = 4.9 Hz, 2H), 8.63 (s, 2H), 8.70 (d, J = 5.1 Hz, 2H). – ^{13}C NMR: δ = 21.2 (+), 118.9 (+), 120.5 (+), 121.3 (+), 122.1 (+), 123.2 (+), 124.8 (+), 130.3 (+), 132.4 (+), 137.6 (+), 145.2 (C_{quat}), 148.2 (C_{quat}), 149.0 (+), 149.6 (+), 153.7 (C_{quat}), 155.8 (C_{quat}), 155.9 (C_{quat}), 156.8 (C_{quat}). – MS (70 eV); *m/z* (%): 544 (100) [M^+]. – $C_{36}H_{28}N_6$: calcd. 544.237; found 544.237 (MS).

Complex **7**: A solution of bis(2,2′-bipyridine)ruthenium(II) dichloride dihydrate (600 mg, 1.15 mmol) in 60 ml ethanol/water (75:25) was refluxed for 20 min. After addition of ligand **3** (280 mg, 0.51 mmol), the reaction mixture was refluxed for a further 15 h, the solvent was evaporated and the residue was purified by CC [MeOH/aqueous NH_4Cl solution (2 M)/$MeNO_2$, 7:2:1; R_f = 0.15, as chloride salt]. The solvent from the appropriate fraction was evaporated invacuo, and the residue was dissolved in water. This solution was filtered and then the complex was precipitated by the addition of 100 ml of aqueous KPF_6 solution (0.1 M), yielding **7** (385 mg, 38%) as an orange solid, m.p. 232 °C. – IR (KBr): $\tilde{\nu} = 1619\ cm^{-1}$, 1444, 841, 762, 557. – UV (CH_3CN): λ_{max} (ε) = 192 nm (181970), 246 (61660), 287 (177500), 453 (29400). – ^1H NMR (400 MHz, CD_3CN): δ = 2.48 (s, 6H), 3.27 (m, 4H), 3.36 (m, 4H), 7.21 (m, 4H), 7.34 (m, 10H), 7.51 (m, 4H), 7.68 (m, 10H), 8.02 (m, 8H), 8.22 (m, 2H), 8.32 (s, 2H), 8.46 (m, 10H). – MS (ESI); *m/z* (%): 1811.4 (6) [$(M^{4+} + 3\ PF_6^-)^+$], 833.2 (45) [$(M^{4+} + 2\ PF_6^-)^{2+}$], 507.1 (63) [$(M^{4+} + PF_6^-)^{3+}$], 451.3 (100), 343.9 (54) [M^{4+}]. – $C_{76}H_{64}N_{14}Ru_2P_4F_{24}$ (1955.4): calcd. C 46.68, H 3.30, N 10.03; found C 45.83, H 3.24, N 9.73. – Mol. mass 1955 (MS).

Complex **8**: A mixture of bis(2,2′-bipyridine)ruthenium(II) dichloride dihydrate (146 mg, 0.28 mmol) and silver perchlorate (127 mg, 0.57 mmol) in 50 ml of dry degassed acetone was stirred for 3 h at room temperature in the dark. The precipitated silver chloride was removed by filtration, ligand **6** (77 mg, 0.14 mmol) was added and the reaction mixture was stirred for 4 d in the dark at room temperature. The solvent was then evaporated and the residue was purified by CC [MeOH/aqueous NH_4Cl solution (2 M)/$MeNO_2$, 7:2:1, R_f = 0.18, as chloride salt]. The solvent from the appropriate fraction was evaporated and the residue was dissolved in water. This solution was filtered and the complex was precipitated by the addition of 100 ml aqueous KPF_6 solution (0.1 M), yielding **8** (65 mg, 24%) as a red solid, m.p. >300 °C. – IR (KBr): $\tilde{\nu} = 1613\ cm^{-1}$, 1465, 1105, 844, 765, 558. – UV (CH_3CN): λ_{max} (ε) = 192 nm (154880), 246 (63100), 287 (144200), 340 (60260), 461 (41020). – ^1H NMR (400 MHz, CD_3CN): δ = 2.57 (s, 6H), 7.26 (m, 2H), 7.41 (m, 8H), 7.56 (m, 4H), 7.63 (m, 2H), 7.68 (m, 2H), 7.74 (m, 8H), 7.82 (m, 2H), 8.02 (m, 12H), 8.50 (m, 8H), 8.54 (s, 2H), 8.63 (m, 2H), 8.74 (s, 2H). – MS (ESI); *m/z* (%): 1805.4 (2) [$(M^{4+} + 3\ PF_6^-)^+$], 830.7 (10) [$(M^{4+} + 2\ PF_6^-)^{2+}$], 413.0 (100).

trans-4-Methyl-4′-[2-(2-pyridyl)vinyl]-2,2′-bipyridine (**10**): A mixture of 4-[(diphenylphosphinoyl)methyl]-4′-methyl-2,2′-bipyridine (**4**; H^+ instead of Na^+) (1.2 g, 3.1 mmol) and NaH (82 mg, 3.4 mmol) in 75 ml THF was heated to 50 °C for 5 min. After addition of 0.33 ml (3.4 mmol) of pyridine-2-aldehyde (**9**), the reaction mixture was stirred for 2 h at room temperature. The organic phase was diluted with 150 ml of dichloromethane, extracted with satd. aqueous NH_4Cl solution (2 × 50 ml), dried over Na_2SO_4, and evaporated to dryness. CC of the crude product [CH_2Cl_2/MeOH/NH_3 (25% in water), 100:2:0.5; R_f = 0.22] yielded **10** (475 mg, 56%) as a yellow solid, m.p. 133 °C. – IR (KBr): $\tilde{\nu} = 1589\ cm^{-1}$, 1468, 990, 828, 554. – UV (CH_3CN): λ_{max} (ε) = 192 nm (30270), 202 (28770), 256 (20560), 280 (22910), 312 (26120). – ^1H NMR: δ = 2.46 (s, 3H), 7.16 (d, J = 4.9 Hz, 1H), 7.21 (m, 1H), 7.42 (m, 2H), 7.50 (d, J = 16.0 Hz, 1H), 7.70 (m, 2H), 8.26 (s, 1H), 8.57 (d, J = 4.9 Hz, 1H), 8.60 (s, 1H), 8.65 (m, 2H). – ^{13}C NMR: δ = 21.1 (+), 118.3 (+), 121.7 (+), 122.0 (+), 122.8 (+), 122.9 (+), 124.8 (+), 130.2 (+), 132.3 (+), 136.7 (+), 145.0 (C_{quat}), 148.1 (C_{quat}), 148.9 (+), 149.6 (+), 149.8 (+), 154.5 (C_{quat}), 155.7 (C_{quat}), 156.6 (C_{quat}). – MS (70 eV); *m/z* (%): 273 (100) [M^+]. – $C_{18}H_{15}N_3$ (273.3): calcd. C 79.10, H 5.53, N 15.30; found C 79.23, H 5.53, N 15.15. – Mol. mass: 273 (MS).

Complex **11**: A mixture of bis(2,2′-bipyridine)ruthenium(II) dichloride dihydrate (262 mg, 0.5 mmol) and silver perchlorate (225 mg, 1 mmol) in 50 ml of dry, degassed acetone was stirred for 3 h at room temperature in the dark. After filtration of the precipitated AgCl, 4-(2-vinylpyridine)-4-methyl-4′-[2-(2-pyridyl)vinyl]-2,2′-bipyridine (**10**) (135 mg, 0.5 mmol) was added. The reaction mixture was stirred overnight at room temperature and then the solvent was removed in vacuo. Recrystallization from methanol gave **11** (120 mg, 26%) as a red solid (R_f = 0.57; SiO_2; MeOH/2 M aq. NH_4Cl/$MeNO_2$, 7:2:1), m.p. 264 °C. – IR (KBr): $\tilde{\nu} = 1636\ cm^{-1}$, 1482, 1089, 766, 622. – UV (CH_3CN): λ_{max} (ε) = 192 nm (83950), 248 (28770), 256 (29510), 288 (69300), 322 (32810), 458 (19910). – ^1H NMR (400 MHz, CD_3CN): δ = 2.55 (s, 3H), 7.24 (m, 1H), 7.31 (m, 1H), 7.39 (m, 4H), 7.54 (m, 3H), 7.65 (m, 1H), 7.72 (m, 5H), 7.80 (m, 2H), 8.04 (m, 4H), 8.50 (m, 5H), 8.62 (m, 1H), 8.68 (m, 1H). – MS (ESI); *m/z* (%): 786.1 (10) [$(M^{2+} + ClO_4^-)^+$], 343.3 (7) [M^{2+}], 272.3 (100).

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