

2,2'-Bipyridine Chelates Substituted with Alkyne Groups, and Their Ru(II) Complexes

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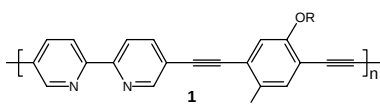
Received February 1st, 1999, respectively June 11th, 1999

Keywords: Chelates, Cross-coupling, Oligomers, Palladium, Ruthenium

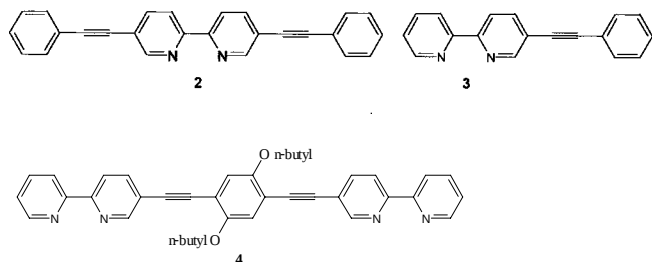
Abstract. The palladium-catalyzed cross-coupling of 5-bromo-2,2'-bipyridine and 5,5'-dibromo-2,2'-bipyridine with phenylacetylene leads to **2** and **3**, and the reaction of 5-ethynyl-2,2'-ethynyl-2,2'-bipyridine with 1,4-diiodo-2,5-dibutyl-oxybenzene provides **4**. Ruthenium complexes were prepared

by reaction of the ligands **2–4** with $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$. The ligands **2** and **4** show a fluorescence quantum yield near 100%. Further photophysical properties of the ligands and their ruthenium complexes were given.

Highly fluorescent conjugated polyarenes have been of increasing interest as potential materials for electroluminescence devices and meet particular attention due to their high non-linear susceptibilities [1, 2] which makes them candidates for all optical switching devices [3]. It is to expect that ruthenium containing polymers increase the non-linear optical properties [4]. A major motivation for oligomer/low molecular model research is to establish relations between chain length/primary structure and physical properties [5]. In order to study the influence of ruthenium coordination on the photophysical properties of the polymer **1** [6] we have prepared model ligands and their rigid rod-like ruthenium(II) complexes.

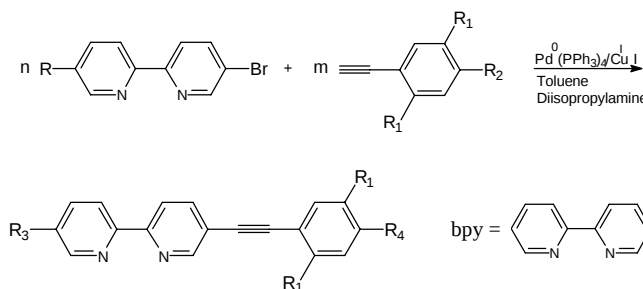


In this communication, we wish to present our results on such hitherto until now unreported ruthenium(II)-2,2'-bipyridine complexes. The ligands **2–4** are low molecular model compounds of the polymers **1**.



Results and Discussion

The 2,2'-bipyridine chelates substituted with alkyne groups were typically prepared on a gram scale by reaction of 5-bromo-2,2'-bipyridine and 5,5'-dibromo-2,2'-bipyridine [7] with phenylacetylene in case of **2** and **3** and by reaction of 5-ethynyl-2,2'-bipyridine [8] with 1,4-diiodo-2,5-dibutyl-oxybenzene [9] in case of **4**, using $\text{Pd}^0(\text{PPh}_3)_4/\text{CuI}$ as catalyst precursor and $(i\text{-Pr})_2\text{NH}$ as base.



Cpd.	n	m	R	R ¹	R ²	R ³	R ⁴
2	1	2	Br	H	H	$\equiv\text{C}_6\text{H}_5$	H
3	1	1	H	H	H	H	H
4	1	2	H	OC_4H_9	$\equiv\text{H}$	H	$\equiv\text{bpy}$

Scheme 1 Synthesis of 2,2'-bipyridines **2–4**

The pure ligands were obtained in good yields, as pale yellow powders and characterized by classical techniques (NMR, MS and elemental analysis). All data were consistent with the proposed structures. The ruthenium complexes of the ligands **2–4** were prepared as orange crystals (**2**, **3**) or amorph powders by reaction of bis-(bipyridine)ruthenium ion $\text{Ru}(\text{bpy})_2^{2+}$ with **4**.

Table 1 Absorption and fluorescence data for the ligands 2–4

Cpd.	$\lambda_{\max}^a$ (nm)	$\lg \epsilon_{\max}$	$\lambda_{\max,\text{exc}}^b$ (nm)	$\lambda_{\max,\text{em}}$ (nm)	λ^{0-0} (nm)	E_g^{0-0} (eV)
2	343	4.80	339	375	368	3.37
3	318	4.53	317	362	340	3.65
4	387	4.68	392	432	417	2.97

$\lambda_{\max,\text{exc}}$: excitation wavelength, $\lambda_{\max,\text{em}}$: emission wavelength, λ^{0-0} : $S_1 \rightarrow S_0$, $E_g^{0-0} = hc/\lambda_{0,1\text{ max}}$

^a) in chloroform, ^b) in dioxan

Table 2 Absorption and fluorescence data for ruthenium complexes 5–7

compound	$\lambda_{\max}^a$ (nm)	$\lg \epsilon_{\max}$	$\lambda_{\max,\text{exc}}^b$ (MLCT) (nm)	$\lambda_{\max,\text{em}}$ (nm)	λ^{0-0} (nm)	E_g^{0-0} (eV)
5	442	3.98	445	596	578	2.08
6	451	4.46	404	651	567	2.18
7	420 ^b)	4.78	457	645	570	2.17

^a) in ethanol, ^b) in acetonitrile

The absorption spectra show a strong band at $\lambda_{\max} \approx 387$ nm, 318 nm, and 343 nm for **4**, **3** and **2**, respectively, which is assigned to the π, π^* transition (Table 1). The absorption of ligand **4** at around 331 nm (Fig. 1) can be allocated to the alkoxy side groups. The value is in agreement with the absorption of alkoxy substituted poly-(1,4-phenylenevinylene)s [10]. The ligands **2** and **4** show a strong fluorescence quantum yield (near unity).

Finally, in preliminary complexation studies we prepared the rigid rod-like ruthenium(II) complexes **5–7**.

The presence of the $(\text{bpy})_2\text{Ru}^{2+}$ -structure is manifested by the appearance of a MLCT absorption band which is close to the reported [11, 12] value for $\text{Ru}(\text{bpy})_3^{2+}$ at 450 nm.

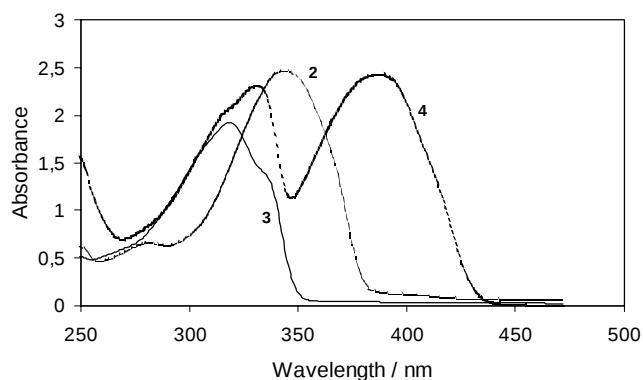


Fig. 1 UV/VIS spectra of the ligands **2–4** in chloroform [$c(2) = 7,7 \times 10^{-5}$ M, $c(3) = 1,0 \times 10^{-4}$ M, $c(4) = 5,1 \times 10^{-5}$ M, $d = 1,0$ cm]

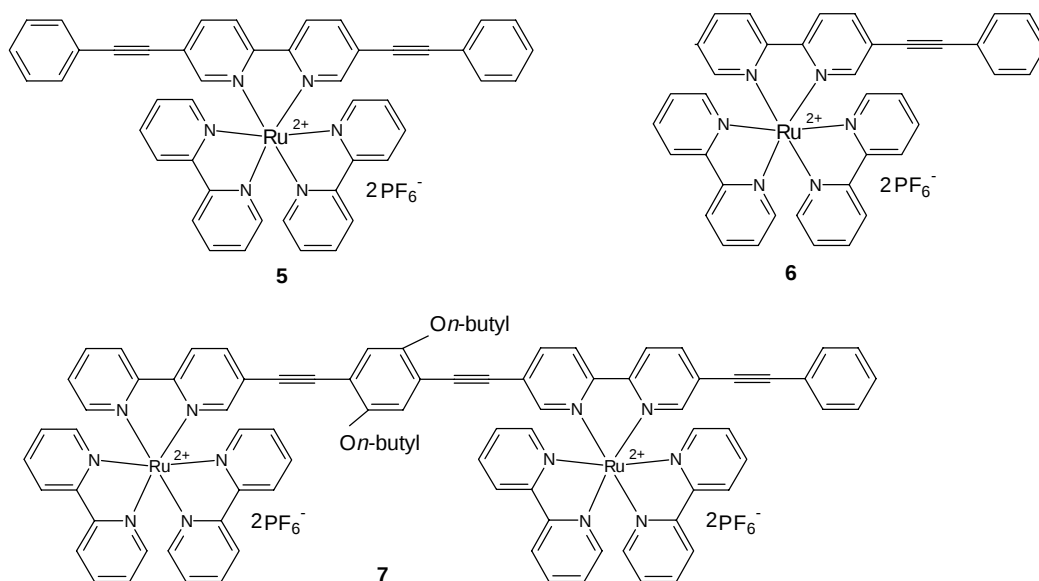


Table 2 summarizes selected data for the new complexes.

The absorption at 420, 442 and 451 nm are assigned to MLCT-bands ($d \rightarrow \pi^*$) (Fig. 2, 3 and Table 2). The ligand centred absorption appears at ≈ 288 nm, which is significant for 2,2'-bipyridine complex.

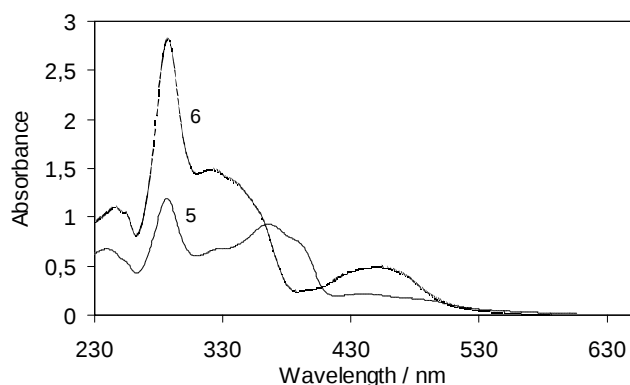


Fig. 2 UV/VIS spectra of the ruthenium(II) complexes **5** and **6** in ethanol [$c(5) = 1,7 \times 10^{-5}$ M, $c(6) = 2,5 \times 10^{-5}$ M, $d = 1,0$ cm]

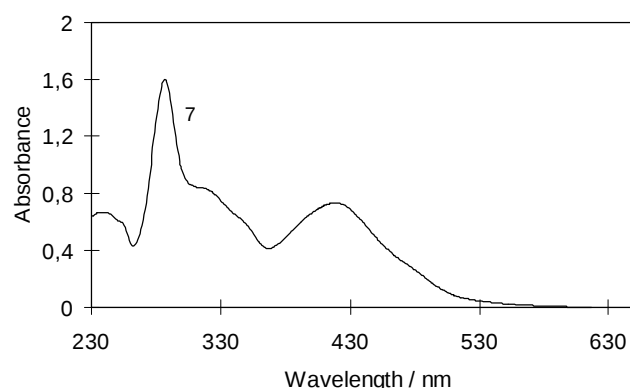


Fig. 3 UV/VIS spectrum of the dinuclear ruthenium(II) complex **7** in acetonitrile [$c(7) = 9,0 \times 10^{-6}$ M, $d = 1,0$ cm]

We gratefully thank Dr. E. Birckner for carrying out the photoluminescence analysis.

Experimental

All chemicals were purchased from Fluka and from Aldrich. Toluene was dried and distilled over CaH_2 , diisopropylamine over KOH. The solvents were degassed by bubbling with argon for 1 h prior to use. All reactions, if not otherwise specified, were carried out under inert gas atmosphere (argon).

Melting points were measured on a Büchi 530 melting point apparatus. Mass spectroscopy was performed as electronic ionisation in case of (**2**, **3**) and with chemical ionisation with H_2O -vapour with gas on a Finnigat Mat SSQ 710. ^1H and ^{13}C NMR spectra were taken on a Bruker AC 250

and a Bruker DRX 400. The absorption spectra were taken in CHCl_3 (for HPLC, Baker) on a Perkin Elmer UV/VIS-NIR Spectrometer Lambda 19. Fluorescence spectra were obtained on a Perkin Elmer LS 50. Quinine sulfate in 0.1N sulfuric acid was used as reference ($\Phi_f = 0.55$). Elemental analysis was performed on a LECO CHNS-932. 5,5'-Dibromo-2,2'-bipyridine [7], 5-bromo-2,2'-bipyridine [7], 5-ethynyl-2,2'-bipyridine [8], 1,4-di-butyl-2,5-diiodobenzene [9] were synthesized by literature methods.

5,5'-Bis(phenylethynylene)-2,2'-bipyridine **2** [6]

Tetrakis(triphenylphosphine)-palladium (110 mg, 9.54×10^{-5} mol, 3 mol%) and copper(I)-iodide (18 mg, 9.54×10^{-5} mol, 3 mol%) were given to a mixture of 5,5'-dibromo-2,2'-bipyridine (1.0 g, 3.18 mmol), phenyl-acetylene (974 mg, 9.54 mmol) and diisopropylamine (30 ml) in dry toluene (70 ml). The reaction mixture was stirred at 65 °C for 14 h. It was filtered warm to remove the inorganic compounds. The precipitate was washed with chloroform, and both filtrates were dried over MgSO_4 , evaporated to dryness and chromatographed with *n*-hexane/ethylacetate (v/v:1/1) on silica gel, yielding 740 mg of pale yellow powder, yield 65.3%; *m.p.* 203–204 °C. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 8.80$ (d, $^4J = 1.5$ Hz, 2H, H6,6'), 8.41 (d, $^3J = 8.1$ Hz, 2H, H3,3'), 7.92 (dd, $^3J = 8.2$ Hz, $^4J = 2.1$ Hz, 2H, H4,4'), 7.55 (m, 4H), 7.36 (m, 6H). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 86.4$, 93.8(C-7,8), 120.5(C-3), 120.6(C-5), 122.6(C-9), 128.5(C-12), 128.8(C-11), 131.7(C-10), 139.3(C-4), 151.7(C-6), 154.1(C-2). – MS (EI): $m/z = 356$ (M/100), 328 (10), 178 (50).

$\text{C}_{26}\text{H}_{16}\text{N}_2$	Calcd.:	C 87.62	H 4.52	N 7.86
(356.43)	Found:	C 87.60	H 4.56	N 7.82.

5-(Phenylethynylene)-2,2'-bipyridine **3**

Synthesis analogue **2**. Tetrakis(triphenylphosphine)-palladium (74 mg, 6.38×10^{-5} mol, 3 mol%) and copper(I)-iodide (12 mg, 6.38×10^{-5} mol, 3 mol%) were given to a mixture of 5-bromo-2,2'-bipyridine (1.0 g, 4.25 mmol), phenylacetylene (651 mg, 6.38 mmol) and diisopropylamine (30 ml) in dry toluene (70 ml). 630 mg of a pale yellow powder were obtained, yield 57.8%. *m.p.* = 108 °C. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 8.80$ (d, $^4J = 1.7$ Hz, 1H, H6), 8.67 (d, $^4J = 4.6$ Hz, 1H, H6'), 8.40 (d, $^3J = 8.3$ Hz, 1H, H3), 8.40 (d, $^3J = 8.3$ Hz, 1H, H3'), 7.91 (dd, $^3J = 8.3$ Hz, $^4J = 2.1$ Hz, 1H, H4), 7.80 (td, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, 1H, H4'), 7.50 (m, 2H), 7.3 (m, 4H). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 86.4$, 93.5(C-7,8), 120.3, 121.3(C-5,5'), 122.6, 123.9(C-3,3'), 128.4 (C-12), 128.7(C-11), 131.7(C-10), 136.9, 139.3(C-4,4'), 149.3, 151.6(C-6,6'), 154.8, 155.5(C-2,2'). – MS (EI): $m/z = 256$ (M/100), 228 (20).

$\text{C}_{18}\text{H}_{12}\text{N}_2$	Calcd.:	C 84.35	H 4.72	N 10.93
(256.31)	Found:	C 84.14	H 5.29	N 10.48.

1,4-Bis(2,2'-bipyridyl-5'-ethynylene)-2,5-dibutyloxybenzene **4**

Synthesis analogues **2**. Tetrakis(triphenylphosphine)-palladium (92 mg, 7.98×10^{-5} mol, 3 mol%) and copper(I)-iodide (15 mg, 7.98×10^{-5} mol, 3 mol%) were given to a mixture of 5-ethynyl-2,2'-bipyridine (1.15 g, 6.38 mmol), 1,4-dibutyloxy-2,5-diiodobenzene (1.26 g, 2.66 mmol) and diisopro-

pylamine (30 ml) in dry toluene (70 ml). 720 mg of a yellow powder were obtained, yield 46.8%; *m.p.* = 191–192 °C. – ¹H NMR (CDCl₃): δ/ppm = 8.80 (d, ⁴J = 1.4 Hz, 2H, H6), 8.67 (d, ⁴J = 4.2 Hz, 2H, H6'), 8.40 (d, ³J = 8.4 Hz, 2H, H3'), 8.40 (d, ³J = 8.4 Hz, 2H, H3), 7.90 (d, ³J = 8.2 Hz, ⁴J = 2.1 Hz, 2H, H4), 7.81 (td, ³J = 7.8 Hz, ⁴J = 1.7 Hz, 2H, H4'), 7.30 (ddd, ³J = 5.6 Hz, ³J = 2.8 Hz, ⁴J = 1.1 Hz, 2H, H5'), 7.05 (s, 2H, Phenyl), 4.05 (t, ³J = 6.4 Hz, 4H, OCH₂), 1.85 (m, 4H, CH₂), 1.57 (m, 4H, CH₂), 1.00 (t, ³J = 7.4 Hz, 4H, CH₃). – ¹³C NMR (CDCl₃), (400 MHz): δ/ppm = 13.9(C-15), 30.9(C-14), 31.3(C-13), 69.3(C-12), 90.1, 92.0(C-7,8), 113.8(C-9), 116.7(C-10), 120.4, 120.4(C-5,5'), 121.3, 123.9(C-3,3'), 137.0, 139.2(C-4,4'), 149.3, 151.6(C-6,6'), 153.7(C-11), 154.8, 155.4(C-2,2'). – MS (CI with H₂O): *m/z* = 579 (M/100), 523 (20), 466 (10).

C₃₈H₃₄N₄O₂ Calcd.: C 78.87 H 5.92 N 9.68
(578.72) Found: C 77.25 H 6.08 N 9.53.

Ruthenium Complexes 5–7 (General Procedure)

(bpy)₂RuCl₂ · 2H₂O was prepared according to the literature method [13], yield 71.4%. – ¹H NMR (DMF-D₇): δ/ppm = 10.20(d, 2H); 8.69(d,2H); 8.53 (d,2H); 8.09 (d,2H); 7.73 (m,6H); 7.15 (m,2H). – ¹³C NMR (DMF-D₇): δ/ppm = 123.01, 123.39, 125.75, 133.77, 135.01, 153.04, 154.22, 159.45, 161.39, 162.91. **5** and **6** were prepared by refluxing of one equivalent (bpy)₂RuCl₂ · 2H₂O with one equivalent of **2** and **3** [14], **7** was prepared with two equivalents of (bpy)₂RuCl₂ · 2H₂O and one equivalent of **4** in 50 ml of EtOH/H₂O (2:1) for 12 h. Because of the insolubility of the ligands, CHCl₃ was added. The dark red solution was evaporated to dryness, after which 10 ml of water was added. The compound was precipitated by adding an excess of aqueous NH₄PF₆. After filtration, the compound was purified by column chromatography on neutral alumina, CH₂Cl₂ was first used as eluent to remove unreacted **2**, **3** or **4**. Acetone was then added to get the pure ruthenium complex.

Ruthenium Complex 5 of 5,5-Bis(phenylethynylene)-2,2'-bipyridine

yield 25%. – ¹H NMR (DMSO-D₆, 200 MHz): δ/ppm = 8.94(d, 2H), 8.84(d, 2H), 8.36(dd, 2H), 8.13–8.23(m, 4H), 7.87(d, 2H), 7.77(s, 2H), 7.71(d, 2H), 7.40–7.57(m, 14H). – ¹³C NMR (Aceton-D₆, 50 MHz): δ/ppm = 85.0, 97.5, 122.2, 124.9, 125.4, 125.5, 128.8, 129.7, 130.8, 132.6, 139.2, 140.8, 152.8, 153.2, 154.3, 156.7, 158.1, 158.2. MS (FAB with NBA). – *m/z* = 1040(–1 F), 915(–1 PF₆), 770(–2 PF₆), 613(–1 bpy).

C₄₆H₃₂N₆RuP₂F₆ (1059.81).
Calcd.: C 52.14 H 3.04 N 7.93
Found: C 52.38 H 3.58 N 7.55.

Ruthenium Complex 6 of 5-(Phenylethynylene)-2,2'-bipyridine

yield 66.8%. – ¹H NMR (DMSO-D₆, 200 MHz): δ/ppm = 8.82–8.92 (m, 6H), 8.33–8.38(m, 1H), 8.13–8.21(m, 5H), 7.8–7.91(m, 1H), 7.64–7.78(m, 5H), 7.39–7.56(m, 10H). – ¹³C NMR (Aceton-D₆, 50 MHz): δ/ppm = 124.8, 124.9, 125.4,

125.5, 125.8, 128.8, 128.8, 128.9, 129.7, 132.5, 139.0, 139.1, 140.8, 152.6, 152.8, 152.9, 153.1, 154.2, 157.2, 157.7, 158.2. – MS (FAB with NBA): *m/z* = 815(–1 PF₆), 670(–2 PF₆), 513(–1bpy), 357(–2 bpy), 257(ligand).

C₃₈H₂₈N₆RuP₂F₁₂ (959.69)
Calcd.: C 47.58 H 2.94 N 8.76
Found: C 47.74 H 3.56 N 8.28.

Ruthenium Complex 7 of 1,4-Bis(2,2'-bipyridyl-5'-ethynylene)-2,5-dibutyloxybenzene

yield 61.7%. – ¹H NMR (DMSO-D₆, 250 MHz): δ/ppm = 8.84(m, 12H), 8.17(m, 12H), 7.53–7.89(m, 22H), 7.13(s, 2H), 3.93(m, 4H, -OCH₂), 1.35–1.56(m, 8H, -CH₂), 0.85(m, 6H, -CH₃). – ¹³C NMR (Aceton-D₆, 50 MHz): δ/ppm = 14.10, 19.76, 31.75, 69.96, 90.64, 94.10, 114.48, 117.89, 124.83, 125.11, 125.38, 125.51, 125.88, 128.80, 139.13, 140.77, 152.61, 152.83, 153.05, 153.71, 154.78, 157.31, 157.63, 158.09, 158.26.

C₇₈H₆₆N₁₂O₂Ru₂P₄F₂₄ (1985.47)
Calcd.: C 47.19 H 3.35 N 8.47
Found.: C 47.00 H 3.71 N 8.36.

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