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The New and Simple 'LEGO' System: Synthesis and Reactions of Ruthenium(II) Complexes

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Dedicated to Professor Dr. Werner Tochtermann on the occasion of his 65th birthday.

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Abstract

The synthesis of ruthenium(II) complexes with 2,2'-bipyridine and 1,10-phenanthroline as ligands is described. These ligands were prepared using reactions of our new and simple 'LEGO' System. 'LEGO' system reactions which are possible with the free, uncoordinated ligands also apply to coordinated ligands.

Keywords: *Complexes; Ruthenium and compounds; Coupling reactions; Pyridines*

INTRODUCTION

In this communication we extend our new 'LEGO' system [1-9], a new and simple high yield route to pyridines via 1,2,4-triazines, to the generation of Ru(II) complexes. In the course of our investigations, we have prepared a large number of various oligopyridines. In this communication we restrict our interest concerning the synthesis of Ru(II) complexes to 2,2'-bipyridine and 1,10-phenanthroline derivatives as ligands.

There are two different ways for the synthesis of complexes. Either direct introduction of ligands in suitable starting complexes or reactions at the coordinated ligand. Both types of reactions are described in this communication.

The Ru(II) complexes obtained possess interesting fluorescence properties, e.g. large Stokes shifts as well as lifetimes up to about 800 ns.

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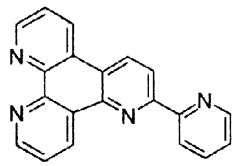
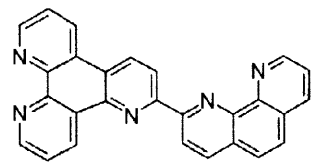
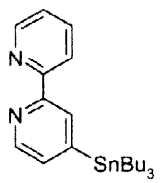
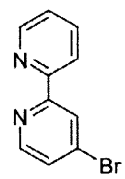
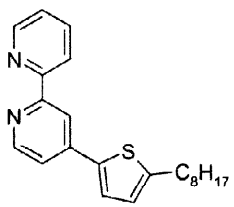
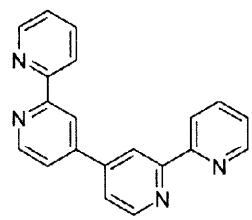
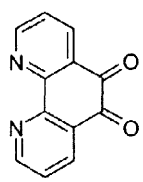
Results and Discussion

Synthesis of the ligands: Ligands **1a** and **1b** were prepared by [4+2] cycloaddition of the corresponding 1,2,4-triazines with norborna-2,5-diene according to the 'LEGO' system [5]. Similarily, compound **1c** was prepared by [4+2] cycloaddition of the corresponding 1,2,4-triazine with ethynyltributyltin [7]. Bromination of **1c** leads to 4-bromo-2,2'-bipyridine (**1d**) [7]. Reactions of tin compound **1c** with aryl bromides under Stille conditions yield cross-coupling products such as **1e** and **1f** [8,9] (Table 1).

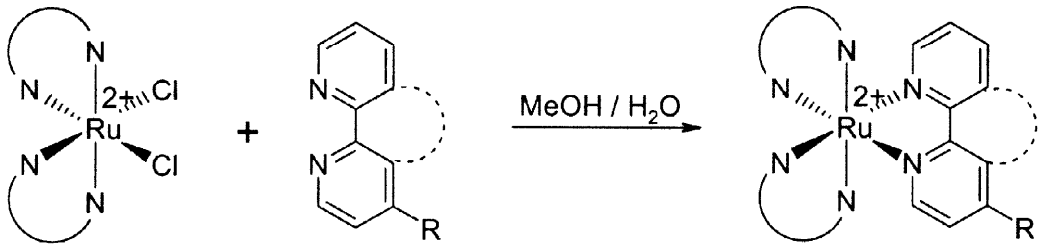
Table 1. Ligands for the synthesis of ruthenium (II) complexes.

Compound		Ref.	Compound		Ref.
1a		[5]	**1b**		[5]
1c		[7]	**1d**		[7]
1e		---	**1f**		---
1g		[11]			

Quaterpyridine **1f** was prepared to compare the yields of Stille cross-coupling reactions of free ligands with those of complexed ligands.

Introduction of ligands into suitable starting complexes: Following the procedure described by Meyer et al. [10], bis-(1,10-phenanthroline)-cis-dichloro ruthenium(II) (**2a**) ($phen_2RuCl_2$) or bis-(2,2'-bipyridine)-cis-dichloro ruthenium(II) (**2b**) (bpy_2RuCl_2)) were treated with a solution

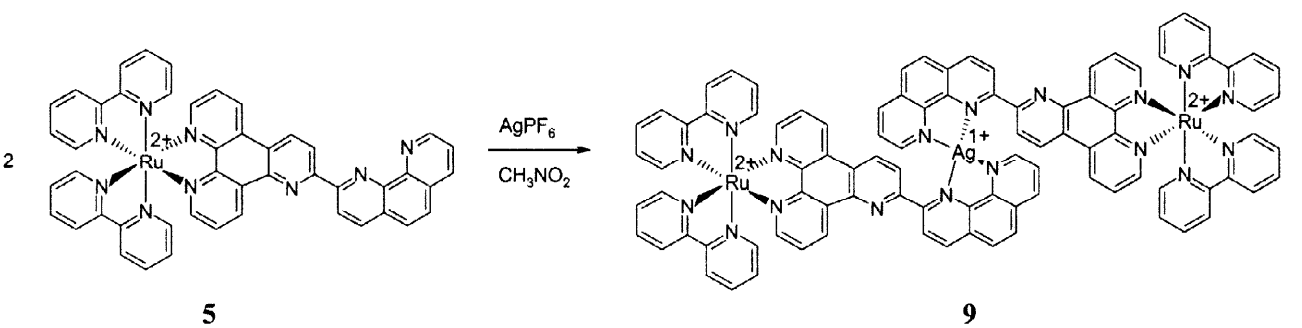
of the ligand **1** in methanol / water. The resulting complexes **3-8** were precipitated with NH_4PF_6 (Scheme 1, Table 2).



2a, 2b **1a-1e** **3-8**

Scheme 1. Synthesis of ruthenium (II) complexes **3-8** via direct introduction of ligands **1**.

Ligand **1b** contains two possible complexing sites. Steric reasons lead to the formation of **5** with the specific coordination of Ru(II) to the less hindered 1,5,12-triaza-triphenylene unit, proved by ^1H NMR coupling constants. The still uncoordinated 1,10-phenanthroline binding site may be occupied by the smaller Ag(I) ion, which prefers tetrahedral coordination (Scheme 2).

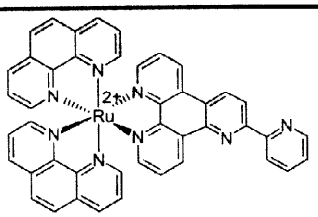
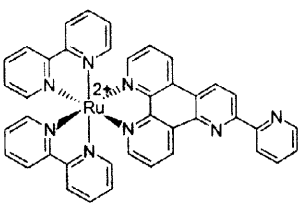
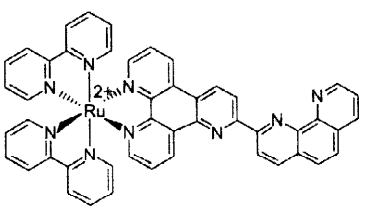
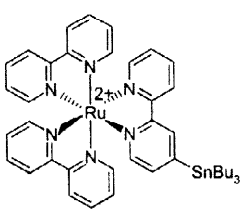
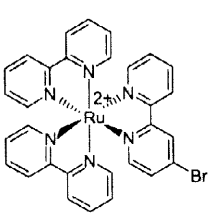
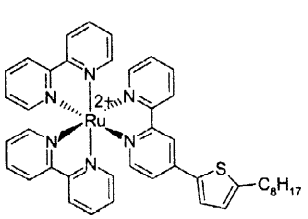
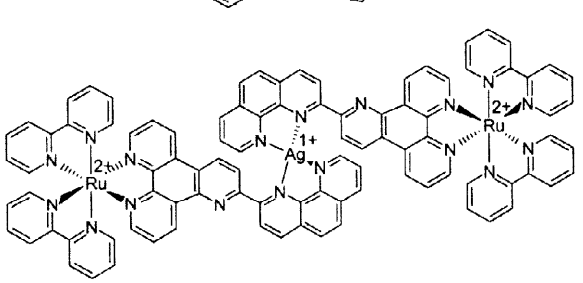


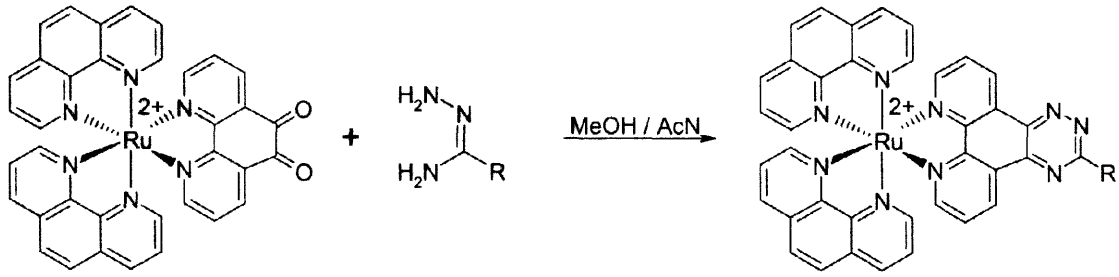
5 **9**

Scheme 2. Synthesis of the triheteronuclear complex **9**.

Reactions with coordinated ligands: Our intention was to check if condensation reactions and Stille cross-coupling reactions, which proceed with the free ligands can be applied to coordinated ligands as well. Hence, bis-(1,10-phenanthroline)Ru(1,10-phenanthroline-5,6-dione)$(PF_6)_2 \cdot 2H_2O$ (**2c**) ($phen_2$Ru(II)phendione) was treated with pyridine-2-carboxamidrazone (**10a**), dicarboxbisamidrazone (**10b**), pyridine-2,6-dicarboxbisamidrazone (**10c**) and pyridine-2,4,6-tricarboxtrisamidrazone (**10d**) [1-9] to furnish mono- and oligonuclear complexes **11a-11d** containing one or more 1,2,4-triazine moieties (Scheme 3, Table 3). The reactions proceed under mild conditions. Preparation of **11b-11d** furnishes the *rac* and *meso* isomer, which were not separated. Attempts to synthesize complexes **11a-11d** following the method described above, i.e. starting from $phen_2RuCl_2$ and the corresponding ligand with triazine unit were

Table 2. Ru(II) complexes synthesized according to Scheme 1.

	Ru(II) complex	Reaction times and Conditions	Yield [%]	M.P. [°C]
3		MeOH / H_2O 24 h, reflux	64	264-268
4		MeOH / H_2O 24 h, reflux	29	228-232
5		MeOH / H_2O 48 h, reflux	77	190-193
6		MeOH / H_2O 15 h, reflux	46	177-180
7		MeOH / H_2O 16 h, reflux	53	175-178
8		MeOH / H_2O 12 h, reflux	46	175-179
9		nitromethane 20 h, r.t.	72	185 begin. decomp.

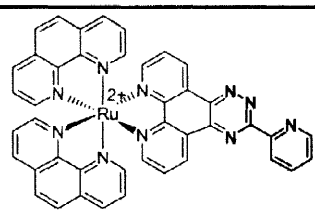
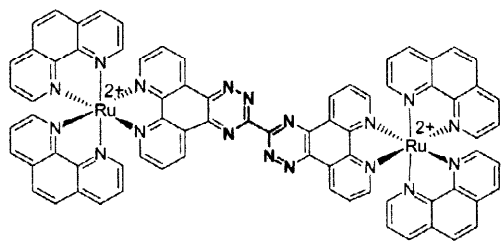
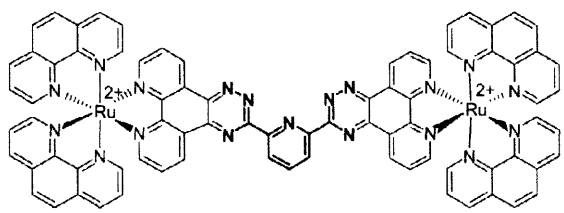
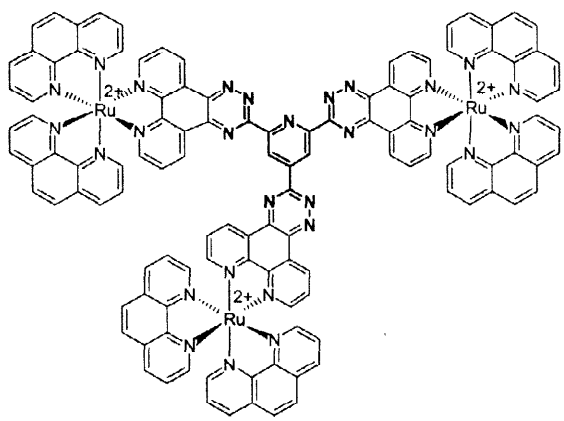


2c **10a-10d** **11a-11d**

Scheme 3. Reaction of $phen_2Ru(II)$ phendione **2c** with various carboxamidrazones **10a-10d**.

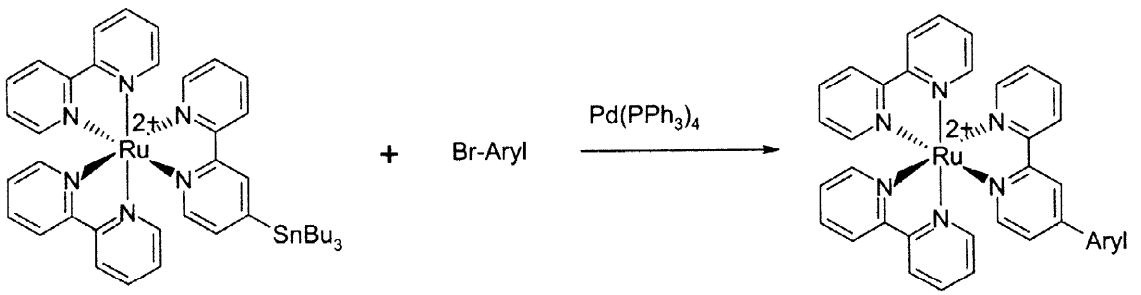
unsuccessful possibly due to oxidative degradation caused by the 1,2,4-triazine moiety at higher reaction temperatures.

Table 3. Ru(II) complexes from reactions of $phen_2Ru(II)$phendione **2c** with carboxamidrazones **10a-10d** (marked in extra bold print).

	Ru(II) complex	Reaction times and Conditions	Yield [%]	M.P. [°C]
11a		MeOH / CH_3CN 24 h, r.t.	55	255-260
11b		MeOH / CH_3CN 24 h, r.t.	72	>300
11c		MeOH / CH_3CN 24 h, r.t.	74	>300
11d		MeOH / CH_3CN 24 h, r.t.	84	>300

The thermal lability of these Ru(II) complexes is the reason why the transformations of 1,2,4-triazines to pyridines via [4+2] cycloaddition reactions with norbornadiene or ethynyltributyltin [1-9] are not possible with Ru(II) complexes **11**. These transformations would require reaction temperatures of about 140-190°C and reaction times of several hours to days.

The second type of 'LEGO' system reaction which we tried to apply to complexed ligands was the Stille cross-coupling reaction (Scheme 4, Table 4). In a first experiment complex **6** was treated with 5-bromo-2,2';5',2''-terthiophene **13** [12] under Pd^0-catalysis in a toluene / acetonitrile mixture. After chromatographic purification analytical data confirmed the identity of coupling product **12a**.

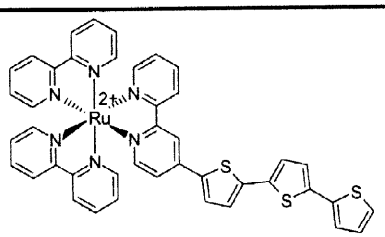
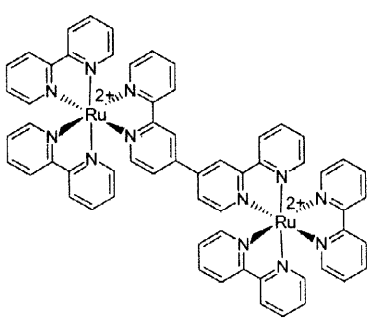


6 **13, 7** **12a, 12b**

Scheme 4. Stille cross-coupling reactions with complexed ligands.

Even the preparation of coupling product **12b** using the coordinated tin compound **6** and coordinated aryl bromide **7** under Stille conditions was successful. The dinuclear complex **12b** was obtained in 41% yield.

Table 4. Ru(II) complexes from Stille cross-coupling reactions.

	Ru(II) complex	Reaction times and Conditions	Yield [%]	M.P. [°C]
12a		toluene / CH_3CN 3d, reflux	46	161-163
12b		toluene / CH_3CN 4d, reflux	41	221-223

The advantage of this method is that after complexation of a tributyltin-bipyridine unit, other oligopyridines may be coupled to the prebuilt complex. In this way it is now possible to direct the regiochemistry of complexation to oligopyridines. The reaction using the same but uncoordinated ligands 4-tributylstannyl-2,2'-bipyridine (**1c**) and 4-bromo-2,2'-bipyridine (**1d**) yielded 61% of 2,2';4',4";2",2"'-quaterpyridine (**1f**).

Fluorescence and fluorescence lifetime spectroscopic data: Ru(II)-bipyridine and Ru(II)-phenanthroline complexes show intense orange-red fluorescence with long lifetime. Compounds like **11a** resemble known systems which interact with DNA and change fluorescence lifetimes upon binding to DNA [13].

Table 5 shows λ_{max} of the UV/VIS absorption with the lowest energy, fluorescence maxima and the resulting Stokes shifts ($\Delta\lambda$) of Ru(II) complexes **3-9** and **11-12**. Also listed in Table 5 are fluorescence lifetimes (LT) and the ratio of lifetimes if the decay is not monoexponential. The fluorescence of compound **11b** was too weak to be measured. Fluorescence of all compounds was excited at 488 nm in acetonitrile or dichloromethane.

Table 5. Fluorescence and fluorescence lifetime spectroscopic data of Ru(II) complexes.

compound	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**11a**	**11c**	**11d**	**12a**	**12b**
solvent	CH_3CN	CH_3CN	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_3CN	CH_3CN	CH_3CN	CH_2Cl_2	CH_2Cl_2
λ_{max} [nm]	448	451	468	454	454	458	452	438	437	436	470	482
emission [nm]	598	606	609	600	616	614	591	641	664	650	597	600
$\Delta\lambda$ [nm]	150	155	141	146	162	156	139	203	227	214	127	118
LT [ns]	174	143	467	396	522	453	120 395	65.3 765	33.6 554	22.1 578	412	186
ratio [%]	100	100	100	100	100	100	57:43	72:28	86:14	83:17	100	100

^1H NMR spectroscopic data: In cases like ligand **1b** with more than one complexing site it is necessary to determine the regiochemistry of complexation. The metal to ligand π-back donation causes an increase of coupling constants of the neighboring protons of about 0.5 - 1.0 Hz compared to the free ligand. To illustrate this effect Figure 1 shows coupling constants and chemical shifts of uncoordinanted **1d** and of the Ru(II) complex **7** which contains **1d** as a ligand.

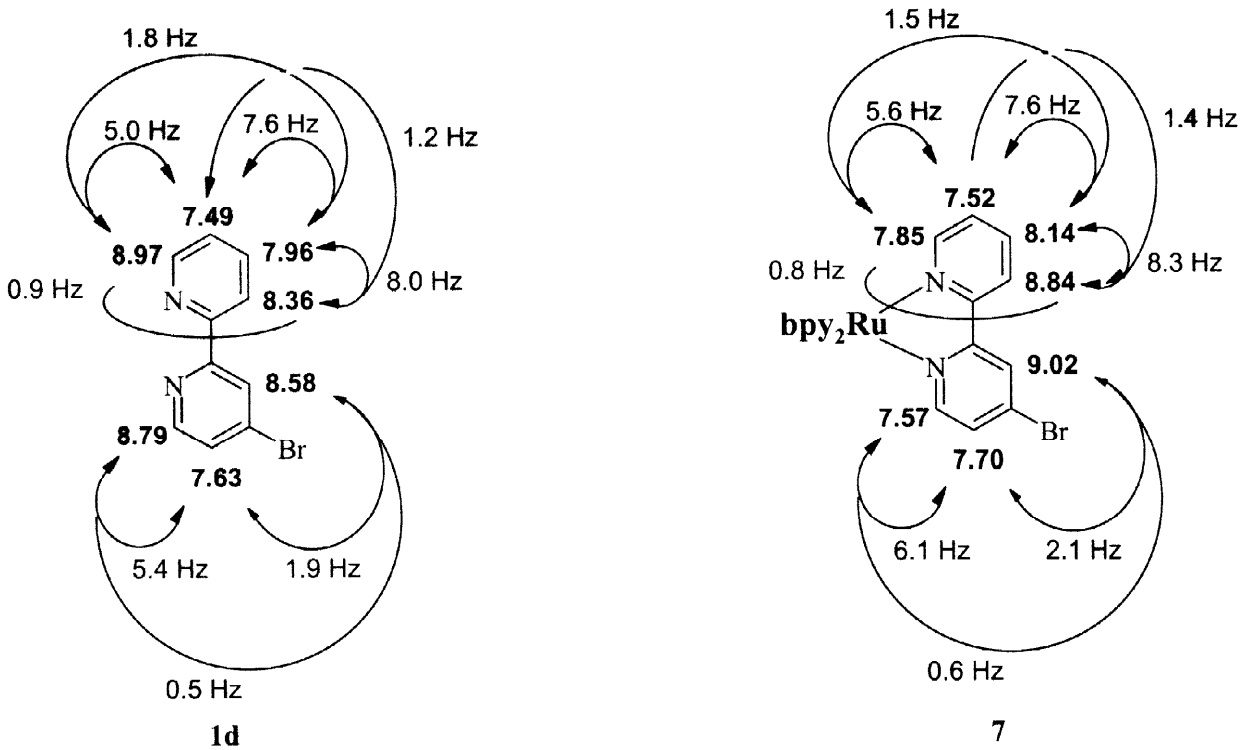


Figure 1. ^{1}H NMR spectroscopic data (DMSO-D_6) of ligand **1d** (left) and of the corresponding bpy$_2$(**1d**)Ru(II) complex **7** (right).

Conclusion

Our 'LEGO' System offers a new and simple approach to numerous substituted or unsubstituted, linear or branched oligopyridines. In this report we successfully extended some of the 'LEGO' system reactions, formation of 1,2,4-triazines and Stille cross-coupling reactions to coordinated ligands. In this way the synthesis of complexes which otherwise would not be accessible is easily possible. Another 'LEGO' system reaction, the transformation of 1,2,4-triazines to pyridines via [4+2] cycloaddition reactions with norbornadiene or ethynyltributyltin is not possible because of thermal lability of the complexes used as 4π components in the cycloaddition step.

Experimental Section

General: IR spectra were recorded with a Beckmann Acculab I. NMR spectra were obtained with a Bruker AC250 and ARX400 (250 MHz / 400 MHz for ^{1}H and 63 MHz / 100 MHz for ^{13}C). The degree of substitution of the C atoms was determined by the DEPT-135 method. Mass spectra were recorded either with an ionizing voltage of 70 eV by electron impact with a Varian CH90 instrument or by fast atom bombardement with a Varian 311A instrument. UV/VIS spectra were recorded with a Karl Zeiss Specord M500. Fluorescence spectra were recorded

with an Aminco-Bowman Series 2 luminescence spectrometer. Fluorescence lifetimes were recorded with an ISS K2 Multifrequency Fluorimeter. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Elemental analyses were performed in the microanalytical laboratory of the University of Regensburg. For analytical thin layer chromatography precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey-Nagel) were used. Alumina (ICN Biomedicals) was used for column chromatography. The alumina used for chromatographic purification of Ru(II) complexes was deactivated with 7% (w/w) water. All reactions were carried out under an atmosphere of nitrogen in solvents dried according to standard procedures.

6-([1,10]-Phenanthrolin-2-yl)-[1,5,12]-triaza-triphenylene (**1b**): A solution of 200 mg (0.49 mmol) of 3-[1,10]-phenanthrolin-2-yl-[1,2,4,8,9]-pentaaza-triphenylene [5] in 15 ml 1,2-dichlorobenzene was heated under an inert atmosphere with bicyclo[2.2.1]hepta-2,5-diene (450 mg, 490 µl, 4.86 mmol) for 48 h at 195°C. After cooling to -20°C overnight, the precipitate was collected by suction filtration and recrystallized from dimethyl sulfoxide to yield 175 mg (0.43 mmol, 88%) of **1b** as beige crystals, m.p. 386-390°C. - IR (KBr): $\tilde{\nu}$ = 3010, 1590, 1580, 1480, 1410, 1340, 850, 830, 740 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.71 (dd, 1 H, J=8.4 Hz, J=4.4 Hz), 7.77 (dd, 1 H, J=8.3 Hz, J=4.4 Hz), 7.84 (dd, 1 H, J=8.2 Hz, J= 4.4 Hz), 7.86 (d, 1 H, J=8.8 Hz), 7.91 (d, 1 H, J=8.8 Hz), 8.32 (dd, 1 H, J=8.2 Hz, J=1.8 Hz), 8.49 (d, 1 H, J=8.5 Hz), 8.99 (dd, 1 H, J=8.4 Hz, J=1.6 Hz), 9.06 (d, 1 H, J=8.6 Hz), 9.25 (dd, 1 H, J=4.4 Hz, J=1.6 Hz), 9.26 (d, 1 H, J=8.5 Hz), 9.30 (dd, 1 H, J=4.4 Hz, J=1.8 Hz), 9.31 (dd, 1 H, J=4.4 Hz, J=1.8 Hz), 9.45 (d, 1 H, J=8.6 Hz), 9.84 (dd, 1 H, J=8.3 Hz, J=1.8 Hz) ppm. - EI MS (70eV); m/z (%): 409 (100) [M^+], 381 (20) [$M^+ - N_2$], 230 (5) [$M^+ - C_{12}H_7N_2$], 204 (20) [M^{2+}], 179 (10) [$M^+ - C_{15}H_8N_3$]. - $C_{27}H_{15}N_5$ (409.5): calcd. C 79.19, H 3.69, N 17.10; found C 78.88, H 3.91, N 16.88.

2-Bromo-5-octyl-thiophene: To a solution of 10.0 g (50.9 mmol) 2-octyl-thiophene [14] in 35 ml dry *N,N*-dimethylformamide was added at 0°C a solution of *N*-bromosuccinimide in 30 ml dry *N,N*-dimethylformamide over a period of 30 min. After stirring over night at room temperature, the solution was poured on 150 ml water. The organic layer was separated and washed with 25 ml water. Fractionated distillation at 0.2 Torr yielded 8.0 g (29.1 mmol, 57%) of 2-bromo-5-octyl-thiophene as a colourless liquid, b.p. 108-112°C / 0.2 Torr. The purity of the product was 99.6% (GC: column 15m DB1, 2 min 50°C, 6°C/min to 240°C, retention time of the product was 20.4 min).

4-(5-Octyl-thiophen)-2-yl-[2,2']-bipyridine (**1e**): $Pd(PPh_3)_4$ (30 mg, 26µmol) and 2-bromo-5-octyl-thiophene (512 mg, 1.86 mmol) were dissolved in 4 ml toluene and stirred for 5 min. 4-

Tributylstannyl-[2,2']-bipyridine **1c** [7] (550 mg, 1.24 mmol) in 2 ml toluene was added and the resulting mixture was heated to reflux for 30 h. Further 2-bromo-5-octyl-thiophene (50 mg, 181 µmol) was added and heating was continued for 30 h. After cooling to room temperature and addition of 50 ml of petroleum ether 40/60 the turbid solution was cooled to -70°C over night. The colourless precipitate was collected by suction filtration. Chromatographic purification with ethyl acetate : petroleum ether 40/60 1 : 9 yielded 330 mg **1e** (942 µmol, 76%) as a colourless solid, m. p. 97-99°C. - IR (KBr): $\tilde{\nu}$ = 3080, 3040, 2920, 2840, 1590, 1560, 1540, 1520, 1460, 1440, 1230, 980, 960, 880, 830, 800, 780, 730, 680 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.86 - 0.95 (m, 3 H), 1.28 - 1.42 (m, 10 H), 1.58 - 1.77 (m, 2 H), 2.85 (td, 2 H, J=7.6 Hz, J=0.9 Hz), 6.84 (dd, 1 H, J=3.7 Hz, J=0.9 Hz), 7.33 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.45 (dd, 1 H, J=5.2 Hz, J=2.0 Hz), 7.47 (d, 1 H, J=3.7 Hz), 7.82 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 8.43 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=1.0 Hz), 8.58 (dd, 1 H, J=5.2 Hz, J=0.7 Hz), 8.59 (dd, 1 H, J=2.0 Hz, J=0.7 Hz), 8.69 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=1.0 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT): δ= 14.21 (1C, +), 23.04 (1C, -), 29.49 (1C, -), 29.60 (1C, -), 29.70 (1C, -), 30.71 (1C, -), 31.97 (1C, -), 32.25 (1C, -), 116.80 (1C, +), 119.06 (1C, 0), 119.65 (1C, +), 121.35 (1C, +), 121.47 (1C, 0), 121.85 (1C, 0), 124.23 (1C, +), 125.83 (1C, +), 126.01 (1C, +), 137.20 (1C, +), 149.11 (1C, 0), 149.52 (1C, +), 149.61 (1C, 0), 150.05 (1C, +) ppm. - EI MS (70eV); m/z (%): 350 (79) [M^+], 321 (1) [M^+ - C_2H_5], 251 (100) [M^+ - C_7H_{15}]. - $C_{22}H_{26}N_2S$ (350.5): calcd. C 75.39, H 7.48, N 7.99; found C 75.62, H 7.09, N 8.11.

[2,2';4',4";2",2"']-Quaterpyridine (**1f**): $Pd(PPh_3)_4$ (12 mg, 10µmol) and 4-bromo-[2,2']-bipyridine **1d** [7] (150 mg, 500 µmol) were dissolved in 5 ml toluene and stirred for 5 min. 4-Tributylstannyl-[2,2']-bipyridine **1c** [7] (223 mg, 500 µmol) in 5 ml toluene was added and the resulting mixture was heated to reflux for 2d. After cooling to r.t. the colourless precipitate was washed 2x with 3 ml toluene. Chromatographic purification with CH_2Cl_2 : methanol 99 : 1 yielded 95 mg **1f** (307 µmol, 61%) as a colourless solid, m. p. 231-233°C. - IR (KBr): $\tilde{\nu}$ = 3080, 3060, 1600, 1570, 1520, 1460, 1390, 940, 800, 740, 690 cm^{-1}. - ^1H NMR (DMSO-d_6, 400 MHz): δ = 7.54 (ddd, 2 H, J=7.5 Hz, J=4.7 Hz, J=1.1 Hz), 7.99 (dd, 2 H, J=5.1 Hz, J=1.9 Hz), 8.02 (ddd, 2 H, J=7.9 Hz, J=7.5 Hz, J=1.8 Hz), 8.49 (ddd, 2 H, J=7.9 Hz, J=1.1 Hz, J=0.9 Hz), 8.78 (ddd, 2 H, J=4.7 Hz, J=1.8 Hz, J=0.9 Hz), 8.83 (dd, 2 H, J=1.9 Hz, J=0.8 Hz), 8.89 (dd, 2 H, J=5.1 Hz, J=0.8 Hz) ppm. - EI MS (70eV); m/z (%): 310 (100) [M^+], 282 (8) [M^+ - N_2], 232 (14) [M^+ - C_5H_4N], 155 (8) [M^{2+}], 78 (5) [M^+ - $C_{15}H_{10}N_3$]. - $C_{20}H_{14}N_4$ (310.4): calcd. C 77.39, H 4.55, N 18.05; found C 77.15, H 4.51, N 18.34.

General procedure for the synthesis of Ru(II) complexes ***3-8***: To a solution of the ligand (slight excess) in a methanol : water 4:1 mixture was added $phen_2RuCl_2$ (**2a**) or bpy_2RuCl_2 (**2b**)

and the resulting mixture was heated to reflux for the time indicated in Table 2. Solvents were stripped off the red solution. The residue was dissolved in a small amout of water and the resulting solution was filtrated in order to remove excess ligand. To the filtrate was added a concentrated aqueous solution of NH_4PF_6 (2 fold excess) and the resulting suspension was cooled to 5°C for 6 h. The precipitate was collected by suction filtration, washed with water followed by diethyl ether (ca. 4 ml each) and dried. The crude product was purified by recrystallization or chromatography. The racemic products contain 1 mol water per mol ruthenium.

Bis-([1,10]-phenanthroline)Ru(6-(pyridin-2-yl)-[1,5,12]-triaza-triphenylene)(PF_6)$_2$ (**3**):
Following the general procedure, $phen_2RuCl_2$ (**2a**) (56.8 mg, 99.9 µmol) and 6-(pyridin-2-yl)-[1,5,12]-triaza-triphenylene (**1a**) [5] yielded after recrystallization from ethanol / acetone 68.3 mg (64.0 µmol, 64%) of **3**, orange solid, m.p. 264-268 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3700-3200, 3660, 3570, 3420, 3090, 1620, 1600, 1580, 1430, 1415, 1405, 1370, 830, 780, 755, 710 cm^{-1}. - ^1H NMR (acetone-d_6, 400 MHz): δ = 7.60 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.82 (dd, 1 H, J=8.3 Hz, J=5.2 Hz), 7.83 (dd, 1 H, J=8.3 Hz, J=5.2 Hz), 7.83 (dd, 1 H, J=8.3 Hz, J=5.3 Hz), 7.83 (dd, 1 H, J=8.3 Hz, J=5.3 Hz), 7.92 (dd, 1 H, J=8.4 Hz, J=5.3 Hz), 7.95 (dd, 1 H, J=8.3 Hz, J=5.3 Hz), 8.09 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 8.42 (dd, 1 H, J=5.2 Hz, J=1.3 Hz), 8.42 (dd, 1 H, J=5.2 Hz, J=1.3 Hz), 8.43 (s, 2 H), 8.44 (s, 2 H), 8.47 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.50 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.58 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.58 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.81 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 8.81 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 8.81 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 8.82 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 8.84 (ddd, 1 H, J=4.8 Hz, 1.8 Hz, J=1.0 Hz), 8.98 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=1.0 Hz), 9.08 (d, 1 H, J=8.7 Hz), 9.51 (ddd, 1 H, J=8.4 Hz, J=1.3 Hz, J=0.4 Hz), 9.55 (dd, 1 H, J=8.7 Hz, J=0.4 Hz), 9.94 (dd, 1 H, J=8.3 Hz, 1.3 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / acetone): 915.2 $[K^{2+} + PF_6^-]^+$, 770.3 $[K^{2+} + e^-]^+$, 588.2 $[K^{2+} + e^- - C_{12}H_{10}N_2]^+$, 460.2 $[K^{2+} + e^- - C_{20}H_{11}N_4]^+$, 385.3 $[K^{2+}]$, 307.3 $[C_{20}H_{11}N_4]$. - UV/VIS (acetonitrile): 222 nm (77900 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.891), 263 (111200 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.046), 448 (20600 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.313). - Fluorescence/-lifetime (acetonitrile, excitation: 488 nm): 598 nm (τ=174 ns). - $C_{44}H_{28}F_{12}N_8P_2Ru \cdot H_2O$ (1077.8): calcd. C 49.03, H 2.81, N 10.40; found C 49.51, H 2.84, N 10.23.

Bis-(2,2'-bipyridine)Ru(6-(pyridin-2-yl)-[1,5,12]-triaza-triphenylene)(PF_6)$_2$ (**4**):
Following the general procedure, bpy_2RuCl_2 (**2b**) (50.0 mg, 103 µmol) and 6-(pyridin-2-yl)-[1,5,12]-triaza-triphenylene (**1a**) [5] yielded after recrystallization from ethanol / acetone 31.3 mg (29.9 µmol, 29%) of **4**, orange solid, m.p. 228-232°C. - IR (KBr): $\tilde{\nu}$ = 3700-3200, 3660, 3640, 3420, 3100, 1600, 1460, 1440, 1415, 1375, 830, 785, 755, 720 cm^{-1}. - ^1H NMR (acetone-

d_6, 400 MHz): δ = 7.42 (ddd, 1 H, J=7.6 Hz, J=5.6 Hz, J=1.3 Hz), 7.42 (ddd, 1 H, J=7.6 Hz, J=5.7 Hz, J=1.3 Hz), 7.59 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.66 (ddd, 1 H, J=7.6 Hz, J=5.6 Hz, J=1.4 Hz), 7.66 (ddd, 1 H, J=7.7 Hz, J=5.6 Hz, J=1.4 Hz), 8.04 (dd, 1 H, J=8.4 Hz, J=5.3 Hz), 8.07 (dd, 1 H, J=8.3 Hz, J=5.3 Hz), 8.09 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.9 Hz), 8.09 (ddd, 1 H, J=5.7 Hz, J=1.5 Hz, J=0.8 Hz), 8.09 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 8.17 (ddd, 2 H, J=8.3 Hz, J=7.6 Hz, J=1.5 Hz), 8.20 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.8 Hz), 8.21 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.8 Hz), 8.28 (ddd, 1 H, J=8.3 Hz, J=7.6 Hz, J=1.5 Hz), 8.29 (ddd, 1 H, J=8.3 Hz, J=7.7 Hz, J=1.5 Hz), 8.50 (dd, 1 H, J=5.3 Hz, J=1.2 Hz), 8.54 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.83 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=0.9 Hz), 8.85 (ddd, 1 H, J=8.3 Hz, J=1.3 Hz, J=0.9 Hz), 8.85 (ddd, 1 H, J=8.3 Hz, J=1.3 Hz, J=0.8 Hz), 8.88 (ddd, 1 H, J=8.3 Hz, J=1.4 Hz, J=0.8 Hz), 8.88 (ddd, 1 H, J=8.3 Hz, J=1.4 Hz, J=0.8 Hz), 8.89 (ddd, 1 H, J=8.3 Hz, J=1.4 Hz, J=0.8 Hz), 8.97 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 9.06 (d, 1 H, J=8.7 Hz), 9.52 (ddd, 1 H, J=8.4 Hz, J=1.2 Hz, J=0.4 Hz), 9.53 (dd, 1 H, J=8.7 Hz, J=0.4 Hz), 9.94 (dd, 1 H, J=8.3 Hz, J=1.3 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / acetone): 867.4 $[K^{2+} + PF_6^-]^+$, 722.4 $[K^{2+} + e^-]^+$, 566.4 $[K^{2+} + e^- - C_{10}H_8N_2]^+$, 361.4 $[K^{2+}]$, 307.3 $[C_{20}H_{11}N_4]$. - UV/VIS (acetonitrile): 243 nm (48700 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.687), 286 (97600 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.990), 451 (18200 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.259). - Fluorescence/-lifetime (acetonitrile, excitation: 488 nm): 606 nm (τ=143 ns). - $C_{40}H_{28}F_{12}N_8P_2Ru \cdot H_2O$ (1029.6): calcd. C 46.66, H 2.94, N 10.89; found C 46.82, H 2.76, N 10.83.

Bis-([2,2']-bipyridine)Ru(6-([1,10]-phenanthrolin-2-yl)-[1,5,12]-triaza-triphenylene)$(PF_6)_2$ (**5**): Following the general procedure, bpy_2RuCl_2 (**2b**) (129 mg, 247 μmol) and 6-([1,10]-phenanthrolin-2-yl)-[1,5,12]-triaza-triphenylene (**1b**) (101 mg, 247 μmol) were heated to reflux for 48 h in 30 ml methanol and 5 ml water. Yield after chromatographic purification on alumina (deactivated with 7% w/w water) with acetone as eluent was 211 mg (190 μmol, 77%) of **5**, orange-red solid, m.p. 190-193 °C. - IR (KBr): $\tilde{\nu}$ = 3600-3200, 3140, 3100, 1600, 1560, 1460, 1440, 1410, 1390, 840, 760 cm^{-1}. - ^1H NMR (acetone-d_6, 400 MHz): δ = 7.42 (ddd, 1 H, J=7.6 Hz, J=5.7 Hz, J=1.3 Hz), 7.44 (ddd, 1 H, J=7.6 Hz, J=5.6 Hz, J=1.4 Hz), 7.67 (ddd, 1 H, J=7.7 Hz, J=5.6 Hz, J=1.3 Hz), 7.68 (ddd, 1 H, J=7.7 Hz, J=5.6 Hz, J=1.4 Hz), 7.88 (dd, 1 H, J=8.1 Hz, J=4.3 Hz), 8.07 (dd, 1 H, J=8.4 Hz, J=5.3 Hz), 8.10 (dd, 1 H, J=8.2 Hz, J=5.2 Hz), 8.10 (ddd, 1 H, J=5.6 Hz, J=1.4 Hz, J=0.8 Hz), 8.11 (d, 1 H, J=8.4 Hz), 8.11 (ddd, 1 H, J=5.7 Hz, J=1.5 Hz, J=0.8 Hz), 8.11 (d, 1 H, J=8.4 Hz), 8.18 (ddd, 1 H, J=8.4 Hz, J=7.6 Hz, J=1.5 Hz), 8.18 (ddd, 1 H, J=8.3 Hz, J=7.6 Hz, J=1.5 Hz), 8.22 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.9 Hz), 8.23 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.8 Hz), 8.29 (ddd, 1 H, J=8.3 Hz, J=7.7 Hz, J=1.5 Hz), 8.30 (ddd, 1 H, J=8.4 Hz, J=7.7 Hz, J=1.4 Hz), 8.53 (dd, 1 H, J=5.2 Hz, J=1.2 Hz), 8.55 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.58 (dd, 1 H, J=8.1 Hz, J=1.7 Hz), 8.76 (d, 1 H, J=8.6 Hz), 8.86 (ddd, 1 H, J=8.4, J=1.3 Hz, J=0.8 Hz), 8.86 (ddd, 1 H, J=8.3 Hz, J=1.4 Hz, J=0.8 Hz), 8.90 (ddd, 1 H,

J=8.4 Hz, J=1.4 Hz, J=0.9 Hz), 8.90 (ddd, 1 H, J=8.3 Hz, J=1.3 Hz, J=0.8 Hz), 9.28 (dd, 1 H, J=4.3 Hz, J=1.7 Hz), 9.36 (d, 1 H, J=8.4 Hz), 9.37 (d, 1 H, J=8.6 Hz), 9.57 (ddd, 1 H, J=8.2 Hz, J=1.2 Hz, J=0.3 Hz), 9.64 (dd, 1 H, J=8.4 Hz, J=0.3 Hz), 10.06 (dd, 1 H, J=8.4 Hz, J=1.3 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / acetone): 968.5 $[K^{2+} + PF_6^-]^+$, 823.5 $[K^{2+} + e^-]^+$, 411.9 $[K^{2+}]$. - UV/VIS (acetonitrile): 244 nm (29600 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.471), 288 (79900 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.903), 468 (16800 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.225). - Fluorescence/-lifetime (CH_2Cl_2, excitation: 488 nm): 609 nm (τ=467 ns). - $C_{47}H_{31}F_{12}N_9P_2Ru \cdot H_2O$ (1130.8): calcd. C 49.92, H 2.94, N 11.15; found C 50.17, H 2.92, N 11.21.

Bis-([2,2']-bipyridine)Ru(4-tributylstannyl-[2,2']-bipyridine)$(PF_6)_2$ (**6**): Following the general procedure, bpy_2RuCl_2 (**2b**) (250 mg, 480 μmol) and 4-tributylstannyl-[2,2']-bipyridine (**1c**) [7] (245 mg, 550 μmol) in 36 ml methanol and 4 ml water yielded after chromatographic purification on alumina (deactivated with 7% w/w water) with CH_2Cl_2 (elution of excess ligand) followed by acetone : water 5:1 as eluent 92.7 mg (88 μmol, 46%) of **5**, orange-red solid, m.p. 177-180 °C. - IR (KBr): ν = 3600-3300, 3140, 3100, 2960, 2940, 2880, 2860, 1600, 1470, 1450, 1430, 1390, 850, 760 cm^{-1}. - ^1H NMR (acetone-d_6, 400 MHz): δ = 0.83-0.87 (m, 9 H), 1.24-1.38 (m, 12 H), 1.55-1.64 (m, 6 H), 7.55 (ddd, 1 H, J=7.7 Hz, J=5.7 Hz, J=1.3 Hz), 7.56 (ddd, 1 H, J=7.7 Hz, J=5.6 Hz, J=1.3 Hz), 7.58 (ddd, 1 H, J=7.6 Hz, J=5.7 Hz, J=1.3 Hz), 7.58 (ddd, 1 H, J=7.9 Hz, J=5.5 Hz, J=1.3 Hz), 7.60 (ddd, 1 H, J=5.5 Hz, J=1.3 Hz, J=0.8 Hz), 7.69 (dd, 1 H, J=5.4 Hz, J=1.0 Hz), 7.89 (dd, 1 H, J=5.4 Hz, J=0.8 Hz), 7.98 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.7 Hz), 8.04 (ddd, 1 H, J=5.7 Hz, J=1.5 Hz, J=0.8 Hz), 8.05 (ddd, 1 H, J=7.5 Hz, J=5.7 Hz, J=1.3 Hz), 8.06 (ddd, 1 H, J=5.7 Hz, J=1.4 Hz, J=0.7 Hz), 8.06 (ddd, 1H, J=5.7 Hz, J=1.6 Hz, J=0.9 Hz), 8.18 (ddd, 1 H, J=8.2 Hz, J=7.7 Hz, J=1.4 Hz), 8.22 (ddd, 1 H, J=8.2 Hz, J=7.7 Hz, J=1.5 Hz), 8.22 (ddd, 1 H, J=8.4 Hz, J=7.6 Hz, J=1.5 Hz), 8.22 (ddd, 1 H, J=8.2 Hz, J=7.9 Hz, J=1.3 Hz), 8.22 (dd, 1 H, J=8.3 Hz, J=7.5 Hz, J=1.6 Hz), 8.83 (ddd, 1 H, J=8.2 Hz, J=1.3 Hz, J=0.7 Hz), 8.83 (ddd, 1 H, J=8.2 Hz, J=1.3 Hz, J=0.7 Hz), 8.83 (ddd, 1 H, J=8.4 Hz, J=1.3 Hz, J=0.8 Hz), 8.83 (ddd, 1 H, J=8.2 Hz, J=1.4 Hz, J=0.8 Hz), 8.88 (ddd, 1 H, J=8.3 Hz, J=1.3 Hz, J=0.9 Hz), 8.93 (dd, 1 H, J=1.0 Hz, J=0.8 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / CH_2Cl_2): 1003.5 $[K^{2+} + PF_6^-]^+$, 858.5 $[K^{2+} + e^-]^+$, 429.4 $[K^{2+}]$. - UV/VIS (acetonitrile): 244 nm (28500 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.458), 288 (87900 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.944), 454 (16300 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.213). - Fluorescence/-lifetime (CH_2Cl_2, excitation: 488 nm): 600 nm (τ=396 ns). - $C_{42}H_{50}F_{12}N_6P_2RuSn \cdot H_2O$ (1166.6): calcd. C 43.44, H 4.41, N 7.20; found C 43.69, H 4.19, N 7.23.

Bis-([2,2']-bipyridine)Ru(4-bromo-[2,2']-bipyridine)$(PF_6)_2$ (**7**): Following the general procedure, bpy_2RuCl_2 (**2b**) (266 mg, 510 μmol) and 4-bromo-[2,2']-bipyridine (**1d**) [7] (120 mg, 510 μmol) were heated to reflux for 16 h in 25 ml methanol and 5 ml water. The crude

product was chromatographed on alumina (deacativated with 7% w/w water) with acetone : toluene 1:1 as eluent. The fractions containing product were freed from solvent, dissolved in 1.2 ml acetone and dropped slowly with stirring in 200 ml diethyl ether. After suction filtration and washing with diethyl ether, the yield was 214 mg (270 μmol, 53%) of **7**, orange-red solid, m.p. 175-178 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3600-3300, 3100, 3080, 1590, 1470, 1450, 1430, 1380, 850, 760, 700 cm^{-1}. - ^1H NMR (DMSO-d_6, 400 MHz, 120°C): δ = 7.49 (ddd, 1 H, J=7.6 Hz, J=5.6 Hz, J=1.3 Hz), 7.49 (ddd, 1 H, J=7.6 Hz, J=5.6 Hz, J=1.3 Hz), 7.50 (ddd, 1 H, J=7.6 Hz, J=5.6 Hz, J=1.3 Hz), 7.51 (ddd, 1 H, J=7.6 Hz, J=5.6 Hz, J=1.4 Hz), 7.52 (ddd, 1 H, J=7.6 Hz, J=5.6 Hz, J=1.4 Hz), 7.57 (dd, 1 H, J=6.1 Hz, J=0.6 Hz), 7.69 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.8 Hz), 7.70 (ddd, 1 H, J=5.6 Hz, J=1.6 Hz, J=0.8 Hz), 7.70 (dd, 1 H, J=6.1 Hz, J=2.1 Hz), 7.71 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.8 Hz), 7.74 (ddd, 1 H, J=5.6 Hz, J=1.5 Hz, J=0.7 Hz), 7.85 (ddd, 1 H, J=5.6 Hz, 1.5 Hz, 0.8 Hz), 8.12 (ddd, 1 H, J=8.4 Hz, J=7.6 Hz, J=1.5 Hz), 8.12 (ddd, 1 H, J=8.3 Hz, J=7.6 Hz, J=1.6 Hz), 8.12 (ddd, 1 H, J=8.3 Hz, J=7.6 Hz, J=1.5 Hz), 8.12 (ddd, 1 H, J=8.1 Hz, J=7.7 Hz, J=1.5 Hz), 8.12 (ddd, 1 H, J=8.3 Hz, J=7.6 Hz, J=1.5 Hz), 8.72 (ddd, 1 H, J=8.4 Hz, J=1.3 Hz, J=0.8 Hz), 8.72 (ddd, 1 H, J=8.3 Hz, J=1.3 Hz, J=0.8 Hz), 8.72 (ddd, 1 H, J=8.3 Hz, J=1.3 Hz, J=0.8 Hz), 8.72 (ddd, 1 H, J=8.1 Hz, J=1.4 Hz, J=0.7 Hz), 8.84 (ddd, 1 H, J=8.3 Hz, J=1.4 Hz, J=0.8 Hz), 9.02 (dd, 1 H, J=2.1 Hz, J=0.6 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / CH_2Cl_2): 795.1 $[K^{2+} + PF_6^-]^+$, 648.2 $[K^{2+} + e^-]^+$, 324.2 $[K^{2+}]$. - UV/VIS (acetonitrile): 235 nm (22600 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.354), 287 (65400 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.816), 454 (11100 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.043). - Fluorescence/-lifetime (CH_2Cl_2, excitation: 488 nm): 616 nm (τ=522 ns). - $C_{30}H_{23}BrF_{12}N_6P_2Ru \cdot H_2O$ (938.5): calcd. C 38.39, H 2.77, N 8.95; found C 38.40, H 2.86, N 8.67.

Bis-([2,2']-bipyridine)Ru(4-[5-(octan-1-yl)-thiophen-2-yl][2,2']-bipyridine)(PF_6)$_2$ (**8**): Following the general procedure, bpy_2RuCl_2 (**2b**) (75.4 mg, 145 μmol) and 4-[5-(octan-1-yl)-thiophen-2-yl]-[2,2']-bipyridine (**1e**) (67.4 mg, 192 μmol) were heated to reflux for 12 h in 16 ml methanol and 4 ml water. The yield after washing with water and diethyl ether was 92.7 mg (88.0 μmol, 46%) of **8**, orange-red solid, m.p. 175-179 °C. - IR (KBr): $\tilde{\nu}$ = 3600-3300, 3100, 3060, 2920, 2840, 1600, 1470, 1450, 1430, 1410, 830, 750, 720 cm^{-1}. - ^1H NMR (acetone-d_6, 400 MHz, 120°C): δ = 0.85-0.89 (m, 3 H), 1.25-1.40 (m, 10 H), 1.68-1.76 (m, 2 H), 2.90-2.95 (m, 2 H), 7.04 (dt, 1 H, J=3.8 Hz, J=0.9 Hz), 7.56-7.63 (m, 4 H), 7.66 (dd, 1 H, J=6.1 Hz, J=2.1 Hz), 7.89 (d, 1 H, J=3.8 Hz), 7.91 (dd, 1 H, J=6.1 Hz, J=0.6 Hz), 8.04-8.12 (m, 3 H), 8.09 (ddd, 1 H, J=5.7 Hz, J=1.5 Hz, J=0.8 Hz), 8.18-8.28 (m, 7 H), 8.79-8.90 (m, 4 H), 8.95 (dd, 1 H, J=2.1 Hz, J=0.6 Hz), 9.02 (ddd, 1 H, J=8.3 Hz, J=1.3 Hz, J=0.8 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / CH_2Cl_2): 909.3 $[K^{2+} + PF_6^-]^+$, 764.4 $[K^{2+} + e^-]^+$, 382.3 $[K^{2+}]$. - UV/VIS (acetonitrile): 244 nm (26800 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.428), 288 (69700 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.843), 338 (21200 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.326), 454 (17000 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.229). - Fluorescence/

-lifetime (CH_2Cl_2, excitation: 488 nm): 614 nm (τ=453 ns). - $C_{42}H_{42}F_{12}N_6P_2RuS \cdot H_2O$ (1071.9): calcd. C 47.06, H 4.14, N 7.84; found C 46.92, H 3.94, N 8.09.

Bis-[(bis-[2,2']-bipyridine)Ru(6-[1,10]-phenanthrolin-2-yl-[1,5,12]-triaza-triphenylene)] $Ag(PF_6)_5$ (**9**): To a solution of Bis-([2,2']-bipyridine)Ru(6-([1,10]-phenanthrolin-2-yl)-[1,5,12]-triaza-triphenylene)$(PF_6)_2$ (**5**) (27.4 mg, 24.6 µmol) in 15 ml nitromethane were added 3.7 mg (14.8 µmol) $AgPF_6$ under an inert atmosphere. The solution was stirred at ambient temperature under exclusion of light. The mixture was warmed to 30-35°C and the solvent was carefully blown off with a moderate stream of argon. The residue was dissolved in 2 ml dry acetone, then 15 ml of dry diethyl ether were slowly added without stirring to avoid mixing of the solvents. The flask was sealed and kept in the dark for 24 h. The precipitate was filtrated with suction and dried. The yield was 21.9 mg (8.84 µmol, 72%) of **9**, orange solid, m.p. 225°C, decomp. beginning at 185°C. - IR (KBr): $\tilde{\nu}$ = 3600-3300, 3080,1610, 1560, 1540, 1470, 1450, 1420, 860, 770, 750, 740 cm^{-1}. - ^1H NMR (DMSO-d_6, 400 MHz, 140°C): δ = 7.35 (ddd, 2 H, J=7.5 Hz, J=5.6 Hz, J=1.4 Hz), 7.37 (ddd, 2 H, J=7.5 Hz, J=5.6 Hz, J=1.5 Hz), 7.57 (ddd, 2 H, J=7.6 Hz, J=5.6 Hz, J=1.6 Hz), 7.58 (ddd, 2 H, J=7.7 Hz, J=5.6 Hz, J=1.4 Hz), 7.71 (ddd, 2 H, J=5.7 Hz, J=1.5 Hz, J=0.8 Hz), 7.74 (ddd, 2 H, J=5.6 Hz, J=1.5 Hz, J=0.9 Hz), 7.84 (dd, 2 H, J=8.0 Hz, J=4.4 Hz), 7.87 (ddd, 2 H, J=5.6 Hz, J=1.5 Hz, J=0.9 Hz), 7.87 (ddd, 2 H, J=5.6 Hz, J=1.5 Hz, J=0.8 Hz), 7.98 (dd, 2 H, J=8.2 Hz, J=5.3 Hz), 7.98 (d, 2 H, J=8.3 Hz), 7.99 (dd, 2 H, J=8.4 Hz, J=5.3 Hz), 7.99 (d, 2 H, J=8.3 Hz), 8.08 (ddd, 2 H, J=8.1 Hz, J=7.5 Hz, J=1.5 Hz), 8.10 (ddd, 2 H, J=8.2 Hz, J=7.6 Hz, J=1.5 Hz), 8.21 (dd, 2 H, J=5.3 Hz, J=1.4 Hz), 8.18 (ddd, 2 H, J=8.3 Hz, J=1.5 Hz), J=0.8 Hz), 8.18 (ddd, 2 H, J=8.2 Hz, J=1.6 Hz, J=0.9 Hz), 8.21 (dd, 2 H, J=5.3 Hz, J=1.3 Hz), 8.51 (dd, 2 H, J=8.0 Hz, J=1.7 Hz), 8.71 (d, 2 H, J=8.6 Hz), 8.74 (ddd, 2 H, J=8.5 Hz, J=7.7 Hz, J=1.5 Hz), 8.75 (ddd, 2 H, J=8.3 Hz, J=7.5 Hz, J=1.5 Hz), 8.77 (ddd, 2 H, J=8.5 Hz, J=1.4 Hz, J=0.9 Hz), ddd, 2 H, J=8.1 Hz, J=1.4 Hz, J=0.8 Hz), 9.09 (d, 2 H, J=8.3 Hz), 9.21 (dd, 2 H, J=4.4 Hz, J=1.7 Hz), 9.27 (d, 2 H, J=8.6 Hz), 9.43 (ddd, 2 H, J=8.4 Hz, J=1.3 Hz, J=0.3 Hz), 9.49 (dd 2 H, J=8.3 Hz, J=0.3 Hz), 9.89 (dd, 2 H, J=8.2 Hz, J=1.4 Hz) ppm. - UV/VIS (acetonitrile): 242 nm (124000 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.093), 286 (177700 $l \cdot mol^{-1}$ cm^{-1}, lg ε 5.250), 338 (71800 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.856), 356 (68200 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.834), 452 (37100 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.570). - Fluorescence/ -lifetime (CH_2Cl_2, excitation: 488 nm): 591 nm (τ_1=120 ns, 57%, τ_2=395 ns, 43%). - $C_{94}H_{62}AgF_{30}N_{18}P_5Ru_2$ (2478.5): calcd. C 45.55, H 2.52, N 10.17; found C 45.21, H 2.79, N 9.71.

*General procedure for the synthesis of Ru(II) complexes **11a-11d***: A solution of bis-([1,10]-phenanthroline)Ru([1,10]-phenanthroline-5,6-dione)$(PF_6)_2 \cdot 2H_2O$ (**2c**) [11] and an equal molar amount of carboxamidrazone **10a-10d** was stirred for 24 h at ambient temperature under an inert atmosphere in acetonitrile / ethanol 1:1 (v/v) . The resulting red solution was heated to

reflux for 1 h. After cooling to r.t. a concentrated aqueous solution of NH_4PF_6 (2 fold excess) was added. The product precipitated upon addition of diethyl ether.

Bis-([1,10]-phenanthroline)Ru(3-(pyridin-2-yl)-[1,2,4,8,9]-pentaaza-triphenylene)(PF_6)$_2$ (**11a**): Following the general procedure, $Phen_2Ru$(II)phendione (**2c**) (500 mg, 475 µmol) and pyridine-2-carboxamidrazone (**10a**) (64.6 mg, 475 µmol) yielded without further purification 286 mg (260 µmol, 55%) of **11a**, orange solid, m.p. 255-260°C, decomposition beginning at 250°C. IR (KBr): $\tilde{\nu}$ = 3700-3200, 3660, 3630, 3570, 1630, 1620, 1590, 1570, 1500, 1490, 1415, 1400, 1385, 1360, 830, 770, 710 cm^{-1}. - ^1H NMR (acetone-d_6, 400 MHz): δ = 7.73 (ddd, 1 H, J=7.6 Hz, J=4.7 Hz, J=1.2 Hz), 7.82 (dd, 1 H, J=8.3 Hz, J=5.3 Hz), 7.83 (dd, 1 H, J=8.3 Hz, J=5.3 Hz), 7.83 (dd, 1 H, J=8.3 Hz, J=5.3 Hz), 7.84 (dd, 1 H, J=8.3 Hz, J=5.3 Hz), 8.03 (dd, 1 H, J=8.3 Hz, J=5.4 Hz), 8.05 (dd, 1 H, J=8.3 Hz, J=5.4 Hz), 8.18 (ddd, 1 H, J=7.9 Hz, J=7.6 Hz, J=1.8 Hz), 8.41 (dd, 1 H, J=5.3 Hz, J=1.3 Hz),), 8.41 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.43 (s, 2 H), 8.44 (s, 2 H), 8.58 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.61 (dd, 1 H, J=5.3 Hz, J=1.3 Hz), 8.63 (dd, 1 H, J=5.4 Hz, J=1.3 Hz), 8.68 (dd, 1 H, J=5.4 Hz, J=1.3 Hz), 8.82 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 8.82 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 8.83 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 8.83 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 8.93 (ddd, 1 H, J=7.9 Hz, J=1.2 Hz, J=0.9 Hz), 8.97 (ddd, 1 H, J=4.7 Hz, J=1.8 Hz, J=0.9 Hz), 9.83 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 9.86 (dd, 1 H, J=8.3 Hz, J=1.3 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / CH_2Cl_2): 917.2 $[K^{2+} + PF_6^-]^+$, 772.2 $[K^{2+} + e^-]^+$, 386.3 $[K^{2+}]$. - UV/VIS (acetonitrile): 223 nm (74300 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.871), 262 (108200 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.034), 338 (21200 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.326), 438 (18400 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.266). - Fluorescence/ -lifetime (CH_2Cl_2, excitation: 488 nm): 641 nm (τ_1=65 ns, 72%, τ_2=765 ns, 28%). - $C_{42}H_{26}F_{12}N_{10}P_2Ru \cdot 2H_2O$ (1097.8): calcd. C 45.95, H 2.75, N 12.76; found C 46.20, H 2.84, N 12.32.

Bis-([1,10]-phenanthroline)Ru([1,2,4,8,9]-pentaaza-triphenylen-3-yl-3-[1,2,4,8,9]-pentaaza-triphenylene)Ru(bis-([1,10]-phenanthroline))(PF_6)$_2$ (**11b**): Following the general procedure, $phen_2Ru$(II)phendione (**2c**) (250 mg, 238 µmol) and dicarboxbisamidrazone (**10b**) (13.8 mg, 119 µmol) yielded after recrystallization from methanol 175 mg (85.7 µmol, 72%) of **11b**, orange solid, m.p. >300°C, decomposition beginning at 250°C. The *rac* and *meso* isomers were not separated. IR (KBr): $\tilde{\nu}$ = 3700-3200, 3660, 3630, 3570, 1630, 1620, 1590, 1570, 1500, 1490, 1415, 1400, 1385, 1360, 830, 770, 710 cm^{-1}. - ^1H NMR (DMSO-d_6, 400 MHz, 100°C): δ = 7.76 (dd, 4 H, J=8.3 Hz, J=5.2 Hz), 7.77 (dd, 4 H, J=8.3 Hz, J=5.2 Hz), 7.77 (dd, 2 H, J=8.3 Hz, J=5.2 Hz), 7.78 (dd, 2 H, J=8.2 Hz, J=5.3 Hz), 7.80 (dd, 2 H, J=8.3 Hz, J=5.2 Hz), 7.80 (dd, 2 H, J=8.3 Hz, J=5.3 Hz), 8.00 (dd, 2 H, J=8.2 Hz, J=5.4 Hz), 8.00 (dd, 2 H, J=8.3 Hz, J=5.4 Hz), 8.04 (dd, 4 H, J=8.3 Hz, J=5.4 Hz), 8.05 (dd, 4 H, J=5.2 Hz, J=1.3 Hz), 8.05 (dd, 4 H, J=5.2 Hz, J=1.3 Hz), 8.23 (dd, 2 H, J=5.3 Hz, J=1.3 Hz), 8.24 (dd, 2 H, J=5.3 Hz, J=1.3 Hz),

8.27 (dd, 2 H, J=5.3 Hz, J=1.3 Hz), 8.27 (dd, 2 H, J=5.3 Hz, J=1.3 Hz), 8.3 (dd, 2 H, J=5.4 Hz, J=1.3 Hz), 8.33 (dd, 2 H, J=5.4 Hz, J=1.3 Hz), 8.35 (dd, 2 H, J=5.4 Hz, J=1.3 Hz), 8.35 (dd, 2 H, J=5.4 Hz, J=1.3 Hz), 8.37 (s, 4 H), 8.38 (s, 8 H), 8.76 (dd, 4 H, J=8.3 Hz, J=1.3 Hz), 8.76 (dd, 4 H, J=8.3 Hz, J=1.3 Hz), 8.78 (dd, 4 H, J=8.2 Hz, J=1.3 Hz), 8.78 (dd, 4 H, J=8.3 Hz, J=1.3 Hz), 9.74 (dd, 2 H, J=8.2 Hz, J=1.3 Hz), 9.74 (dd, 2 H, J=8.3 Hz, J=1.3 Hz), 9.89 (dd, 4 H, J=8.3 Hz, J=1.3 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / CH_2Cl_2): 1823.0 $[K^{4+} + 3PF_6^-]^+$, 1678.1 $[K^{4+} + 2PF_6^- + e^-]^+$, 1532.3 $[K^{4+} + PF_6^- + 2e^-]^+$, 839.2 $[K^{4+} + 2PF_6^-]^{2+}$, 766.3 $[K^{4+} + PF_6^- + e^-]^{2+}$, 460.4 $[(phen)_2 Ru^{2+} + e^-]^+$. - UV/VIS (acetonitrile): 223 nm (109100 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.038), 262 (163900 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.215), 338 (21200 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.326), 438 (28000 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.447). - Fluorescence/ -lifetime (acetonitrile, excitation: 488 nm): too weak (τ_1=10 ns, 81%, τ_2=241 ns, 19%). - $C_{74}H_{44}F_{24}N_{18}P_4Ru_2 \cdot 4H_2O$ (2039.3): calcd. C 43.58, H 2.57, N 12.37; found C 43.64, H 2.71, N 12.39.

2,6-Bis-[bis-([1,10]-phenanthroline)Ru([1,2,4,8,9]-pentaaza-triphenylen-3-yl)]-pyridine $(PF_6)_4$ (**11c**): Following the general procedure, $phen_2Ru$(II)phendione (**2c**) (500 mg, 475 μmol) and pyridine-2,6-dicarboxbisamidrazone (**10c**) (45.9 mg, 238 μmol) yielded without further purification 371 mg (175 μmol, 74%) of **11c**, orange solid, m.p. >300°C, decomposition beginning at 250°C. The *rac* and *meso* isomers were not separated. IR (KBr): $\tilde{\nu}$ = 3700-3200, 3630, 3080, 1635, 1625, 1590, 1575, 1505, 1420, 1405, 1375, 1365, 830, 770, 710 cm^{-1}. - ^1H NMR (DMSO-d_6, 400 MHz, 100°C): δ = 7.76 (dd, 4 H, J=8.3 Hz, J=5.3 Hz), 7.76 (dd, 4 H, J=8.3 Hz, J=5.3 Hz), 7.77 (dd, 4 H, J=8.3 Hz, J=5.3 Hz), 7.79 (dd, 4 H, J=8.3 Hz, J=5.3 Hz), 7.99 (dd, 4 H, J=8.3 Hz, J=5.4 Hz), 8.01 (dd, 4 H, J=8.3 Hz, J=5.4 Hz), 8.05 (dd, 2 H, J=5.3 Hz, J=1.3 Hz), 8.05 (dd, 2 H, J=5.3 Hz, J=1.3 Hz), 8.05 (dd, 4 H, J=5.3 Hz, J=1.3 Hz), 8.23 (dd, 2 H, J=5.3 Hz, J=1.3 Hz), 8.23 (dd, 2 H, J=5.3 Hz, J=1.3 Hz), 8.27 (dd, 4 H, J=5.3 Hz, J=1.3 Hz), 8.28 (dd, 4 H, J=5.4 Hz, J=1.3 Hz), 8.31 (dd, 2 H, J=5.4 Hz, J=1.3 Hz), 8.31 (dd, 2 H, J=5.4 Hz, J=1.3 Hz), 8.37 (s, 4 H), 8.37 (s, 4 H), 8.37 (s, 8 H), 8.58 (dd, 2 H, J=8.1 Hz, J=7.7 Hz), 8.75 (dd, 4 H, J=8.3 Hz, J=1.3 Hz), 8.76 (dd, 4 H, J=8.3 Hz, J=1.3 Hz), 8.77 (dd, 4 H, J=8.3 Hz, J=1.3 Hz), 8.77 (dd,4 H, J=8.3 Hz, J=1.3 Hz), 9.14 (d, 4 H, J=7.9 Hz), 9.78 (dd, 4 H, J=8.3 Hz, J=1.3 Hz), 9.80 (dd, 4 H, J=8.3 Hz, J=1.3 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / CH_2Cl_2): 1898.5 $[K^{4+} + 3PF_6^-]^+$, 1755.8$[K^{4+} + 2PF_6^- + e^-]^+$, 1609.9 $[K^{4+} + PF_6^- + 2e^-]^+$, 1148.0 $[(phen)_2Ru^{2+}L + PF_6^-]^+$, 1004.2 $[(phen)_2Ru^{2+}L + e^-]^+$, 877.8 $[K^{4+} + 2PF_6^-]^{2+}$, 805.4 $[K^{4+} + PF_6^- + e^-]^{2+}$, 733.8 $[K^{4+} + 2e^-]^{2+}$. - UV/VIS (acetonitrile): 223 nm (172800 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.238), 262 (265100 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.423), 437 (44700 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.650). - Fluorescence/ -lifetime (acetonitrile, excitation: 488 nm): 664 nm (τ_1=34 ns, 86%, τ_2=554 ns, 14%). - $C_{79}H_{47}F_{24}N_{19}P_4Ru_2 \cdot 4H_2O$ (2116.4): calcd. C 44.83, H 2.62, N 12.57; found C 45.08, H 2.87, N 12.69.

2,4,6-Tris-[bis-([1,10]-phenanthroline)Ru([1,2,4,8,9]-pentaaza-triphenylen-3-yl)]-pyridine(PF_6)$_6$ (**11d**): Following the general procedure, $phen_2Ru$(II)phendione (**2c**) (500 mg, 475 µmol) and pyridine-2,4,6-tricarboxtrisamidrazone (**10d**) (42.5 mg, 158 µmol) yielded without further purification 416 mg (133 µmol, 84%) of **11d**, orange solid, m.p. >300°C. The *rac* and *meso* isomers were not separated. IR (KBr): $\tilde{\nu}$ = 3700-3200, 3630, 3080, 1635, 1625, 1590, 1505, 1415, 1405, 1355, 830, 770, 710 cm^{-1}. - ^1H NMR (DMSO-d_6, 400 MHz, 100°C): δ = 7.73-7.82 (m, 12 H), 7.98-8.10 (m, 12 H), 8.22-8.42 (m, 24 H), 8.72-8.80 (m, 12 H), 9.79 (dd, 2 H, J=8.3 Hz, J=1.3 Hz), 9.82 (dd, 1 H, J=8.2 Hz, J=1.3 Hz), 9.83 (dd, 2 H, J=8.3 Hz, J=1.3 Hz), 9.86 (dd, 1 H, J=8.3 Hz, J=1.3 Hz), 10.32 (s, 2 H) ppm. - ESI-MS ($CH_3CN/H_2O/CH_3COOH$): 611.5 $[K^{6+} + 2PF_6^-]^{4+}$, 459.8 $[K^{6+} + PF_6^-]^{5+}$, 454.2 $[K^{6+} - N_2 + PF_6^-]$, 430.8 $[K^{6+} + e^-]^{5+}$, 359.3 $[K^{6+}]$. - UV/VIS (acetonitrile): 223 nm (255800 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.408), 262 (374000 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.573), 436 (69800 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.844). - Fluorescence/ -lifetime (acetonitrile, excitation: 488 nm): 650 nm (τ_1=22 ns, 83%, τ_2=578 ns, 18%). - $C_{116}H_{68}F_{36}N_{28}P_6Ru_3 \cdot 6H_2O$ (3135.1): calcd. C 44.44, H 2.57, N 12.51; found C 44.43, H 2.72, N 12.72.

Bis-([2,2']-bipyridine)Ru(4-[2,2';5',2'']-terthiophen-5-yl-[2,2']-bipyridine)(PF_6)$_2$ (**12a**): A solution of $Pd(PPh_3)_4$ (10.0 mg, 10.3 µmol), bis-([2,2']-bipyridine)Ru(4-tributylstannyl-[2,2']-bipyridine)(PF_6)$_2$ (**6**) (106 mg, 92.1 µmol) and 5-bromo-[2,2';5',2'']-terthiophene [12] (45.2 mg, 138 µmol) in 15 ml toluene and 3 ml acetonitrile was heated to reflux for 3 d. The solution was filtrated to remove a small amount of black precipitate and the solvents were stripped off. After chromatographic purification on alumina (deactivated with 7% w/w water) with acetone, the oily product was dissolved in a small amount of CH_2Cl_2 and poured in 150 ml diethyl ether. The yield of **12a** was 92.7 mg (88.0 µmol, 46%), orange-red solid, m.p. 161-163°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3600-3200, 3120, 3080, 1610, 1470, 1450, 1430, 850, 770, 740 cm^{-1}. - ^1H NMR (acetone-d_6, 400 MHz): δ = 7.13 (dd, 1 H, J=5.1 Hz, J=3.6 Hz), 7.31 (d, 1 H, J=3.8 Hz), 7.37 (dd, 1 H, J=3.6 Hz, J=1.1 Hz), 7.41 (d, 1 H, J=3.8 Hz), 7.51 (d, 1 H, J=4.0 Hz), 7.51 (dd, 1 H, J=5.1 Hz, J=1.1 Hz), 7.55-7.65 (m, 5 H), 7.74 (dd, 1 H, J=6.1 Hz, J=2.1 Hz), 7.98 (dd, 1 H, J=6.1 Hz, J=0.6 Hz), 8.07 (d, 1 H, J=4.0 Hz), 8.08-8.11 (m, 4 H), 8.21-8.28 (m, 6 H), 8.81-8.89 (m, 4 H), 9.06 (dd, 1 H, J=2.1 Hz, J=0.6 Hz), 9.09 (ddd, 1 H, J=8.5 Hz, J=1.3 Hz, J=0.9 Hz) ppm. - FAB-MS (nitrobenzyl alcohol matrix / CH_2Cl_2): 961.3 $[K^{2+} + PF_6^-]^+$, 816.3 $[K^{2+} + e^-]^+$, 408.3 $[K^{2+}]$. - UV/VIS (acetonitrile): 244 nm (32100 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.507), 288 (71500 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.855), 420 (32300 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.509), 470 (31700 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.501). - Fluorescence/ -lifetime (CH_2Cl_2, excitation: 488 nm): 597 nm (τ=412 ns). - $C_{42}H_{30}F_{12}N_6P_2RuS_3 \cdot H_2O$ (1054.0): calcd. C 47.87, H 3.06, N 7.97; found C 47.45, H 3.25, N 7.85.

Bis-([2,2']-bipyridine)Ru([2,2';4',4";2",2"']-quaterbipyridine)Ru(bis-([2,2']-bipyridine)) $(PF_6)_4$ (**12b**): A solution of $Pd(PPh_3)_4$ (25.0 mg, 28.1 µmol), bis-([2,2']-bipyridine)Ru(4-tributylstannyl-[2,2']-bipyridine)$(PF_6)_2$ (**6**) (140 mg, 122 µmol) and bis-([2,2']-bipyridine)Ru(4-bromo-[2,2']-bipyridine)$(PF_6)_2$ (**7**) (126 mg, 134 µmol) in 10 ml toluene and 10 ml acetonitrile was heated to reflux for 4 d. The solution was filtrated and the solvents were stripped off. After chromatographic purification on alumina (deactivated with 7% w/w water) with acetone : toluene 2:1 (v/v) the yield of **12b** was 82.6 mg (47.6 µmol, 41%), orange-red solid, m.p. 221-223°C. - IR (KBr): $\tilde{\nu}$ = 3600-3200, 3100, 3020, 1600,1590, 1450, 1430, 1390, 860, 750, 720 cm^{-1}. - ^1H NMR (acetone-d_6, 400 MHz): δ = 7.53-7.64 (m, 10 H), 8.00-8.12 (m, 4 H), 8.19-8.27 (m, 8 H), 8.82-8.86 (m, 14 H), 8.81-8.86 (m, 8 H), 9.01-9.08 (m, 2 H) ppm. - ESI-MS ($CH_3CN/H_2O/CH_3COOH$): 713 $[K^{2+} + 2PF_6^-]^{2+}$, 427 $[K^{4+} + PF_6^-]^{3+}$, 284 $[K^{4+}]$. - UV/VIS (acetonitrile): 246 nm (48000 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.681), 286 (104100 $l \cdot mol^{-1}cm^{-1}$, lg ε 5.017), 482 (24100 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.381). - Fluorescence/ -lifetime (CH_2Cl_2, excitation: 488 nm): 600 nm (τ=186 ns). - $C_{60}H_{46}F_{24}N_{12}P_4Ru_2 \cdot H_2O$ (1735.1): calcd. C 41.53, H 2.79, N 9.69; found C 41.91, H 2.88, N 9.85.

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