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<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p>	
Scheme1.cdx Figure1.cdx Figure 4.hgl	



Article

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The Combination of 4-Hydroxythiazoles with Azaheterocycles: Efficient bidentate Ligands for novel Ruthenium Complexes

R. Menzel^[a], E. Täuscher^[a], D. Weiß^{[a]*}, R. Beckert^{[a]*} and H. Görls^[b]

Dedicated to ... on the Occasion of ... ((optional))

Keywords: Thiazoles; Fluorescence; Ruthenium Complexes; Emission, Lifetime

We report here on the synthesis of three novel ligands in which an azaheterocycle is connected with a thiazole subunit: 4-methoxy-5-methyl-2-pyridine-2-yl-1,3-thiazole (**1**), 4-methoxy-5-methyl-2-pyrimidine-2-yl-1,3-thiazole (**2**) and 4-methoxy-5-phenyl-2-pyridine-2-yl-1,3-thiazole (**3**). Being cyclic versions of 1,4-diazadienes, they offer good prerequisites for the synthesis of metal complexes and have been employed as chelating ligands. Three novel heteroleptic cationic complexes of the type

$\text{Ru}(\text{bpy})_2(\text{L})$, with $\text{bpy} = 2,2'$ -bipyridine have been successfully synthesized. The Ru(II) complexes as well as the ligands were characterized by means of mass spectrometry, NMR, UV/Vis and IR spectroscopy and elemental analysis. Furthermore, an X-ray structure of $\text{Ru}(\text{bpy})_2\text{2}(\text{PF}_6)$, as far as we know the first example where a thiazole is directly connected to a Ru(II) core, is presented in this paper.

Introduction

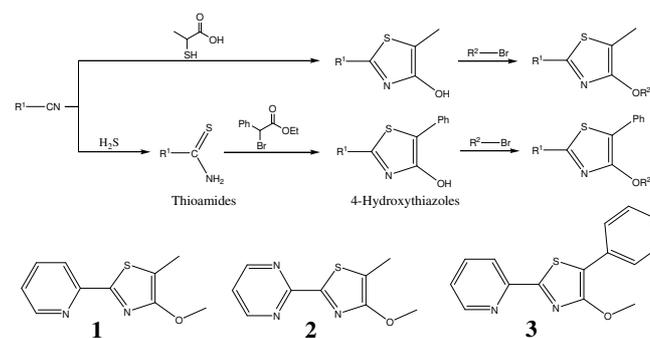
Ruthenium compounds, in particular Ru(II) polypyridine complexes, are one class of transition metal complexes showing outstanding photochemical properties and the development of novel Ru(II) complexes has undergone an impressive growth, especially in the last 15 years. Exhaustive reviews concerning Ru(II) polypyridine complexes have been published [1]. They play a central role in artificial photosynthesis, in particular, in the design of dye-sensitized solar cells (DSC's) [2]. Furthermore, they are used in supramolecular chemistry, organic light emitting diodes (OLED's), electroluminescent devices and as catalysts. A new increasingly important research field where Ru complexes are utilized is in the photoelectrochemical reduction of CO_2 to form a useful fuel [3]. A recently published paper, for example, describes an unexpected high activity of similar benzothiazole and bithiazole Ru(II) complexes for CO_2 reduction [4].

Because of their various capabilities, there still exists an immense interest in new Ru(II) complexes with distinct properties. The class of Ru(II) complexes containing a thiazole based ligand is absolute underrepresented and only a few examples are known [5].

Thiazoles connected to an aromatic heterocycle show interesting photophysical properties [6] and might act as light harvesting or bridging ligands in several transition metal complexes. In addition, due to the strong fluorescence of the thiazole ligands connected with the versatile hydroxy group, they might be employed as easily binding sensor molecules [7].

Results and Discussion

The 4-hydroxythiazoles which lead to ligand **1** and **2** have been prepared following a protocol established by our group [8]. The 4-hydroxythiazole of ligand **3** was synthesized using a slightly modified method. At first, a nitrile, here pyridine-2-carbonitrile, reacts with hydrogen sulfide forming the corresponding thioamide which was then cyclized with ethyl 2-bromophenylacetate to yield the 4-hydroxythiazole. Methyl iodide was chosen as the electrophile for a Williamson type etherification of the 4-hydroxythiazoles. Both methods and the structures of the ligands are depicted in Scheme 1



Scheme 1. General synthetic routes and structures of the three thiazole ligands obtained.

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The complexes were synthesized using the precursor *cis*-(bpy)₂RuCl₂, which was prepared by following a literature procedure [9]. The structures of the synthesized complexes are shown in Figure 1.

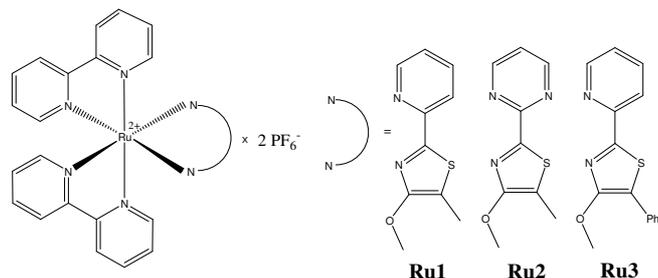


Figure 1. Structures of the Ru(bpy)₂(L)(PF₆)₂ complexes.

A standard synthesis with the precursor was not successful. The *cis*-(bpy)₂RuCl₂ must be transformed to the activated precursor *cis*-Ru(bpy)₂(acetone)₂PF₆ before being used. Therefore, *cis*-(bpy)₂RuCl₂ was stirred with AgPF₆ in dry and degassed acetone under an inert atmosphere [10]. The complexes were finally obtained by heating the activated precursor with an equimolar amount of ligand in acetone. Gel filtration was used to remove traces of ligand and silver impurities. The yield was moderate to good (53 - 68 %).

Electronic Properties

The ligands show various absorption bands in the UV/Vis-spectra with a molar extinction coefficient of over 70000 M⁻¹cm⁻¹ and hence are $\pi \rightarrow \pi^*$ and not $n \rightarrow \pi^*$ transitions. The absorption and emission spectra of the ligands are depicted in Figure 2. The shortest wave-length absorptions, at about 240 nm, correspond to the $\pi \rightarrow \pi^*$ transition based on the azaheterocyclic moiety. The second, thiazole based $\pi \rightarrow \pi^*$ transition is at 350 nm and is red-shifted (25 nm) for **3** to 375 nm, due to the additional aromatic phenyl ring lowering the energy gap between ground (S₀) and excited state (S₁). Additionally, a third absorption band at 273 nm can be observed for **3** which belongs to the $\pi \rightarrow \pi^*$ transition (*K*-band) based on the phenyl ring [11]. The thiazoles show strong blue room temperature fluorescence in solution (CH₂Cl₂). The λ_{max} of the emission is at 420 nm for **1** and **2**. For **3** the λ_{max} is red shifted (29 nm) to 448 nm, which is in accordance with the absorption spectra. Additionally, this indicates that the fluorescence arises basically from the S₁ state located at the thiazole moiety. The Stokes shift is comparatively large for these small molecules and can be assigned to a significant geometry change in the S₁ state [6]. The fluorescence quantum yields are high and almost unity for **3**. The fluorescence lifetimes are in the normal range and vary from 2 - 4 ns [6].

The absorption and emission spectra of the complexes, together Ru(bpy)₃²⁺ as a reference, are shown in Figure 3. All complexes show strong ligand centered (LC) absorptions of the bpy ligands at around 285 nm. The LC transitions of the coordinated thiazole ligands are also present in the complexes and are located at 352 nm, 332 nm and 368 nm for **Ru1**, **Ru2** and **Ru3**, respectively. The shoulders at 322 nm in **Ru1** and **Ru3** can be assigned to metal center MC transitions which are superimposed in **Ru2** with the intense thiazole-based LC transition. The bands at 240 and 450 nm

are metal to ligand (MLCT) transitions. The λ_{max} of the longest wave-length absorption is slightly red-shifted (4 nm) for **Ru1** and **Ru3** compared to Ru(bpy)₃²⁺. Due to the especially broad nature of the MLCT of **Ru2**, an exact assignment of the longest wave-length absorption is not possible (a shoulder is present at around 465 nm). The λ_{max} of the emission varies from 637 to 665 nm and is correlated to the electronic properties of the thiazole ligands. A strong π -acceptor such as pyrimidine lowers the π^*_L (LUMO) of the complex and therefore decreases the energy of the MLCT state. This leads to a bathochromic shift of the λ_{max} of the absorption (¹MLCT) and also the emission band (³MLCT) of the MLCT transitions. This can be observed for **Ru2** compared to **Ru1**. The higher π -acceptor strength of the pyrimidine heterocycle is also expressed in a higher oxidation potential of 0.85 V for **Ru1** compared to 0.81 V for **Ru2**. Additionally, a more extended π system, like in ligand **3**, lowers the energy of the π^*_L orbital (π^* -tuning). Therefore, the λ_{max} of the emission of **Ru3** is also red-shifted compared to **Ru1**. A second effect is a higher energy gap between the ³MLCT and the non-radiative ³MC state leading to a less probable population of the latter and, consequently, to an extended lifetime of the emitting state. This is in accordance with the measured values of **Ru3** compared to **Ru1**. The emission quantum yields obtained at room temperature are good and in the range of 2 % despite the use of aerated CH₂Cl₂ in which oxygen acts as a quencher. All values are summarized in Table 1.

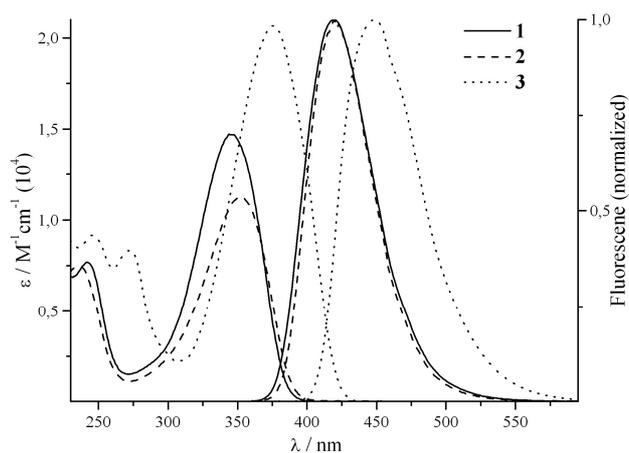


Figure 2. UV/Vis and fluorescence spectra of the ligands **1** to **3** measured in CH₂Cl₂ at room temperature.

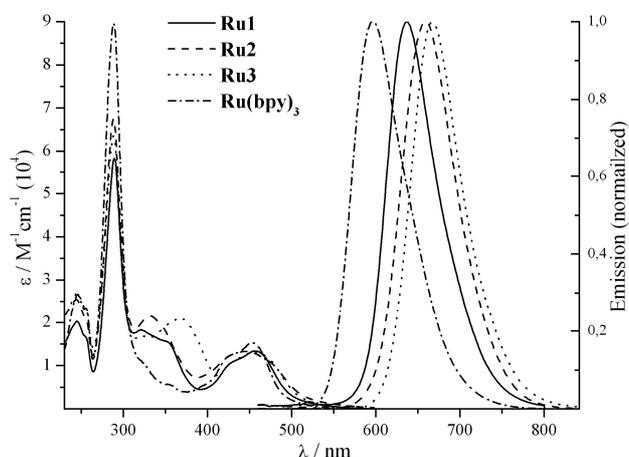


Figure 3. UV/Vis and emission spectra of **Ru1** to **Ru3** and Ru(bpy)₃²⁺, measured in CH₂Cl₂ at room temperature ($c \approx 1.5 \times 10^{-5}$ mol/L).

Table 1. Spectroscopic data of ligands **1-3** and the complexes **Ru1 - Ru3** and Ru(bpy)₃²⁺. All measurements were made in aerated CH₂Cl₂ at 298 K

Ligands	$\lambda_{\text{Abs}} / \text{nm} [\log \epsilon]$	$\lambda_{\text{Fl}} / \text{nm}^{[a]}$	Stokes-Shift / $\text{cm}^{-1}^{[b]}$	$\tau / \text{ns}^{[d]}$	Φ in %
1	241 [3.89], 344 [4.17]	419	5203	3.6	90
2	236 [3.87], 352 [4.05]	421	4656	2.8	60
3	246 [3.96], 273 [3.92], 376 [4.32]	448	4345	3.9	100
Complexes	$\lambda_{\text{Abs}} / \text{nm} [\log \epsilon]$	$\lambda_{\text{Em.}} / \text{nm}^{[c]}$		$\tau / \text{ns}^{[d]}$	Φ in %
Ru(bpy)₃	246 [4.43], 289 [4.95], 322 [4.04], 453 [4.19]	608		885 ^[e]	6.2 ^[e]
Ru1	244 [4.31], 288 [4.80], 321 [4.26], 457 [4.12]	637		378	2.0
Ru2	245 [4.40], 289 [4.83], 332 [4.33], 446 [4.12]	659		253	1.9
Ru3	246 [4.43], 289 [4.83], 368 [4.32], 457 [4.12]	667		412	2.0

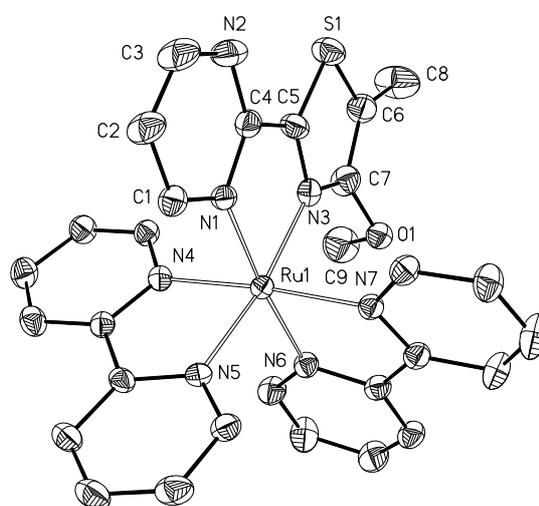
[a] excitation in the absorption maximum, [b] related to the maximum of the longest wave-length absorption, [c] excitation at $\lambda = 450 \text{ nm}$, [d] excitation at $\lambda = 435 \text{ nm}$, [e] value obtained from Ref. [12].

Crystal structure of Ru(bpy)₂(PF₆)₂

Single crystals suitable for X-ray structure analysis were obtained by slow ether diffusion in an acetonitrile solution of the corresponding complex **Ru2**. An ORTEP draw of the complex is shown in Figure 4. The complex **Ru2** crystallizes as red needles in the monoclinic space group $P2_1/c$. The methoxy group of the complex is slightly displaced, which does not effect the relevant information. The typical distorted octahedral coordination geometry of the complex forces the aromatic rings of the thiazole ligand into an almost coplanar orientation (torsion angles N1-C4-C5-N3 0.24°, N2-C4-C5-S1 1.29°). The Ru-N bond lengths and N-Ru-N bond angles for the bpy ligands are in the normal range (e.g. Ru1-N4 2.059(5) Å, Ru1-N5 2.047(5) Å) as reported for this type of Ru(II) complexes [13]. The Ru-N bond lengths from the thiazole ligand to the metal centre are elongated (Ru1-N1 2.078(5) Å, Ru1-N3 2.085(5) Å). This can be ascribed to a less π^* backbonding from the thiazole to the Ru(II), which has been observed for similar complexes like [Ru(bpy)₂(cept)]⁺ (cept = 3-(ethoxycarbonyl)-5-(pyrid-2'-yl)-1,2,4-triazolate) [14] and [Ru(bpy)₂TPZ]²⁺ (TPZ = 2-(1*H*-tetrazol-5-yl)pyrazine) [15]. The bond angle N1-Ru1-N3 of the bidentate thiazole to the Ru(II) core is slightly diminished (78.4(2)°) compared to the bond angle formed from the bpy ligands (e.g. N5-Ru1-N4 79.23(19)°). This can be explained with the elongated N1/N3-Ru1 bonds, leading to a diminished N1-Ru1-N3 bond angle. This effect also compensates for the influence of the smaller bond angle N3-C5-S1 (114.7(6)°) of the five-membered thiazole-ring, which normally should lead to an expand N1-Ru1-N3 bond angle.

Table 2. Selected bond lengths / Å and angles / ° of **Ru2**.

Bond lengths		Bond angles	
Ru1-N1	2.078(5)	N1-Ru1-N3	78.4(2)
Ru1-N3	2.085(5)	N1-Ru1-N4	88.12(88)
Ru1-N4	2.059(5)	N1-Ru1-N5	93.94(19)
Ru1-N5	2.047(5)	N1-Ru1-N7	96.46(18)
Ru1-N6	2.050(5)	N3-Ru1-N4	95.75(19)
Ru1-N7	2.054(5)	N3-Ru1-N6	98.7(2)
Torsion angles		N5-Ru1-N4	79.23(19)
N1-C4-C5-N3	0.24	N6-Ru1-N7	79.09(19)
N2-C4-C5-S1	1.29		

**Figure 4.** ORTEP drawing of **Ru2** showing the labeling scheme of selected atoms. Solvent molecules, hydrogen atoms and the anions PF₆⁻ are omitted for the sake of clarity. Ellipsoids are at a probability level of 30 %.

Conclusions

The presented results, which include the first time X-ray structure of a Ru(II) complex with a 4-hydroxythiazole derivative as a ligand, are promising in terms of the spectroscopic properties of the compounds. The versatile hydroxy group of the ligands allows the connection of the complexes with biological systems *via* an ester linkage, for example [8]. Together with the easily tunable room temperature emission they can be used as possible sensor molecules. This will be the subject of further research. Also, the application as possible catalysts for CO₂ reduction, with the sulfur as the reactive site (as reported already) will be investigated.

Experimental Section

¹H-, ¹³C-NMR and the corresponding correlation spectra were recorded on a Bruker AC-250 (250 MHz) and a Bruker AC-400 (400 MHz) spectrometer. Chemical shifts (δ) are

given relative to solvents and all coupling constants are given in Hz. Fluorescence spectra were measured on a *Jasco FP 6500*. UV/Vis data were collected on a *Lambda 19* from PERKIN-ELMER. Elemental analysis was carried out on a *Leco CHNS-932*. Mass spectra were measured either on a *Finnigan MAT SSQ 710* (EI) or *MAZ 95 XL* (FAB) system.

The quantum yield measurements were carried out on a *Hamamatsu C9920-02 QY* system. The home-made system consists of an integrated sphere which allows the measurement of absolute quantum yields of dilute solutions of the corresponding compounds. The emission lifetimes were obtained by time-correlated single photon counting (TCSPC) after excitation with a frequency-doubled Ti-sapphire laser (Tsunami, Newport Spectra-Physics GmbH) as the light source. Repetition rate was reduced to 0.4 MHz by a pulse selector (*Model 3980*, Newport Spectra-Physics GmbH). The laser beam was frequency doubled in a second harmonic generator (Newport Spectra-Physics GmbH) to create the 435 nm excitation beam. The emission was detected using a *PMC-100-4* photon-counting module from Becker & Hickel. A biexponential (to include the response function) fitting function was used to determine luminescence lifetimes.

The intensity data for X-ray structure analysis was collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects [16], [17]. The structure was solved by direct methods (SHELXS [18]) and refined by full-matrix least-squares techniques against Fo² (SHELXL-97 [18]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non hydrogen atoms were refined anisotropically [18]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Starting materials were commercially obtained from Aldrich and used as received. TLC was from Merck (Polygram SIL G/UV₂₅₄, aluminum oxide 60 F₂₅₄). The material for Column chromatography was also obtained from Merck (Silica gel 60 or Merck aluminum oxide 90 active or neutral; activity stage 1 till 15 with 15 m% water).

4-Methoxy-5-methyl-2-pyridine-2-yl-1,3-thiazole (1): A mixture of 1.43 g (7.45 mmol) of 5-methyl-2-pyridine-2-yl-1,3-thiazole-4-ol and 0.48 g (8.63 mmol) K₂CO₃ were dissolved in 15 mL of DMSO and stirred for 20 min at RT. The colour of the solution turned deep red and 1.18 g (8.32 mmol) methyl iodide was added. After the reaction was finished (TLC), water was added and a yellow precipitate was formed. The mixture was filtered, the residue was washed with water and dried *in vacuo*. Purification by column chromatography (silica, EtOAc/heptane 1:1) yielded 1.3 g of the product as a pale yellow solid (yield: 85 %). ¹H-NMR (250 MHz, CDCl₃): δ = 2.32 (s, 3H), 4.05 (s, 3H), 7.24 (ddd, J₁ = 7.6, J₂ = 4.9, J₃ = 1.0, 1H), 7.73 (ddd, J₁ = 7.8, J₂ = 7.8, J₃ = 1.7, 1H), 8.06 (dd, J₁ = 8.0, J₂ = 1.0, 1H), 8.54 (dd, J₁ = 4.8, J₂ = 1.6, 1H); ¹³C-NMR (250 MHz, CDCl₃): δ = 9.5, 57.7, 109.6, 118.7, 123.7, 136.8, 149.3, 151.6, 159.5, 160.7; MS (EI): *m/z* (%) = 206 (70), 105 (100); EA C₁₀H₁₀N₂OS (206.26 g/mol): C 58.23 (calc. 58.29), H 4.89 (5.03), N 13.58 (13.41), S 15.55 (15.63)%; UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ) = 242 nm (3.88), 344 nm (4.12); m.p.: 45.1 °C.

4-Methoxy-5-methyl-2-pyrimidine-2-yl-1,3-thiazole (2): A mixture of 0.16 g (0.77 mmol) 5-methyl-2-pyrimidine-2-yl-1,3-thiazole-4-ol and 134 mg (0.97 mmol) K₂CO₃ were suspended in 10 mL of DMF. After 30 min, the colour of the solution turned deep red and 109 mg (0.77 mmol) methyl iodide dissolved in 5 mL of DMF was added over a period of 30 min. The mixture was stirred for 24 h. After removal of the solvent *in vacuo*, the crude product was purified by column chromatography (silica, CH₂Cl₂) yielding 90 mg of a brown solid. Recrystallization from an MeOH/H₂O (50:50, v/v) mixture afforded the product as light tan needles (yield: 55 %). ¹H-NMR (250 MHz, CDCl₃): δ = 2.34 (s, 3H), 4.12 (s, 3H), 7.20 (t, J = 4.9, 1H), 8.77 (d, J = 4.9, 2H); ¹³C-NMR (250 MHz, CDCl₃): δ = 9.53, 58.0, 112.5, 119.9, 157.0, 157.6, 159.6, 161.9; MS (EI): *m/z* (%) = 207 (70), 105 (100); EA C₉H₉N₃OS (207.25 g/mol) C 52.16 (calc. 52.33), H 4.38 (4.53), N 20.27 (20.11), S 15.44 (15.44)%; UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ) = 236 nm (3.87), 352 nm (4.05); m.p.: 61 °C.

General procedure for the formation of thioamides: The nitrile (0.1 mol) was dissolved in 200 mL of ethanol and triethylamine (0.05 mol) was added. Then hydrogen sulfide was passed through the solution until no more gas was consumed. After 1 hour the mixture was filtered and the crude material was recrystallized from EtOH. The compound 2-pyridinethioamide was identical with a sample obtained from Aldrich (m.p.: 138 °C (lit: 137 °C, EtOH)).

5-Phenyl-2-(pyridin-2-yl)-1,3-thiazol-4-ol: A mixture of 13.9 g (0.1 mol) 2-pyrimidinethioamide, 24.3 g (0.1 mol) ethyl 2-bromophenylacetate and 2.4 g (30 mmol) pyridine was stirred under an argon atmosphere at 100-110 °C. After the mixture has solidified, ethanol was added (20 mL) and the stirring was continued at room temperature for 30 min. After filtration, the crude product was recrystallized from EtOH yielding 18.3 g of the 4-hydroxythiazole as a yellow crystalline compound (yield: 72 %). ¹H-NMR (250 MHz, DMSO-d₆): δ = 7.25 (d, J = 7.3, 2H), 7.48 (m, 3H), 7.77 (d, J = 7.3, 2H), 8.00 (m, 2H), 8.61 (d, J = 1.3, 1H), 11.60 (s, 1H); ¹³C-NMR (250 MHz, DMSO-d₆): δ = 110.8, 116.8, 125.4, 126.6, 126.8, 129.3, 132.3, 138.2, 150.2, 150.6, 159.1, 160.9; EA C₁₄H₁₀N₂OS (254.31 g/mol): C 66.12 (calc. 66.10), H 3.96 (4.13), N 11.02 (10.95), S 12.61 (12.75)%; m.p.: 236.3 °C.

4-Methoxy-5-phenyl-2-pyridine-2-yl-1,3-thiazole (3): 2.54 g (10 mmol) of the 5-phenyl-2-(pyridin-2-yl)-1,3-thiazol-4-ol was dissolved in 50 mL of DMSO and the mixture was stirred for 30 min. 3.54 g (90 mmol) NaOH dissolved in 20 mL of H₂O were added and the solution was stirred again for 5 min. 1.7 g (12 mmol) methyl iodide was then added to the red solution. After the reaction was finished (TLC), water was added until a precipitate appeared. The mixture was filtered and the crude product was recrystallized from EtOH/CHCl₃ yielding 1.9 g of a yellow compound (Yield: 71 %). ¹H-NMR (400 MHz, CDCl₃): δ = 4.2 (s, 3H), 7.23 - 7.32 (m, 2H), 7.38 - 7.43 (m, 2H), 7.76 - 7.82 (m, 3H), 8.14 (dd, J₁ = 8.0, J₂ = 1.0, 1H), 8.61 (dd, J₁ = 4.9, J₂ = 1.7, 1H); ¹³C-NMR (400 MHz, CDCl₃): δ = 57.6, 114.4, 118.9, 124.0, 126.7, 126.9, 128.7, 131.6, 136.9, 149.3, 151.2, 159.7, 160.2; MS (EI): *m/z* (%) = 268 (60 %), 121 (100 %); EA C₁₅H₁₂N₂OS (268.33 g/mol): C 67.14 (calc. 67.01), H 4.51 (4.49), N 10.44 (10.39), S 11.95 (11.81); UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ) = 246 nm (3.96), 273 nm (3.92), 376 [4.32]; m.p.: 213 °C decomp.

General procedure for the synthesis of the complexes; example for $[Ru(bpy)_2(1)](PF_6)_2$ (**Ru1**):

The activated precursor *cis*-Ru(bpy)₂(acetone)₂PF₆ was synthesized by stirring 180 mg (0.37 mmol) of *cis*-(bpy)₂RuCl₂ and 187 mg (0.74 mmol) AgPF₆ in 10 mL of degassed and dried acetone for 6 h at RT under an argon atmosphere. The suspension was filtered inert to remove the developed AgCl. 76 mg (0.37 mmol) of **1** dissolved in 5 mL of acetone were added to the solution and the mixture was refluxed for 24 h. Subsequently, the reaction mixture was allowed to cool down to RT and the solvent was removed *in vacuo*. The crude product was purified by gel filtration (Al₂O₃, basic, 15, acetone/toluene 1:1) to remove additionally developed AgCl and traces of the ligand. After evaporation of the solvents, the solid was dissolved in a small amount of CH₂Cl₂ and precipitated with diethyl ether to yield 169 mg of the complex as a bright orange powder (yield: 50 %). ¹H-NMR (400 MHz, CD₃CN): δ = 2.42 (s, 3H), 3.18 (s, 3H), 7.3 - 7.4 (m, 2H), 7.4 (ddd, J₁ = 7.2, J₂ = 5.7, J₃ = 1.1, 1H), 7.45 (ddd, J₁ = 7.2, J₂ = 5.7, J₃ = 1.1, 1H), 7.55 (ddd, J₁ = 7.2, J₂ = 5.7, J₃ = 1.1, 1H), 7.61 (d, J = 5.5, 1H), 7.67 (d, J = 5.4, 1H), 7.76 (t, J₁ = 5.2, 2H), 7.9 - 8.01 (m, 3H), 8.02 - 8.11 (m, 3H), 8.18 (d, J = 8.0, 1H), 8.4 - 8.6 (m, 4 H); ¹³C-NMR (400 MHz, CD₃CN): δ = 10.4, 61.6, 120.2, 123.2, 123.4, 123.8, 124.28, 124.32, 126.7, 127.0, 127.6, 127.7, 127.8, 137.4, 137.8, 137.81, 138.0, 151.8, 152.06, 152.1, 152.5, 153.5, 157.0, 157.1, 157.46, 157.51, 162.1; MS (FAB): *m/z* (fragment) = 765 (Ru(bpy)₂L x PF₆⁻), 620 (Ru(bpy)₂L); EA C₃₀H₂₆F₁₂N₆OP₂RuS (909.63): C 39.61 (calc. 39.82), H 2.88 (2.93), N 9.24 (9.08), S 3.53 (3.47)%; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 244 nm (4.31), 288 nm (4.80), 321 nm (4.26), 352 nm (4.19), 457 nm (4.12); IR (ATR): ν̄ = 3095 (w), 2987 (w), 1605 (m), 1547 (m), 1474 (m), 1447 (m), 1316 (m), 1267 (w), 1242 (w), 1162 (m), 1139 (w), 1034 (w), 1003 (m), 880 (m), 833 (vs), 760 (s), 730 (s) cm⁻¹; m.p.: 290 °C decomp.

$[Ru(bpy)_2(2)](PF_6)_2$ (**Ru2**): This complex was prepared from 140 mg (0.29 mmol) of *cis*-(bpy)₂RuCl₂ with 146 mg (0.58 mmol) AgPF₆ and 60 mg (0.29 mmol) of **2** to afford 140 mg of the product as an orange-red powder (yield: 53 %). ¹H-NMR (400 MHz, CD₃CN): δ = 2.44 (s, 3H), 3.19 (s, 3H), 7.30 - 7.40 (m, 3H), 7.48 (ddd, J₁ = 1.3, J₂ = 5.6, J₃ = 7.5, 1H), 7.54 (ddd, J₁ = 1.3, J₂ = 5.7, J₃ = 7.5, 1H), 7.66 (dd, J₁ = 1.2, J₂ = 5.3, 1H), 7.74 (dd, J₁ = 1.1, J₂ = 5.5, 1H), 7.86 (dd, J₁ = 5.8, J₂ = 2.0, 1H), 7.93 (dd, J₁ = 1.2, J₂ = 5.5, 1H), 7.98 - 8.10 (m, 3H), 8.08 - 8.14 (m, 2H), 8.46 - 8.54 (m, 4 H), 8.86 (dd, J₁ = 4.8, J₂ = 2.0, 1H); ¹³C-NMR (400 MHz, CD₃CN): δ = 11.58, 62.61, 118.22, 123.06, 124.44, 124.78, 124.83, 125.33, 125.37, 127.70, 128.58, 128.66, 128.98, 138.53, 138.99, 153.01, 153.02, 153.48, 153.77, 156.44, 157.90, 158.28, 158.46, 158.49, 158.59, 160.39, 163.72, 163.84; MS (FAB): *m/z* (fragment) = 766 (Ru(bpy)₂L x PF₆⁻); EA C₂₉H₂₅F₁₂N₇OP₂RuS (910.62): C 38.25 (calc. 38.56), H 2.77 (3.08), N 10.77 (10.82), S 3.52 (3.73)%; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 245 nm (4.40), 289 nm (4.83), 332 nm (4.33), 446 nm (4.12); IR (ATR): ν̄ = 3095 (w), 2987 (w), 1605 (m), 1571 (w), 1543 (m), 1474 (s), 1447 (m), 1424 (m), 1335 (m), 1316 (m), 1274 (w), 1243 (w), 1165 (w), 1139 (w), 1049 (w), 1002 (w), 880 (m), 823 (vs), 760 (s), 729 (s) cm⁻¹; m.p.: 255 °C decomp.

Crystal Data for **Ru2** [19]: [C₂₉H₂₅N₇ORuS]²⁺ 2[PF₆]⁻, 0.5 C₂H₈O₂, 0.5 C₂H₃N, Mr = 963.20 g mol⁻¹, red-brown prism, size 0.05 x 0.05 x 0.05 mm³, monoclinic, space group *P* 2₁/c,

a = 12.4229(3), *b* = 25.9841(5), *c* = 13.5263(3) Å, β = 117.081(2)°, *V* = 3887.56(15) Å³, *T* = -90 °C, *Z* = 4, ρ_{calcd.} = 1.646 g cm⁻³, μ_{Mo-Kα} = 6.38 cm⁻¹, *F*(000) = 1932, 27450 reflections in *h*(-14/16), *k*(-33/33), *l*(-17/17), measured in the range 2.90° ≤ θ ≤ 27.49°, completeness θ_{max} = 99%, 8835 independent reflections, *R*_{int} = 0.0535, 5982 reflections with *F*_o > 4σ(*F*_o), 496 parameters, 0 restraints, *R*_{1obs} = 0.0773, *wR*_{2obs} = 0.2025, *R*_{1all} = 0.1168, *wR*_{2all} = 0.2262, GOOF = 1.050, largest difference peak and hole: 1.341 / -0.754 e Å⁻³.

$[Ru(bpy)_2(3)](PF_6)_2$ (**Ru3**): This complex was prepared from 140 mg (0.29 mmol) of *cis*-(bpy)₂RuCl₂ with 146 mg (0.58 mmol) AgPF₆ and 75 mg (0.28 mmol) of **3** to afford 138 mg of the product as an orange powder (yield: 68 %). ¹H-NMR (400 MHz, CD₃CN): δ = 2.96 (s, 3H), 7.32 - 7.42 (m, 3H), 7.44 - 7.59 (m, 7 H), 7.67 (t, J₁ = 4.8, 2H), 7.80 (dd, J₁ = 9.3, J₂ = 5.4, 2H), 7.95 - 8.15 (m, 6 H), 8.26 (d, J = 8.0, 1H); ¹³C-NMR (400 MHz, CD₃CN): δ = 62.4, 124.42, 124.47, 124.68, 124.91, 125.35, 125.39, 127.7, 128.45, 128.70, 128.74, 128.89, 128.98, 129.22, 130.43, 130.89, 138.45, 138.89, 138.92, 139.11, 152.84, 153.07, 153.13, 153.25, 153.74, 154.34, 158.05, 158.49, 158.56, 159.37, 162.0; MS (FAB): *m/z* (fragment) = 827 (Ru(bpy)₂L x PF₆⁻), 682 (Ru(bpy)₂L); MS (micro-ESI): exact molecular mass C₃₅H₂₈N₆OSRuPF₆ for ⁹⁶Ru = 821.0763, found 821.0764; EA C₃₅H₂₈F₁₂N₆OP₂RuS (971.70): C 43.26 (calc. 42.82), H 2.90 (3.39), N 8.65 (8.38), S 3.30 (2.97)%; UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 246 nm (4.43), 289 nm (4.83), 368 nm (4.32), 457 nm (4.12); IR (ATR): ν̄ = 3095 (w), 3025 (w), 1628 (w), 1620 (m), 1574 (w), 1540 (m), 1470 (m), 1447 (m), 1428 (w), 1402 (w), 1332 (w), 1316 (m), 1267 (w), 1242 (w), 1162 (m), 1127 (w), 1070 (w), 1030 (w), 1003 (m), 972 (w), 945 (w), 880 (m), 830 (vs), 764 (s), 730 (s), 700 (s) cm⁻¹; m.p.: 190 °C, CH₃CN/diethylether.

Acknowledgments

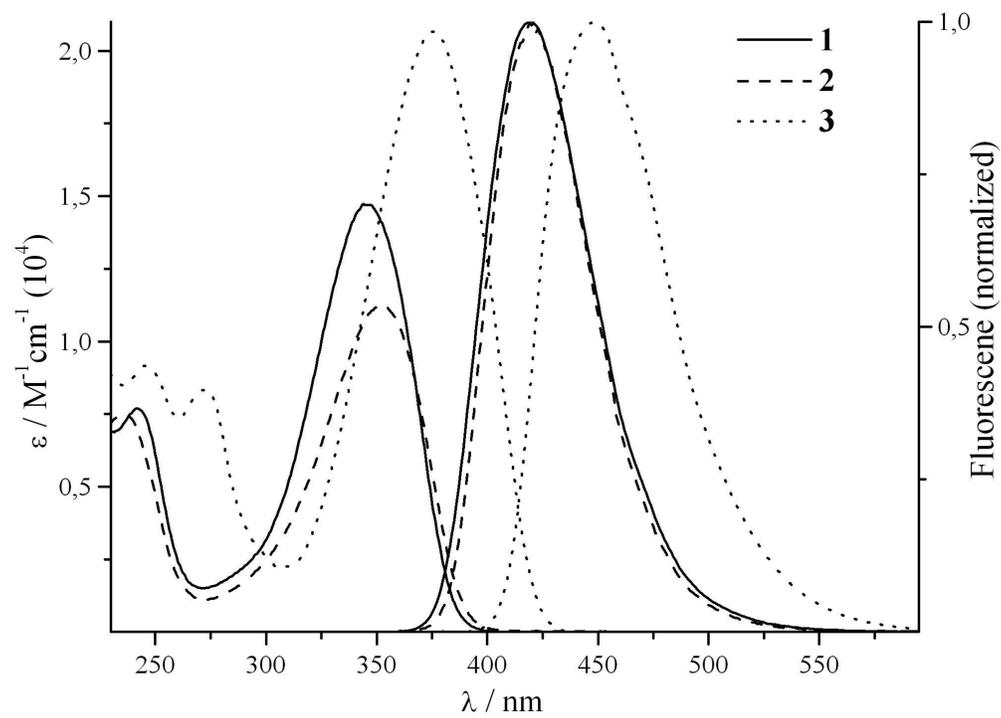
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- [1] S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, V. Balzani, *Top. Curr. Chem.*, **2007**, *280*, 117-214; b) V. Balzani, G. Bergamini, S. Campagna, F. Puntoriero, *Top. Curr. Chem.*, **2007**, *280*, 1-36; c) L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, *Top. Curr. Chem.*, **2007**, *281*, 143-203; d) V. Balzani, A. Juris, *Coord. Chem. Rev.*, **2001**, *211*, 97-115; e) V. Balzani, A. Juris, M. Venturi, *Chem. Rev.*, **1996**, *96*, 759-833; f) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.*, **1988**, *84*, 85-277.
- [2] G. J. Meyer, *Inorg. Chem.*, **2005**, *44*, 6852-6864; b) A. Hagefeld, M. Grätzel, *Acc. Chem. Res.*, **2000**, *33*, 269; c) M. Grätzel, *Inorg. Chem.*, **2005**, *44*, 6841-6851.
- [3] R. P. S. Chaplin, A. A. Wragg, *J. Appl. Electrochem.*, **2003**, *33*, 1107; b) K. Tanaka, D. Ooyama, *Coord. Chem. Rev.*, **2002**, *226*, 211.
- [4] A. Begum, P. G. Pickup, *Electrochem. Commun.*, **2007**, *9*, 2525-2528.

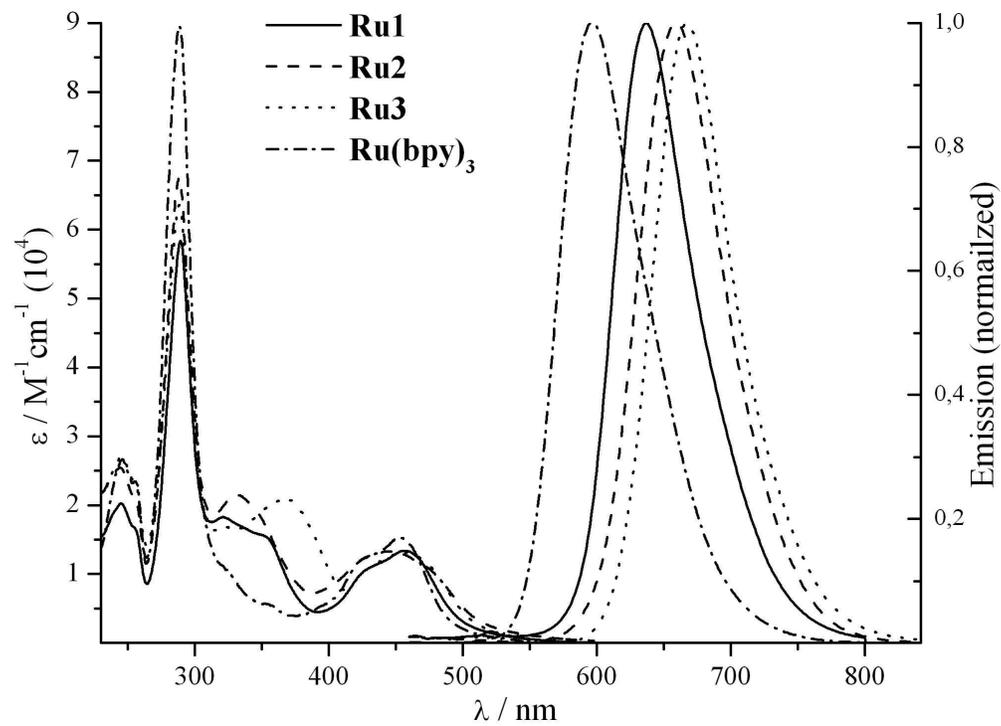
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- [5] B. J. MacLean, P. G. Pickup, *J. Mater. Chem.* **2001**, *11*, 1357-1363; b) G. Orellana, A. M. Braun, *J. Photochemistry and Photobiology A: Chemistry*, **1989**, *48*, 277-289
- [6] U.-W. Grummt, D. Weiß, E. Birckner, R. Beckert, *J. Phys. Chem. A.*, **2007**, *111*, 1104-1110.
- [7] C. D. Geddes, J. R. Lakowitz in *Reviews in Fluorescence*, Kluwer Academics/Plenum Publishers, New York, **2004**, vol.1, pp. 137-149.
- [8] D. Weiss, S. Trupp, L. F. M. L. Ciscato, R. Beckert, E. Anders, *Journal of Sulfur Chemistry*, **2009**, *30*, 109-118.
- [9] B. P. Sullivan, D. J. Salmon, T. J. Meyer, *Inorg. Chem.*, **1978**, *17*, 3334.
- [10] D. N. Leea, J. K. Kima, H. S. Parka, Y. M. Juna, R. Y. Hwangb, W.-Y. Leeb, B. H. Kim, *Synthetic Metals*, **2005**, *150*, 93-100.
- [11] J. Popp, M. Reichenbaecher in *Strukturanalytik organischer und anorganischer Verbindungen*, B. G. Teubner Verlag, Wiesbaden, **2007**, vol.1, p. 136.
- [12] W. Zhang, J.-H. Liu, J.-X. Pan, P. Li, L.-C. Sun, *Polyhedron*, **2008**, *27*, 1173
- [13] D. P. Rillema, T. G. Taghdiri, D. S. Jones, C. D. Keller, L. A. Worl, T. J. Meyer, H. A. Levy, *Inorg. Chem.*, **1987**, *26*, 578.
- [14] B. Mehmetaj, J. G. Haasnoot, L. De Cola, G. A. van Albada, T. Mutikainen, U. Turpeinen, J. Reedijk, *Eur. J. Inorg. Chem.*, **2002**, *7*, 1765-1771.
- [15] S. Stagni, E. Orselli, A. Palazzi, L. De Cola, S. Zacchini, C. Femoni, M. Marcaccio, F. Paolucci, S. Zandarini, *Inorg. Chem.*, **2007**, *46*, 9126-9138.
- [16] COLLECT, Data Collection Software; Nonius B.V., Netherlands, **1998**.
- [17] Z. Otwinowski & W. Minor, „Processing of X-Ray Diffraction Data Collected in Oscillation Mode“, in *Methods in Enzymology*, Macromolecular Crystallography, Part A, edited by C.W. Carter & R.M. Sweet, Academic Press, San Diego, **1997**, vol. 276, pp. 307-326.
- [18] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A*, **1990**, *46*, 467-473; b) G. M. Sheldrick “SHELX-97”, University of Göttingen, Germany, **1997**.
- [19] CCDC-753509 (**Ru2**) and CCDC-752318 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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UV/Vis and fluorescence spectra of the ligands 1 to 3 measured in CH₂Cl₂ at room temperature
84x61mm (600 x 600 DPI)



UV/Vis and emission spectra of Ru1 to Ru3 and Ru(bipy)3 measured in CH₂Cl₂ at room temperature
84x62mm (600 x 600 DPI)