DOI: 10.1002/ejic.200600469

Synthesis of New Phenanthroline-Based Heteroditopic Ligands – Highly Efficient and Selective Fluorescence Sensors for Copper(II) Ions

Peter Comba,*[a] Roland Krämer,[a] Andriy Mokhir,[a] Kyaw Naing,[a] and Erik Schatz[a]

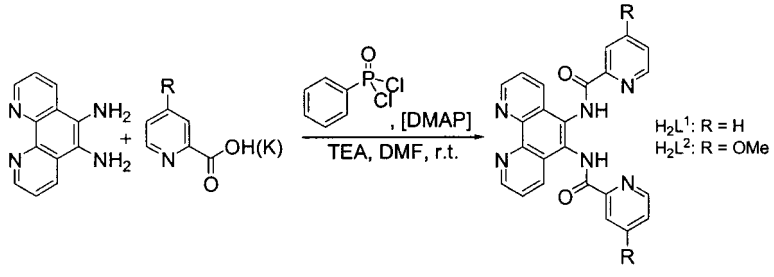
Keywords: Sensor / Fluorescence / Copper(II) / Selectivity / Ruthenium

The heteroditopic phenanthroline derivatives 5,6-bis(2-pyridylcarboxamido)-1,10-phenanthroline (H_2L^1) and 5,6-bis[(4-methoxy-2-pyridyl)carboxamido]-1,10-phenanthroline (H_2L^2) have been prepared and characterized, together with their luminescent ruthenium(II) complexes $[Ru(bpy)_2(H_2L^{1,2})](PF_6)_2$ and $[Ru(H_2L^1)_3](PF_6)_2$ and the corresponding iron(II) complex $[Fe(H_2L^1)_3](PF_6)_2$. In these complexes, the metal ion is coordinated by the bidentate phen site of H_2L. The luminescence of the ruthenium complexes (λ_{ex} = 450 nm, λ_{em} ca. 620 nm) is completely quenched by Cu^{2+} ions in the micromolar concentration range and, to a lesser extent, by other metal ions. At pH 5, the response of the luminescent sensors is highly Cu^{2+}-selective. Heterodinuclear complexes $[Ru(bpy)_2(LM)](PF_6)_2$, $[Ru(LM)_3](PF_6)_2$, and $[Fe(LM)_3](PF_6)_2$ have been isolated for M = Cu^{2+}, Ni^{2+}, Co^{2+}, and Pd^{2+}. It is suggested that M is coordinated to the tetradentate N4 site of L by two deprotonated amide N atoms and two pyridyl groups. This coordination type is confirmed by the EPR spectrum of the compound $[Ru^{II}(bpy)_2(L^1Cu^{II})](PF_6)_2$.

Introduction

For many good reasons di- and oligonuclear transition-metal complexes are attracting much interest. Cooperativity in general and, more specifically, electron and energy transfer as well as magnetic interactions have been recognized as important and rather general features in biological systems,[1,2] and there is an increasing range of applications in areas such as catalysis,[3,4] analytical chemistry (metal-ion- and anion-selective sensors),[5,6] and information technology (switches).[7] Most of these applications imply that the two metal centers in a dinuclear complex have different functions and, therefore, different properties. Synthetically, the required ligand asymmetry is often a demanding task.[8] An attractive approach is to couple a photoactive coordination site covalently to a ligand, which selectively coordinates another metal ion or has a second coordination center that selectively binds anions or activates substrates. Tris(bipyridine)ruthenium(II)-derived systems have been used frequently in this area,[9,10] and metal-ion- and anion-selective sensors,[10–16] photocatalysts,[12–14] and photoactive pharmaceuticals[15,16] have been reported.

Generally, the synthesis of this type of system relies on a suitable ditopic ligand with a multidentate or macrocyclic donor set, coupled to 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy). We report here on the synthesis of the two heteroditopic ligands H_2L^1 and H_2L^2 (Scheme 1) based on 5,6-diamino-1,10-phenanthroline and the synthesis of the corresponding ruthenium(II) complexes ($[Ru(bpy)_2(H_2L^{1,2})]^{2+}$ and $[Ru(H_2L^1)_3]^{2+}$) and their hetero-oligonuclear transition-metal complexes ($[Ru(bpy)_2\{(L^{1,2})M\}]^{2+}$ and $[Ru\{(L^1)M\}_3]^{2+}$, M = divalent transition-metal ion, e.g. Cu^{2+}). Of specific interest are the strong and selective coordination of first-row transition-metal ions to the coordina-



Scheme 1.

[a] Universität Heidelberg, Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: +49-6221-54-66-17
E-mail: peter.comba@aci.uni-heidelberg.de

tion site offered by L^1 and L^2 and the quenching of the fluorescence of the tris(bipyridine-type)ruthenium(II) site by this selective coordination event.

Results and Discussion

Syntheses and Characterization

The heteroditopic ligands H_2L^1 and H_2L^2 are prepared in respectable yields from 5,6-diamino-1,10-phenanthroline[17–19] (obtained in high yield by the reduction of 1,10-phenanthroline-5,6-dione dioxime with sodium dithionite[20] or formamidinesulfinic acid[21]) and picolinic acid or its methoxy derivative, respectively (Scheme 1). Because of solubility problems, air sensitivity, and poor reactivity of the amine groups, the acylation is performed under inert conditions in DMF, with DMAP[22] as the acylation catalyst, phenylphosphonic acid dichloride[23–26] as the activation reagent for the carboxylic group, and TEA as base. The Ru^{2+} complexes $[Ru(bpy)_2(H_2L^{1,2})]^{2+}$ and $[Ru(H_2L^1)_3]^{2+}$ are obtained by the usual methods and in high yields.[10] Low-spin Fe^{2+} complexes have also been obtained but are not discussed here in detail. The red mononuclear Ru^{2+} complexes have the characteristic MLCT transitions at around 450 nm, they show resonances in the ^1H NMR spectra for the amide protons at around 10.5 ppm and have the expected vibrations for amide bonds in the infrared spectra at approximately 1680 and 1570 cm^{-1}, as well as the amide N–H transitions at approximately 3300 cm^{-1}. Upon coordination of metal ions to the L^1 (L^2) sites, the N–H vibration disappears, the amide transitions shift to a lower energy (ca. 30–50 cm^{-1}), and the MLCT transitions are shifted to a higher energy.

The EPR spectra of the mono- and tris-Cu^{II} complexes are similar to each other and typical for tetragonal Cu^{II} sites, with g and A values ($g_\parallel = 2.213$, $A_\parallel = 180 \times 10^{-4}$ cm^{-1}) that are typical for tetrahedrally distorted coordination sites.[9] The similarity of the EPR spectra indicates that there is no $Cu^{II}\cdots Cu^{II}$ magnetic exchange interaction and only a very weak, i.e. negligible, dipolar coupling interaction (Figure 1b). A model of the structure (Figure 1a), obtained by force field calculations,[27,28] visualizes the Cu^{II} planes that are distorted because of the α-H atoms of the pyridine donors and indicates a distance of ca. 13 Å between the Cu^{II} centers.

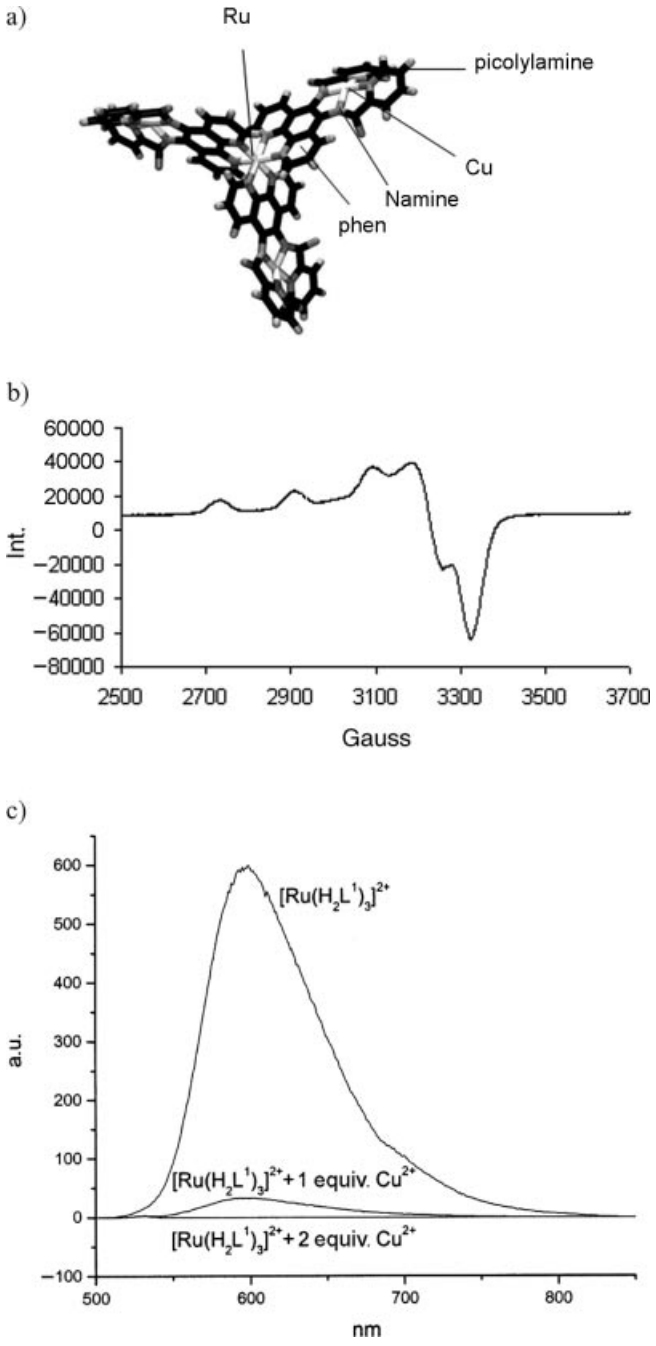


Figure 1. (a) Structural model of $[Ru\{(L^1)Cu\}_3]^{2+}$; (b) X-band EPR spectrum of $[Ru\{\mu\text{-}(L^1)Cu\}_3](PF_6)_2$ (ca. 10^{-3} M, DMF-H_2O-glass (2:1), 110 K); and (c) relative fluorescence intensities (λ_{ex} = 450 nm, λ_{em} = 620 nm) in aqueous solution at pH 7 (lutidine buffer) of $[Ru(H_2L^1)_3](PF_6)_2$ alone (10 μM), and after addition of 1 or 2 equiv. $CuSO_4$.

Fluorescence Measurements

The luminescence spectra of $[Ru(bpy)_2(H_2L^1)]^{2+}$, $[Ru(bpy)_2(H_2L^2)]^{2+}$, and $[Ru(H_2L^1)_3]^{2+}$ are as expected for Ru^{2+} polypyridine chromophores (transition at ca. 620 nm,[13] see Figure 1c); also shown in Figure 1c is the efficient fluorescence quenching of $[Ru(H_2L^1)_3]^{2+}$ with Cu^{2+} ($[Ru^{2+}]/[Cu^{2+}]$ = 1:0, 1:1, 1:2). Similar effects are observed with $[Ru(bpy)_2(H_2L^1)]^{2+}$ and $[Ru(bpy)_2(H_2L^2)]^{2+}$, i.e. these complexes are, as expected, good on/off sensors for metal ions, specifically for Cu^{2+} and Ni^{2+}, which have electronic transitions at similar energies and are known to strongly bind to amide donors already at physiological pH.[10,29]

To fully characterize the L^1- and L^2-based Cu^{2+} sensors, the luminescence intensities (aqueous solutions, $[Ru^{2+}] = 10^{-5}$ M) were studied as a function of pH, buffer base, anion, and M^{n+} concentration (M = Cu^{2+}, Ni^{2+}, Co^{2+}, $Fe^{2+/3+}$, Zn^{2+}, Al^{3+}, Nd^{3+}, Mn^{2+}, Pb^{2+}, alkali, and alkaline earth

metal ions; see Table 1 for an overview of the most relevant results.). Buffer bases such as acetate, citrate, carbonate, phosphate, and lutidine as well as EDTA do not quench the fluorescence. Aminoalkylsufonates (e.g., MOPS, MES) lead to an approximately 50% reduction of the luminescence intensity, i.e., these are not suited as buffer bases in our systems. Usual inorganic anions or carboxylates do not affect the fluorescence intensity (see Table 1 and above). In addition, Al^{3+}, Nd^{3+}, Mn^{2+}, Pb^{2+}, and group 1 and 2 cations do not alter the luminescence spectra. Interestingly, protonation of the pyridine donors and deprotonation of an amide site lead to drastic changes in the luminescence properties (Figure 2). This is in contrast to other $Ru(bpy)_2$-amide sensors,[10] which have pH-independent luminescence intensities over a pH range of 2–12. This indicates that the published and present systems probably differ with respect to the mechanism of quenching of the excited state [electron (PET) vs. energy transfer (EET)].[12]

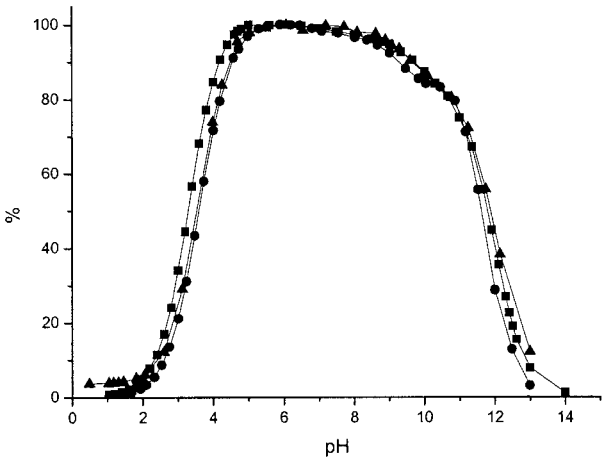


Figure 2. pH-dependence of the relative fluorescence intensity of 10 μM aqueous solutions of the complexes (λ_{ex} = 450 nm, λ_{em} = 620 nm) $[Ru(bpy)_2(H_2L^1)]^{2+}$ (■), $[Ru(H_2L^1)_3]^{2+}$ (▲), and $[Ru(bpy)_2(H_2L^2)]^{2+}$ (●).

Table 1. Reduction of the fluorescence intensity (in %) of $[Ru(bpy)_2(H_2L^1)]^{2+}$ as a function of added metal ions and pH.

Added metal ion	pH	% Reduction of fluorescence intensity of $[Ru(bpy)_2(H_2L^1)]^{2+}$
1 equiv. Cu^{2+}	5	99
2 equiv. Cu^{2+}	5	99
10 equiv. Co^{2+}	5	2
10 equiv. Fe^{2+}	5	1
1 equiv. Ni^{2+}	5	0
10 equiv. Ni^{2+}	5	5
10 equiv. Zn^{2+}	5	1
10 equiv. Fe^{2+} + 1 equiv. Cu^{2+}	5	98
100 equiv. Ni^{2+} + 1 equiv. Cu^{2+}	5	99
10 equiv. Zn^{2+} + 1 equiv. Cu^{2+}	5	99
1 equiv. Cu^{2+}	7	98
1 equiv. Co^{2+}	7	70
10 equiv. Co^{2+}	7	90
10 equiv. Fe^{2+}	7	80
10 equiv. Mn^{2+}	7	3
1 equiv. Ni^{2+}	7	80
10 equiv. Ni^{2+}	7	85
1 equiv. Zn^{2+}	7	40
10 equiv. Pb^{2+}	7	0
10 equiv. Cu^{2+}	7	0
10 equiv. Mg^{2+}	7	0
1 equiv. Cu^{2+} + 10 equiv. Co^{2+}	7	99
1 equiv. Cu^{2+} + 10 equiv. Fe^{2+}	7	99
1 equiv. Cu^{2+} + 10 equiv. Pb^{2+}	7	99

From the plot in Figure 2, it follows that for $[Ru(bpy)_2(H_2L^1)]^{2+}$ the luminescence intensity is virtually constant over the pH range 4.5–8.5. For $[Ru(bpy)_2(H_2L^2)]^{2+}$ and $[Ru(H_2L^{1,2})_3]^{2+}$ the pH ranges of approximately constant luminescence are similar (pH 4.7–9.0). At a lower pH, the fluorescence intensity drops sharply to nearly zero at pH < 2. The sigmoidal curves suggest pK_a values of ≈3, which is in the expected range for substituted pyridine groups [pK_a(20–25 °C) = 2.1–2.4].[30] The decrease in the luminescence intensity at high pH (luminescence intensity approximately zero at pH > 14, pK_a ≈ 11.5) suggests a deprotonation of an amide donor, and this also occurs in the expected range [pK_a(25 °C) ≈ 12].[33]

Figure 3 shows the pH-dependent luminescence of $[Ru(bpy)_2(H_2L^1)]^{2+}$ together with that of the $[Ru(bpy)_2(H_2L^1)]^{2+}/Cu^{2+}$ system (1 equiv. Cu^{2+}). Also shown in Figure 3 is the Cu^{2+}-concentration dependence of the fluorescence intensity at pH 4.9 (acetate buffer). At pH 5, no other metal ion leads to any fluorescence quenching, i.e. at pH 5 the $[Ru(bpy)_2(H_2L^1)]^{2+}$ on/off fluorescence sensor is selective for Cu^{2+}.

All three systems, $[Ru(bpy)_2(H_2L^1)]^{2+}$, $[Ru(bpy)_2(H_2L^2)]^{2+}$, and $[Ru(H_2L^1)_3]^{2+}$, show very similar behavior with respect to the metal-ion-induced fluorescence quenching, specifically in terms of the metal-ion- and pH-dependencies and the competition with other ligands (Table 1): (i) at pH 5 (acetate buffer), Cu^{2+} is the only metal ion that leads to significant quenching; the addition of an excess of any other metal ion does not have any influence on the fluorescence intensity observed with Cu^{2+} alone; (ii) at pH 7 (lutidine buffer), the reduction of the fluorescence intensity with one equivalent of Cu^{2+} is ≈100%, those due to Ni^{2+}, $Fe^{2+/3+}$, Co^{2+}, and Zn^{2+} are significantly smaller (40–85%), all other metal ions studied do not lead to any quenching; the kinetics of complex formation with Ni^{2+} is very slow, full equilibration (pH 7; 1 or 10 equiv. Ni^{2+}) needs at least 1 h (complexation of all other metal ions is fast, i.e., equilibration within minutes); (iii) at pH 7, acetate does not lead to any significant reduction of the quenching efficiency of Cu^{2+}, with citrate there is some competition, and with EDTA fluorescence quenching is only observed after complexation with EDTA is complete [from semiquantitative experiments and the known stability constants $\log K^{ML}$(Cu–acetate) = 1.75,[31] $\log K^{ML}$(Cu–citrate) = 4.5,[32] $\log K^{ML}$(Cu–EDTA) = 19.2,[33] an approximate value of $\log K^{ML}([Ru(bpy)_2\{(H_2L^1)Cu\}]^{2+}) = 12 \pm 2$ may be deduced].

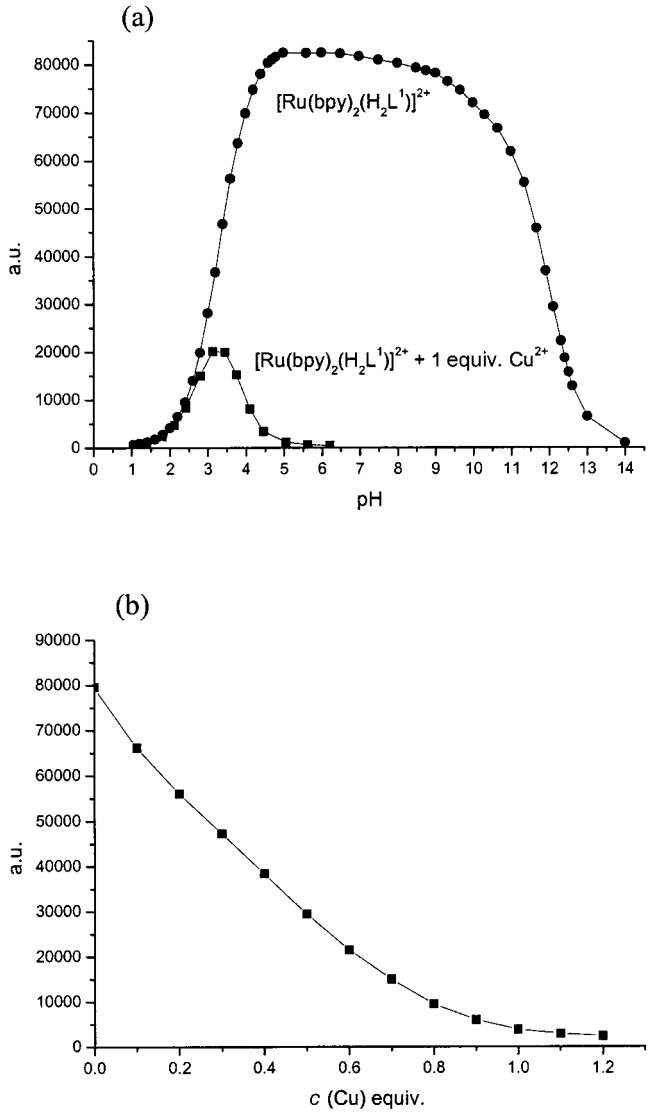


Figure 3. (a) pH-dependence of the luminescence of $[Ru(bpy)_2(H_2L^1)]^{2+}$ (10 μM aqueous solution) with or without 1 equiv. of Cu^{2+}, λ_{ex} = 450 nm, λ_{em} = 620 nm. (b) Fluorimetric titration of $[Ru(bpy)_2(H_2L^1)]^{2+}$ (10^{-5} M) with Cu^{2+} in acetate buffer (100 equiv.) at pH 4.9.

Conclusions

The synthesis of a rigid ditopic ligand with a 1,10-phenanthroline and a bis(pyridinamide) coordination site, based on a general strategy, which may be used to prepare a variety of 1,10-phenanthroline-derived ditopic ligands with a range of donor sets, has led to Ru^{2+}-polypyridine-based fluorescence on/off sensors that are highly selective for Cu^{2+} in aqueous solution at low pH. The rational design of the structure and donor set of the host, which, upon coordination of a metal ion, leads to fluorescence quenching,[34–36] should make possible the development of systems that show a range of specific selectivities in various pH regions.

Experimental Section

Materials and Measurements: Commercially available chemicals were used without further purification; solvents were dried by standard methods; solvents and chemicals for spectroscopy were of the highest possible grade and used as purchased. 1,10-Phenanthroline-5,6-dione dioxime was obtained by oxidation of 1,10-phenanthroline to 1,10-phenanthroline-5,6-dione[37] and subsequent reaction with hydroxylamine.[18] (4-Chloro-2-pyridyl)carboxylic acid methyl ester and (4-methoxy-2-pyridyl)carboxylic acid methyl ester were obtained as described from picolinic acid.[38]

UV/Vis/NIR spectra (CH_3CN, ambient temperature) were recorded with a Cary 1E or a JASCO V-570 spectrophotometer. IR spectra (KBr pellets) were obtained with a Perkin–Elmer 16C FTIR instrument. ^1H NMR spectra were recorded at room temperature with a Bruker ARX 200 or a Bruker Avance 500 spectrometer; the chemical shifts are relative to the solvent that is used as the internal standard. Electrochemical data were obtained by cyclic voltammetry [100 mV/sec., complex solutions (2×10^{-3} M), ambient temperature, tetrabutylammonium hexafluorophosphate (0.1 M) in CH_3CN], measured with a BAS100B electrochemical analyzer (data analysis with Digisim), by using a glassy carbon working electrode, a Pt-wire auxiliary, and a $Ag/AgNO_3$ reference electrode (0.01 M $AgNO_3$); ferrocene was used as an external standard. EPR spectra were recorded with a Bruker ELEXSYS E500 spectrometer [frozen solutions (approx. 10^{-3} M) in DMF/H_2O = 2:1] at 110 K. Mass spectra were recorded with a Finnigan 8400 or a JEOL JMS700 sector field instrument (EI or FAB) with a nitrobenzyl alcohol matrix (Nibeol, NBA) for the FAB spectra; electrospray mass spectra were recorded with a Finnigan TSQ 700 triple-quadrupole or a Q-Tof Ultima API mass spectrometer (Micromass/Waters, ESI) with analyte solutions in acetonitrile or methanol in the concentration range 10^{-6}–10^{-5} M. For HR-EI, HR-FAB, and HR-ESI spectra deviations from the theoretical mass are generally smaller than 5 mD, the internal standards used are reported with the experimental data. Emission spectra were recorded with a Varian Cary Eclipse fluorescence spectrophotometer at an excitation wavelength of 450 nm (intensities not calibrated). Fluorimetric titrations were performed in aqueous solutions (equilibrated in air, μ = 0.1; NaCl; the concentrations of the ruthenium complexes were 10^{-5} M). Metal ions were added as the chloride, perchlorate, or sulfate salts, and there was no dependence on the type of anion within this group. Standard HCl and NaOH solutions were used for adjusting the pH. Buffers at pH 4.7–5 and 7 were made by using the acetate/acetic acid and the lutidine/lutidinium couples, respectively.

Syntheses

5,6-Diamino-1,10-phenanthroline[17–19]

Method A: A suspension of phenanthroline-5,6-dione dioxime (2.88 g, 12 mmol) in ethanol (80 mL) was heated under N_2 (70 °C). A solution of sodium dithionite (85%, 9 g, 45 mmol) in aqueous ammonia (3%, 80 mL) was quickly added. An additional amount of sodium dithionite (85%, 3 g, 15 mmol) in aqueous ammonia (3%, 40 mL) solution was added when the yellow product started to precipitate as yellow flakes after dissolution of the dioxime. The reaction was then kept for 45 min at 85 °C. After being cooled to ambient temperature, the product was filtered under N_2, washed 3 times with diluted ammonia and then with THF, and dried overnight under high vacuum. Yield: 2.17 g (10.3 mmol, 86%), deep yellow solid.

Method B: Ethanol (150 mL, 50%) and a concentrated ammonia solution (10 mL) were added to a mixture of phenanthroline-5,6-dione dioxime (2.4 g, 10 mmol) and thiourea *S*,*S*-dioxide (5 g, 46.3 mmol) under nitrogen whilst stirring. The mixture was placed in a preheated (80 °C) oil bath and left to react for 45 min. The 5,6-diamino-1,10-phenanthroline started to precipitate after ≈15 min. After being cooled to room temperature, the product was isolated

as described above. Yield: 1.79 g (8.1 mmol, 81%). $C_{12}H_{10}N_4 \cdot \frac{1}{6}H_2O$ (213.23): calcd. C 67.59, H 4.88, N 26.27; found C 67.81, H 4.62, N 26.03. MS (EI+): m/z = 210 [M^+].

Potassium Salts of Substituted Picolinic Acids: KOH (0.95 equiv.) in a minimum amount of EtOH was added to a stirred solution of the methyl ester of the corresponding substituted picolinic acid derivative in dry ethanol (2 mL/mmol). After 6 h, Et_2O (1/5 volume) was added. The product was filtered, washed with EtOH/Et_2O, and dried under high vacuum.

Potassium (4-Cloro-2-pyridyl)carboxylate: Yield: 84%. M.p. > 350 °C. $C_6H_3ClKNO_2$ (195.64): calcd. C 36.83, H 1.55, N 7.16; found C 36.98, H 1.82, N 7.22. MS (ESI-): m/z = 156 [M – H^-]. ^{1}H NMR (200 MHz, D_2O): δ = 7.63 (dd, ^3J = 5.3 Hz, ^4J = 1.9 Hz, 1 H), 7.99 (d, ^4J = 1.90 Hz, 1 H), 8.55 (d, ^3J 5.3 Hz, 1 H) ppm.

Potassium (4-Methoxy-2-pyridyl)carboxylate: (4-Methoxy-2-pyridyl)carboxylic acid methyl ester (0.84 g, 5 mmol) and KOH (0.27 g) were added together to give (4-methoxy-2-pyridyl)carboxylic acid potassium salt (0.76 g). Yield: 80%. M.p. > 350 °C. $C_7H_6KNO_3 \cdot \frac{1}{4}H_2O$ (195.73): calcd. C 42.95, H 3.35, N 7.16; found C 43.06, H 3.21, N 7.17. MS (ESI-): m/z = 152 [M – H^-]. ^{1}H NMR (200 MHz, D_2O): δ = 3.92 (s, 3 H, OCH_3), 7.07 (dd, ^3J = 5.8 Hz, ^4J = 2.5 Hz, 1 H), 7.46 (d, ^4J = 2.5 Hz, 1 H), 8.38 (d, ^3J = 5.76 Hz, 1 H) ppm.

5,6-Bis(2-pyridylcarboxamido)-1,10-phenanthroline, H_2L^1: Picolinic acid (1.11 g, 9 mmol) and DMAP (0.12 g, 1 mmol, 33 mol-%) in absolute DMF (25 mL) were added to a stirred suspension/solution of 5,6-diamino-1,10-phenanthroline (0.63 g, 3 mmol) in a 100-mL Schlenk flask under nitrogen at ambient temperature. TEA (1.4 mL, 10 mmol) was then added by syringe, followed by the addition of phenylphosphonic acid dichloride (0.9 mL, 6.4 mmol) and more TEA (2.8 mL, 20 mmol) over a period of 5 h. After an additional 4 h, the reaction was quenched by the addition of water (1 mL). The product was isolated by precipitation (addition of H_2O, 5 volumes), filtration, washing with H_2O, and drying under high vacuum. Yield: 0.68 g (1.62 mmol, 54%). M.p. 294–298 °C. $C_{24}H_{16}N_6O_2 \cdot 1\frac{2}{3}\ H_2O$ (450.45): calcd. C 63.99, H 4.33, N 18.66, found C 64.01, H 4.10, N 18.39. MS (ESI+): m/z = 421 [M + H^+]. ^{1}H NMR (500 MHz, [D_7]DMF): δ = 7.70 (ddd, ^3J = 7.6 Hz, ^3J = 4.7 Hz, ^4J = 1.2 Hz, 2 H, py-*H*), 7.85 (dd, ^3J = 8.3 Hz, ^3J = 4.2 Hz, 2 H, phen-*H*), 8.11 (td, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 2 H, py-*H*), 8.25 (ddd,^3J = 7.7 Hz, ^4J = 1.2 Hz, ^5J = 0.6 Hz, 2 H, py-*H*), 8.62 (dd, ^3J = 8.3 Hz, ^4J = 1.6 Hz, 2 H, phen-*H*), 8.75 (ddd, ^3J = 4.7 Hz, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 2 H, py-*H*), 9.21 (dd, ^3J = 4.2 Hz, ^4J = 1.6 Hz, 2 H, phen-*H*), 11.10 (s, 2 H, N*H*) ppm. IR (KBr): 3298 (m), 3236 (m) (N–H); 3076 (w), 3050 (m) (C–H); 1676 (s), 1570 (m) (C=O_{amide}); 1616 (m) (C=N); 1590 (m), 1496 (m) (C=C) cm^{-1}.

5,6-Bis[(4-methoxy-2-pyridyl)carboxamido]-1,10-phenanthroline, H_2L^2: Obtained as described above by using 5,6-diamino-1,10-phenanthroline (0.21 g,1 mmol). Yield: 0.25 g, (0.52 mmol, 52%). M.p. 246–249 °C. $C_{26}H_{20}N_6O_4 \cdot 2H_2O$ (516.51): calcd. C 60.46, H 4.68, N 16.27, found C 60.57, H 4.76, N 15.96. MS (ESI+): m/z = 481 [M + H^+]. ^{1}H NMR (500 MHz, [D_7]DMF): δ = 4.00 (s, 6 H, OCH_3), 7.26 (dd, ^3J = 5.7 Hz, ^4J = 2.6 Hz, 2 H, py-*H*), 7.73 (d, ^4J = 2.6 Hz, 2 H, py-*H*), 7.85 (dd, ^3J = 8.4 Hz, ^3J = 4.2 Hz, 2 H, phen-*H*), 8.57 (d, ^3J = 5.7 Hz, 2 H, py-*H*), 8.59 (dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 2 H, phen-*H*), 9.20 (dd, ^3J = 4.2 Hz, ^4J = 1.5 Hz, 2 H, phen-*H*), 11.02 (s, 2 H, N*H*) ppm. IR (KBr): 3298 (s) (N–H); 3090 (w), 3066 (w), 3010 (w), 2934 (w) (C–H); 1684 (s), 1566 (m) (C=O_{amide}); 1602 (s), 1496 (s) (C=N, C=C) cm^{-1}.

5,6-Bis[(4-chloro-2-pyridyl)carboxamido]-1,10-phenanthroline: Obtained as described above by using 5,6-diamino-1,10-phenanthroline (0.21 g, 1 mmol) and (4-chloro-2-pyridyl)carboxylic acid potassium salt (0.59 g, 3 mmol). Yield: 0.37 g crude product. HR-ESI-MS: calcd. for [M + H^+] ($C_{24}H_{15}Cl_2N_6O_2$) 489.0634; found 489.0610 (–2.4 mD, standard: H_3PO_4).

Tris[5,6-bis(2-pyridylcarboxamido)-1,10-phenanthroline]ruthenium Hexafluorophosphate, $[Ru(H_2L^1)_3](PF_6)_2$: A mixture of $RuCl_3 \cdot 3H_2O$ (0.026 g, 0.1 mmol) and 5,6-bis(2-pyridylcarboxamido)-1,10-phenanthroline (0.15 g, 0.35 mmol) was heated (160 °C) in ethylene glycol (5 mL) for 30 min. After being cooled to room temperature, the mixture was diluted with water (1/6 volume), and the excess ligand was removed by filtration. The complex was precipitated by the addition of NH_4PF_6, filtered off, washed with small amounts of H_2O and Et_2O, and dried under high vacuum. Yield: 0.11 g (0.06 mmol, 66%) black-violet powder. $C_{72}H_{48}F_{12}N_{18}O_6P_2Ru \cdot 6H_2O$ (1760.25): calcd. C 49.12, H 3.44, N 14.32; found C 49.29, H 3.54, N 13.87. HR-FAB-MS: calcd. for [M – PF_6^-] ($C_{72}H_{48}F_6N_{18}O_6PRu$) 1507.2689; found 1507.2656 (–3.3 mD, standard: PEG1500). ^{1}H NMR (500 MHz, CD_3CN): δ = 7.61 (dd,^3J = 7.5 Hz, ^3J = 4.5, 6 H, py-*H*), 7.72 [m(br), 6 H, phen-*H*], 8.01 (t, ^3J = 7.5 Hz, 6 H, py-*H*), 8.19 [s(sh), 6 H, phen-*H*], 8.20 (d, ^3J = 7.5 Hz, 6 H, py-*H*), 8.65 (d, ^3J = 4.5 Hz, 6 H, py-*H*), 8.69 (d, ^3J = 7.8 Hz, 6 H, phen-*H*), 10.71 (s, 6 H, N*H*) ppm. IR (KBr): 3280 (s) (N–H); 3076 (m), 3054 (m) (C–H); 1680 (s), 1570 (m) (C=O_{amide}); 1620 (m) (C=N); 1590 (m), 1496 (s) (C=C); 844 (s) (PF_6^-) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 451 nm (ε = 2.2×10^4 L mol^{-1} cm^{-1}).

Bis(2,2′-bipyridine)[5,6-bis(2-pyridylcarboxamido)-1,10-phenanthroline]ruthenium Hexa-fluorophosphate, $[Ru(bpy)_2(H_2L^1)](PF_6)_2$: $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (0.15 g, 0.3 mmol) and 5,6-bis(2-pyridylcarboxamido)-1,10-phenanthroline (0.15 g, 0.35 mmol) were refluxed in 50% aqueous ethanol (20 mL) under nitrogen for 4 h. After being evaporated to near dryness, the residue was treated with water (10 mL), and the excess ligand was removed by filtration. The complex was precipitated with NH_4PF_6, filtered off, washed with H_2O and Et_2O, and dried under vacuum. Yield: 0.27 g (0.233 mmol, 78%) orange-red powder. $C_{44}H_{32}F_{12}N_{10}O_2P_2Ru \cdot 2H_2O$ (1159.80): calcd. C 45.56, H 3.13, N 12.08; found C 45.40, H 3.13, N 11.90. HR-FAB-MS: calcd. for [M – PF_6^-] ($C_{44}H_{32}F_6N_{10}O_2PRu$) 979.1395; found 979.1415 (+2.0 mD, standard: PEG1000). ^{1}H NMR (500 MHz, CD_3CN): δ = 7.29 (ddd, ^3J = 7.3 Hz, ^3J = 5.4 Hz, ^4J = 1.0 Hz, 2 H, bpy-*H*), 7.46 (ddd, ^3J = 7.3 Hz, ^3J = 5.4 Hz, ^4J = 1.0 Hz, 2 H, bpy-*H*), 7.61 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J = 1.0 Hz, 2 H, py-*H*), 7.63 (d, ^3J = 5.4 Hz, 2 H, bpy-*H*), 7.75 (dd, ^3J = 8.4 Hz, ^3J = 5.2 Hz, 2 H, phen-*H*), 7.85 (d, ^3J = 5.4 Hz, 2 H, bpy-*H*), 8.00 (ddd, ^3J = 8.2 Hz, ^3J = 7.3 Hz, ^4J = 1.0 Hz, 2 H, bpy-*H*), 8.02 (ddd, ^3J = 8.2 Hz, ^3J = 7.3 Hz, ^4J = 1.0 Hz, 2 H, bpy-*H*), 8.10 (ddd, ^3J = 8.0 Hz, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 2 H, py-*H*), 8.12 (dd, ^3J = 5.2 Hz, ^4J = 0.8 Hz, 2 H, phen-*H*), 8.19 (d, ^3J = 8.0 Hz, 2 H, py-*H*), 8.51 (d, ^3J = 8.2 Hz, 2 H, bpy-*H*), 8.54 (d, ^3J = 8.2 Hz, 2 H, bpy-*H*), 8.65 (d, ^3J = 4.8 Hz, 2 H, py-*H*), 8.66 (d, ^3J = 8.4 Hz, 2 H, phen-*H*), 10.67 (s, 2 H, NH) ppm. IR (KBr): 3322 (s) (N–H); 3076 (m) (C–H); 1684 (m), 1570 (w) (C=O_{amide}); 1622 (m) (C=N); 1604 (m), 1496 (m) (C=C); 842 (s) (PF_6^-) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 450 nm ($\varepsilon \approx 1.3 \times 10^4$ L mol^{-1} cm^{-1}).

Bis(2,2′-bipyridine){5,6-bis[(4-methoxy-2-pyridyl)carboxamido]-1,10-phenanthroline}ruthenium Hexafluorophosphate, $[Ru(bpy)_2(H_2L^2)](PF_6)_2$: Obtained as described above by using $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (0.09 g, 0.173 mmol) and 5,6-bis[(4-methoxy-2-pyridyl)-carboxamido]-1,10-phenanthroline (0.1 g, 0.2 mmol). Yield: 0.19 g (0.152 mmol, 88%) orange-red powder. $C_{46}H_{36}F_{12}N_{10}O_4P_2Ru \cdot 3.5H_2O$ (1246.87): calcd. C 44.31, H 3.48, N 11.23; found C 44.02, H 3.15, N 11.06. HR-FAB-MS: calcd. for [M – PF_6^-]

($C_{46}H_{36}F_6N_{10}O_4PRu$) 1039.1608; found 1039.1649 (+4.1 mD, standard: PEG1000); calcd. for [M – 2 PF_6^-] ($C_{46}H_{36}N_{10}O_4PRu$) 894.1966; found 894.1955 (–1.1 mD). ^{1}H NMR (500 MHz, CD_3CN): δ = 3.92 (s, 6 H, OCH_3), 7.12 (dd, ^3J = 5.2 Hz, ^4J = 2.8 Hz, 2 H, py-*H*), 7.29 [m(br), 2 H, bpy-*H*], 7.46 [m(br), 2 H, bpy-*H*], 7.63 (d, ^3J = 4.2 Hz, 2 H, bpy-*H*), 7.70 (d, ^4J = 2.8 Hz, 2 H, py-*H*), 7.74 (dd, ^3J = 8.2 Hz, ^3J = 4.8 Hz, 2 H, phen-*H*), 7.85 (d, ^3J = 4.2 Hz, 2 H, bpy-*H*), 8.02 [m(br), 2 H, bpy-*H*], 8.10 [m(br), 2 H, bpy-*H*], 8.11 (d, ^3J = 4.8 Hz, 2 H, phen-*H*), 8.46 (d, ^3J = 5.2 Hz, 2 H, py-*H*), 8.51 (d, ^3J = 7.9 Hz, 2 H, bpy-*H*), 8.54 (d, ^3J = 7.9 Hz, 2 H, bpy-*H*), 8.63 (d, ^3J = 8.2 Hz, 2 H, phen-*H*), 10.67 (s 2 H, N*H*) ppm. IR (KBr): 3318 (s) (N–H); 3074 (m), 2932 (w) (C–H); 1684 (m), 1566 (m) (C=O_{amide}); 1614 (m) (C=N); 1600 (s), 1308 (s) (C=C); 840 (s) (PF_6^-) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 447 nm ($\varepsilon \approx 1.9 \times 10^4$ $L\,mol^{-1}\,cm^{-1}$).

[Ru(bpy)$_2$(μ-L^{1}M)](PF$_6$)$_2$, M = Cu^{2+}, Ni^{2+}, Pd^{2+}: [Ru(bpy)$_2$-(H_2L^1)](PF_6)$_2$·2H_2O (0.034 g, 0.03 mmol) and the corresponding metal salt (0.03 mmol) were refluxed in MeOH (15 mL) for 20 min. After being cooled to room temperature, the dinuclear complexes were precipitated by addition of Et_2O, isolated by centrifugation or filtration, and dried under high vacuum.

[Ru(bpy)$_2$(μ-L^{1}Cu)](PF$_6$)$_2$: Cu$(AcO)_2$·H_2O (0.006 g). Yield: 0.022 g (0.017 mmol, 57%) dark brown solid. $C_{44}H_{30}CuF_{12}N_{10}O_2P_2Ru$·6$H_2O$ (1293.39): calcd. C 40.86, H 3.27, N 10.83; found C 40.63, H 3.03, N 10.60. IR (KBr): 3074 (m) (C–H); 1654 (m) (C=O_{amide}); 1624 (m) (C=N); 1600 (m), 1488 (m) (C=C); 838 (PF_6^-) cm^{-1}.

[Ru(bpy)$_2$(μ-L^{1}Ni)](PF$_6$)$_2$: Ni$(AcO)_2$·4H_2O (0.0075 g). Yield: 0.027 g (0.023 mmol, 75%) bright red solid.

[Ru(bpy)$_2$(μ-L^{1}Pd)](PF$_6$)$_2$: Pd(benzonitrile)$_2Cl_2$ (0.0115 g) in CH_3CN (2 mL), followed by 0.05 mL TEA. Yield: 0.031 g (0.024 mmol, 80%) orange-red solid. $C_{44}H_{30}F_{12}N_{10}O_2P_2PdRu$·2MeOH (1292.26): calcd. C 42.75, H 2.96, N 10.84; found C 42.59, H 3.16, N 11.12. IR (KBr): 3062 (m) (C–H); 1684 (w) (C=O_{amide}); 1626 (m) (C=N); 1600 (m), 1494 (w) (C=C); 842 (s) (PF_6^-) cm^{-1}.

[Ru(bpy)$_2$(μ-L^{2}M)](PF$_6$)$_2$, M = Cu^{2+}, Ni^{2+}, Pd^{2+}: Obtained as described above, but with [Ru(bpy)$_2$(H_2L^2)](PF_6)$_2$·3.5H_2O (0.038 g, 0.03 mmol).

[Ru(bpy)$_2$(μ-L^{2}Cu)](PF$_6$)$_2$: Cu$(AcO)_2$·H_2O (0.006 g). Yield: 0.027 g (0.02 mmol, 68%) red-brown solid. $C_{46}H_{34}CuF_{12}N_{10}O_2P_2Ru$·3$H_2O$·1.5MeOH (1319.42): calcd. C 42.34, H 3.44, N 10.39; found C 42.40, H 3.64, N 10.61. IR (KBr): 3072 (w), 2926 (w) (C–H); 1656 (m) (C=O_{amide}); 1634 (s) (C=N); 1604 (s), 1310 (m) (C=C); 842 (s) (PF_6^-) cm^{-1}.

[Ru(bpy)$_2$(μ-L^{2}Ni)](PF$_6$)$_2$: Ni$(AcO)_2$·4H_2O (0.0075 g). Yield: 0.029 g (0.022 mmol, 74%) red solid. $C_{46}H_{34}NiF_{12}N_{10}O_2P_2Ru$·3$H_2O$ (1268.02): calcd. C 42.68, H 3.11, N 10.82; found C 42.69, H 3.16, N 10.77. IR (KBr): 3074 (m), 2934 (w) (C–H); 1640 (m) (C=O_{amide}); 1612 (s) (C=N); 1584 (w), 1310 (m) (C=C); 838 (s) (PF_6^-) cm^{-1}.

[Ru(bpy)$_2$(μ-L^{2}Pd)](PF$_6$)$_2$: Pd(benzonitrile)$_2Cl_2$ (0.0115 g) in CH_3CN (2 mL), followed by 0.05 mL TEA. Yield: 0.03 g (0.022 mmol, 74%) orange-red solid. $C_{46}H_{34}PdF_{12}N_{10}O_2P_2Ru$·4$H_2O$ (1333.77): calcd. C 40.62, H 3.11, N 10.30; found C 40.45, H 3.13, N 10.22. IR (KBr): 3066 (m), 2926 (w) (C–H); 1654 (sh) (C=O_{amide}); 1626 (s) (C=N); 1604 (s), 1308 (m) (C=C); 842 (s) (PF_6^-) cm^{-1}.

[Ru(μ-L^{1}M)$_3$](PF$_6$)$_2$, M = Cu^{2+}, Ni^{2+}, Pd^{2+}: The synthesis was carried out as described above, but with [Ru(H_2L^1)$_3$](PF_6)$_2$·6H_2O (0.035 g, 0.02 mmol), along with double the amount of the corresponding metal salts and double the volume of solvent.

[Ru(μ-L^{1}Cu)$_3$](PF$_6$)$_2$: Cu$(AcO)_2$·H_2O (0.012 g). Yield after recrystallization from DMF/MeOH: 0.029 g (0.014 mmol, 69%) dark brown solid. $C_{72}H_{42}Cu_3F_{12}N_{18}O_6P_2Ru$·2DMF·5$H_2O$·MeOH (2105.06): calcd. C 45.07, H 3.35, N 13.31; found C 45.21, H 3.46, N 13.15. HR-ESI-MS: calcd. for [M – 2 PF_6^-] ($C_{72}H_{42}Cu_3$-$N_{18}O_6Ru$) 1545.0466; found 1545.0432 (–3.4 mD, standard: H_3PO_4). IR (KBr): 3066 (w) (C–H); 1650 (sh) (C=O_{amide}); 1620 (s) (C=N); 1596 (s) (C=C); 842 (s) (PF_6^-) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 419 nm ($\varepsilon \approx 1.0 \times 10^4$ $L\,mol^{-1}\,cm^{-1}$), λ_{max} = 473 nm ($\varepsilon \approx 0.9 \times 10^4$ $L\,mol^{-1}\,cm^{-1}$).

[Ru(μ-L^{1}Ni)$_3$](PF$_6$)$_2$: Ni$(AcO)_2$·4H_2O (0.015 g). Yield: 0.031 g (0.017 mmol, 85%) red solid. HR-ESI-MS: calcd. for [M – 2 PF_6^-] ($C_{72}H_{42}N_{18}Ni_3O_6Ru$) 1530.0639; found 1530.0640 (+0.1 mD, standard: H_3PO_4).

[Ru(μ-L^{1}Pd)$_3$](PF$_6$)$_2$: Pd(benzonitrile)$_2Cl_2$ (0.023 g) in CH_3CN (4 mL), followed by TEA (0.1 mL). Yield: 0.037 g (0.022 mmol, 74%) red solid. ESI-MS: calcd. for [M – 2 PF_6^-] ($C_{72}H_{42}N_{18}O_6P$-d_3Ru) 1673.97; found 1674.

Tris[5,6-bis(2-pyridylcarboxamido)-1,10-phenanthroline]iron Hexafluorophosphate, [Ru(H$_2$L^1)$_3$](PF$_6$)$_2$: A mixture of $FeSO_4$·7H_2O (0.028 g, 0.1 mmol), 5,6-bis(2-pyridylcarboxamido)-1,10-phenanthroline (0.15 g, 0.35 mmol), hydroxylammonium chloride (0.01 g), and sulfuric acid (50 μL) was stirred in H_2O (10 mL) for 6 h at ambient temperature. After filtration (excess ligand), the complex was precipitated from the dark red solution by addition of NH_4PF_6, collected on a filter, washed with small amounts H_2O and Et_2O, and dried under high vacuum. Yield: 0.15 g (0.09 mmol, 90%) bordeaux red powder. $C_{72}H_{48}F_{12}FeN_{18}O_6P_2$·4$H_2O$ (1679.00): calcd. C 51.50, H 3.36, N 15.02; found C 51.67, H 3.55, N 15.13. HR-ESI-MS: calcd. for [M – 2PF_6^-] ($C_{72}H_{48}FeN_{18}O_6$) 1316.3354; found 1316.3366 (+1.2 mD, standard: H_3PO_4). ^{1}H NMR (500 MHz, CD_3CN): δ = 7.62 (dd, ^3J = 7.5 Hz, ^3J = 4.2 Hz, 6 H, py-*H*), 7.69 [m(br), 6 H, phen-*H*], 7.82 (d, ^3J = 3.4 Hz, 6 H, phen-*H*), 8.01 (t, ^3J = 7.5 Hz, 6 H, py-*H*), 8.21 (d, ^3J = 7.5 Hz, 6 H, py-*H*), 8.65 (d, ^3J = 4.2 Hz, 6 H, py-*H*), 10.74 (s, 6 H, N*H*) ppm. IR (KBr): 3274 (m) (N–H); 3074 (w), 3054 (w) (C–H); 1570 (m), 1680 (s) (C=O_{amide}); 1622 (m) (C=N); 1588 (m), 1500 (s) (C=C); 844 (s) (PF_6^-) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 515 nm ($\varepsilon \approx 0.8 \times 10^4$ $L\,mol^{-1}\,cm^{-1}$).

[Fe(μ-L^{1}M)$_3$](PF$_6$)$_2$, M = Cu^{2+}, Ni^{2+}, Pd^{2+}: [Fe($LpicH_2$)$_3$](PF_6)$_2$·4H_2O (0.034 g, 0.02 mmol) and the corresponding metal salt (0.06 mmol) were refluxed in MeOH (15 mL) for 20 min. After cooling, the tetranuclear complexes were precipitated by addition of Et_2O, isolated by centrifugation or filtration, and dried under high vacuum.

[Fe(μ-L^{1}Cu)$_3$](PF$_6$)$_2$: Cu$(AcO)_2$·H_2O (0.012 g). Yield: 0.03 g (0.0157 mmol, 79%) dark red-brown solid. $C_{72}H_{42}Cu_3F_{12}FeN_{18}$-$O_6P_2$·6$H_2O$ (1899.62): calcd. C 45.52, H 2.87, N 13.27; found C 45.56, H 3.04, N 13.17. HR-ESI-MS: calcd. for [M – 2PF_6^-] ($C_{72}H_{42}Cu_3FeN_{18}O_6$) 1499.0772; found 1499.0804 (+3.2 mD, standard: H_3PO_4). IR (KBr): 3068 (m) (C–H); 1654 (m) (C=O_{amide}); 1622 (s) (C=N); 1596 (s) (C=C); 844 (s) (PF_6^-) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 387 nm ($\varepsilon \approx 1.0 \times 10^4$ $L\,mol^{-1}\,cm^{-1}$), λ_{max} = 524 nm ($\varepsilon \approx 0.9 \times 10^4$ $L\,mol^{-1}\,cm^{-1}$).

[Fe(μ-L^{1}Ni)$_3$](PF$_6$)$_2$: Ni$(AcO)_2$·4H_2O (0.015 g). Yield: 0.025 g (0.0132 mmol, 66%) red solid. $C_{72}H_{42}F_{12}FeN_{18}Ni_3O_6P_2$·2$H_2O$·3MeOH (1906.09): calcd. C 47.18, H 3.06, N 13.21; found C 47.22, H 2.92, N 12.96. ESI-MS: calcd. for [M – 2 PF_6^-] ($C_{72}H_{42}FeN_{18}Ni_3O_6$) 1484; found 1483.9. IR (KBr): 3078 (w) (C–H); 1660 (sh) (C=O_{amide}); 1636 (s) (C=N); 1604 (w), 1586 (m) (C=C); 842 (s) (PF_6^-) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 451 nm ($\varepsilon \approx$

1.3×10^4 L mol^{-1} cm^{-1}), λ_{max} = 485 nm ($\varepsilon \approx 1.3 \times 10^4$ L mol^{-1} cm^{-1}), λ_{max} = 527 nm ($\varepsilon \approx 1.3 \times 10^4$ L mol^{-1} cm^{-1}).

[Fe(μ-L^{1}Pd)$_3$](PF$_6$)$_2$: Pd(benzonitrile)$_2$Cl$_2$ (0.023 g) in CH_3CN (4 mL), followed by TEA (0.1 mL). Yield: 0.032 g (0.0164 mmol, 82%) red solid. $C_{72}H_{42}F_{12}FeN_{18}O_6P_2Pd_3 \cdot 9H_2O$ (2082.29): calcd. C 41.53, H 2.90, N 12.11; found C 41.28, H 2.76, N 11.97. ESI-MS: calcd. for [M – 2 PF_6^-] ($C_{72}H_{42}FeN_{18}O_6$ Pd_3) 1628; found 1628. IR (KBr): 3064 (m) (C–H); 1650 (sh) (C=O$_{amide}$); 1626 (s) (C=N); 1598 (s) (C=C); 844 (m) (PF_6^-) cm^{-1}.

Acknowledgments

Generous financial support by the Deutsche Forschungsgemeinschaft (DFG) and a generous gift of palladium and ruthenium salts by Degussa AG are gratefully acknowledged.

[1] S. J. Lippard, J. M. Berg, *Principles of Bioinorganic Chemistry*, University Science Books, **1994**.
[2] R. J. P. Williams, *Bringing Chemistry to Life*, Oxford University Press, **2000**.
[3] P. Braunstein, X. Morise, *Organometallics* **1998**, *17*, 540.
[4] P. Comba, A. Mayboroda, H. Pritzkow, *Eur. J. Inorg. Chem.* **2003**, 3042.
[5] P. D. Beer, *Acc. Chem. Res.* **1998**, *31*, 71.
[6] P. D. Beer, M. W. Wong, *Macrocyclic Chemistry – Current Trends and Future Perspectives* (Ed.: E. K. Gloe), Springer, **2005**.
[7] V. Balzani, A. Credi, M. Venturi, *ChemPhysChem* **2003**, *3*, 49.
[8] C. Fraser, L. Johnston, A. L. Rheingold, B. S. Haggerty, G. K. Williams, J. Whelan, B. Bosnich, *Inorg. Chem.* **1992**, *31*, 1835.
[9] E. Kimura, S. Wada, M. Shionoga, T. Takahashi, Y. Iitaca, *J. Chem. Soc., Chem. Commun.* **1990**, 397.
[10] F. Bolletta, I. Costa, L. Fabbrizzi, M. Licchelli, M. Montalti, P. Pallavicini, L. Prodi, N. Zaccheroni, *J. Chem. Soc., Dalton Trans.* **1999**, 1381.
[11] C. Lodeiro, F. Pina, A. J. Parola, A. Bencini, A. Bianchi, C. Bazzicalupi, S. Ciattini, C. Giorgi, A. Masotti, B. Valtancoli, J. S. de Melo, *Inorg. Chem.* **2001**, *40*, 6813.
[12] V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, **1991**.
[13] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85.
[14] M. K. Nazeeruddin, M. Graetzel in *Conversion and Storage of Solar Energy Using Dye-Sensitized Nanocrystalline TiO_2 Cells* (Eds.: M. K. Nazeeruddin, M. Graetzel), Oxford, **2004**.
[15] V. Nikolenko, R. Yuste, L. Zayat, L. M. Baraldo, R. Etchenique, *Chem. Commun.* **2005**, *13*, 1752.
[16] A. Bouskila, E. Amouyal, C. Verchere-Beaur, I. Sasaki, A. Gaudemer, *J. Photochem. Photobiol. B* **2004**, *76*, 69.
[17] J. Bolger, A. Gourdon, E. Ishow, J.-P. Launay, *Inorg. Chem.* **1996**, *35*, 2937.
[18] S. Bodige, F. M. MacDonnell, *Tetrahedron Lett.* **1997**, *38*, 8159.
[19] H. Camren, M.-Y. Chang, L. Zeng, M. E. McGuire, *Synth. Commun.* **1996**, *26*, 1247.
[20] O. Luis-Andre, G. Gelbard, *Bull. Soc. Chim. Fr.* **1986**, 565.
[21] E. de Barry Barnet, *J. Chem. Soc.* **1910**, 63.
[22] R. Murugan, E. F. V. Scriven, *Aldrichim. Acta* **2003**, *36*, 21.
[23] A. Michaelis, F. Rothe, *Ber. Dtsch. Chem. Ges.* **1892**, *25*, 1747.
[24] K. Sasse in *Organische Phosphorverbindungen, Teil 1* (Ed.: K. Sasse), **1963**.
[25] L. Anschütz, H. Wirth, *Ber. Dtsch. Chem. Ges.* **1956**, 688.
[26] M. F. Hershman, L. F. Audrieth, *J. Org. Chem.* **1958**, *23*, 1889.
[27] P. Comba, T. W. Hambley, N. Okon, G. Lauer, *MOMEC97, A Molecular Modeling Package for Inorganic Compounds*, ed. CVS, **1997**.
[28] J. E. Bol, C. Buning, P. Comba, J. Reedijk, M. Ströhle, *J. Comput. Chem.* **1998**, *19*, 512.
[29] H. A. O. Hill, K. A. Raspin, *J. Chem. Soc., Sect. A* **1968**, 3036.
[30] A. Weiss, S. Fallab, H. Erlenmeyer, *Helv. Chim. Acta* **1955**, *38*, 263.
[31] P. W. Lindner, R. G. Torrington, U. A. Seemann, *Talanta* **1983**, *30*, 295.
[32] H. Azab, A. M. El-Nady, A. Hassan, R. S. A. Akzal, *Monatsh. Chem.* **1993**, *124*, 637.
[33] E. Baumann, *J. Inorg. Nucl. Chem.* **1974**, *36*, 1827.
[34] P. Comba, *Coord. Chem. Rev.* **1999**, *185*, 81.
[35] P. Comba, T. W. Hambley, *Molecular Modeling of Inorganic Compounds*, 2nd ed., with a tutorial based on MOMEClite, Wiley-VCH, **2001**.
[36] P. Comba, B. Martin in *Modeling of Macrocyclic Ligand Complexes* (Ed.: K. Gloe), **2005**.
[37] W. Paw, R. Eisenberg, *Inorg. Chem.* **1997**, *36*, 2287.
[38] R. J. Sundberg, S. Jiang, *Org. Prep. Proc. Int.* **1997**, *29*, 117.

Received: May 19, 2006
Published Online: September 12, 2006

