Intramolecular Luminescence Quenching in Amino Acid Bridged Ruthenium(II)-Copper(II) Complexes with Negligible Ground-State Coupling

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A series of heterobimetallic complexes [{Ru(bipy)$_2$}m-AA{Cu(phen)(H$_2$O)}](PF$_6$)$_3$ (m-AA = N^{ω}-(4-carbonyl-4′-methyl-2,2′-bipyridyl)-L-α,ω-diamino acid; diamino acid (AA): **1b**, L-2,3-diaminopropionic acid; **2b**, L-2,4-diaminobutyric acid; **3b**, L-ornithine, **4b**, L-lysine) has been synthesized and characterized starting from the 2,2′-bipyridineruthenium(II)-substituted amino acids [{Ru(bipy)$_2$}m-AA-$^{\alpha}N$-^{t}Boc]$^{2+}$ ($^{\alpha}N$-^{t}Boc-**1a–4a**, $^{\alpha}N$-^{t}Boc = N^{α}-*tert*-butoxycarbonyl). The metal centers in **1b–4b** are bridged by insulating alkyl chains. Consequently, spectroscopic and electrochemical investigations confirmed the absence of any appreciable ground-state coupling between ruthenium(II) and copper(II). However, the luminescence of **1b–4b** is significantly quenched compared to that of the parent compounds **1a–4a**. Quenching was found to proceed only intramolecularly and to be most efficient in **1b** with the shortest alkyl spacer. Equilibrium constants for the formation of **1b–4b** were determined from luminescence titrations of the respective ruthenium-substituted amino acid with [Cu(phen)(NO$_3$)$_2$]. The complexes **2b–4b** (K = 1.61–2.08 × 10^7 M^{-1}) were found to be significantly more stable than **1b** (K = 5.7 × 10^6 M^{-1}). This is explained by a stronger electrostatic repulsion between the two metal centers in the latter compound.

Introduction

Owing to their fundamental importance in biological photosynthesis, photoinduced electron- and energy-transfer processes have attracted much attention in the context of supramolecular chemistry.[1][2][3][4] A particularly interesting challenge for synthetic chemists is the design of redox-active devices in which a photoinduced electron-transfer process triggers a chemical reaction. The light-dependent reduction of CO$_2$ by macrocyclic Ni^{II} complexes which have been covalently tethered to a polypyridineruthenium moiety may illustrate this goal.[5][6] In these compounds the electron-accepting nickel complex functions as a catalytically active site for substrate turnover, whereas the ruthenium chromophore serves the purpose of converting light into chemical energy.

Work in our laboratories has focussed on the design and synthesis of modified amino acids with well-defined binding sites for transition-metal complexes.[7] Our aim is to use these ligands as building blocks for the construction of polyfunctional supramolecular systems. Here we report the synthesis and characterization of novel dinuclear Ru^{II}-Cu^{II} complexes [{Ru(bipy)$_2$}m-AA{Cu(phen)(H$_2$O)}](PF$_6$)$_3$, **1b−4b** (Figure 1), with bridging bipyridyl-substituted α,ω-diamino acids (m-AA). The photoredox active [Ru(bipy)$_3$] subunit in **1b−4b** is thought to be suitable for the photochemical generation of phenanthrolinecopper(I).

It has been known for twenty years that phenanthroline-copper(I) complexes can function as efficient chemical nucleases, catalysing the oxidative cleavage of ribose links of DNA in the presence of oxygen and a reducing agent.[8] This has stimulated considerable interest in using these systems as chemical probes for DNA structures.[9] DNA-strand scission occurs through a series of reactions starting with hydrogen-atom abstraction from a ribose unit.[9] The active agent is probably a metal-oxo or metal-hydroxyl intermediate formed upon reaction of hydrogen peroxide with a [Cu(phen)$_2$]$^+$ molecule bound to the surface of DNA within the minor groove.[9][10]

An interesting approach to the in situ generation of active Cu^{I} species has been reported by Strekas et al.[11] The authors have synthesized and characterized heterobimetallic complexes containing Cu^{I} and Cu^{II} fragments, and a bis(diimine)ruthenium(II) complex. It was shown that the compounds interact with DNA and that oxidative strand cleavage occurs in the presence of reducing agents. The combination of [Cu(phen)]$^{2+}$ fragments with photoredox-active polypyridineruthenium(II) complexes thus seems to be a promising route to bimetallic DNA-cleavage reagents. Photoinduced electron transfer should be possible between the ruthenium and the copper centers in dinuclear complexes, triggering oxidative strand-scission reactions upon irradiation with visible light.

Furthermore, both metal fragments are expected to interact with DNA with different affinities and selectivities. Polypyridineruthenium compounds typically intercalate into the base stacks of DNA,[12][13] whereas bis(phenanthroline-)copper(I) predominantly binds to the minor groove.[9][14] The combination of metal fragments with different DNA

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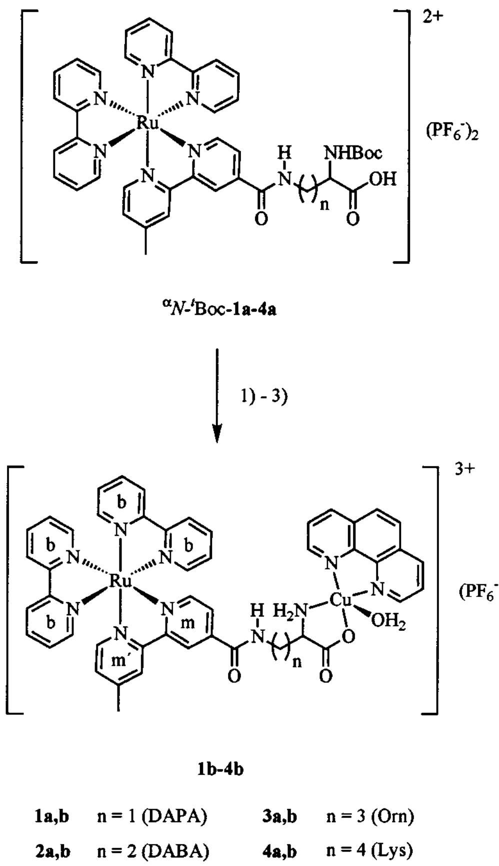
Figure 1. Synthesis of the Ru^{II}-Cu^{II} complexes **1b−4b**[a]



[a] 1) 4 N HCl/dioxane, 1 h, 0°C. − 2) 1 equiv. [Cu(phen)(NO$_3$)$_2$]/methanol. − 3) NH$_4$PF$_6$/H$_2$O.

binding patterns has been exploited by Brewer and co-workers for the synthesis of Ru^{II}-Pt^{II} and Os^{II}-Pt^{II} heterobimetallic complexes.[15] These compounds can interact with DNA by intercalation and/or covalent bonding.

It was first the aim of our studies on **1b−4b** to establish fundamental structure-function relationships in order to provide a basis for the applications described above. The compounds were investigated structurally by NMR and EPR spectroscopy. UV/Vis spectroscopy and cyclic voltammetry were used to confirm the absence of an efficient electronic coupling between the two metal centers. Finally, luminescence spectroscopy was applied as a tool to determine the effects of bridge structures on quenching efficiencies and complex stability constants.

Synthesis and Characterization of the Complexes

Synthesis

Our synthesis of the dinuclear Ru^{II}-Cu^{II} complexes **1b−4b** started from the $^{\alpha}N$-^{t}Boc-protected (amino acid)ruthenium(II) complexes [{Ru(bipy)$_2$}m-AA-$^{\alpha}N$-^{t}Boc](PF$_6$)$_2$ [$^{\alpha}N$-^{t}Boc-**1a−4a**; AA = L-2,3-diaminopropionic acid; L-2,4-diaminobutyric acid; L-ornithine; L-lysine (Figure 1)]. The latter compounds were prepared by coupling the succinimido ester [Ru(bipy)$_2$(m-OSu)](PF$_6$)$_2$ with the appropriate $^{\alpha}N$-^{t}Boc-protected α,ω-amino acid according to a procedure reported earlier for the lysine derivative $^{\alpha}N$-^{t}Boc-**4a**.[16] Full experimental details will be published elsewhere.[17]

The ^{t}Boc protecting groups of $^{\alpha}N$-^{t}Boc-**1a−4a** were removed by acid deprotection in dioxane/HCl.[18] Deprotonation of the amine hydrochloride and subsequent reaction with one equivalent of commercially available [Cu(phen)(NO$_3$)$_2$] in methanol yielded the desired complexes **1b−4b** (Figure 1). The compounds were isolated as PF$_6^-$ salts from water in approximately 70% yield. Coprecipitated salts can be removed by stirring the complexes with water for one day. However, it is advantageous to use only a small excess (< 5 times) of NH$_4$PF$_6$ in order to prevent coprecipitation of ammonium hexafluorophosphate.

^{1}H NMR

Proton-NMR spectroscopy proved to be a valuable tool for structural investigations of the Ru^{II}-Cu^{II} mixed-metal complexes **1b−4b**. Binding of the paramagnetic [Cu](phen)$^{2+}$ fragment is easily confirmed by the disappearance of all signals related to the $^{\alpha}$CH and $^{\beta-\omega}$CH$_2$ protons of the amino acid moieties.[19][20] In contrast, the resonances of the [Ru(bipy)$_2$m]$^{2+}$ fragments in **1b−4b** are broader than those of the parent compounds **1a−4a** but readily observable. This is a consequence of the $1/r^6$ dependence of longitudinal relaxation rates, $1/T_1$, on the distance between protons and paramagnetic centers such as Cu^{2+}.[19]

Most interesting are changes of the signals assigned to the m3 protons of **1b−4b** at δ ≈ 8.96 (notation see Figure 1). A clear dependence on the Ru−Cu distance is evident as the intensities decrease with the number of methylene spacers, n. Assuming fully extended hydrocarbon chains, the Ru−Cu distances can be calculated to range from ca. 13 A in **4b** to ca. 9 A in **1b**. We think this model is justified because of the electrostatic repulsion between the positively charged metal centers.

EPR

The EPR spectra of **1b−4b** in frozen methanol solutions at 77 K are anisotropic with $g_{\parallel} > g_{\perp} > 2.04$ and large parallel hyperfine splittings ($A_{\parallel} \approx 180 \times 10^{-4}$ cm^{-1}). These values are typical for copper(II) complexes with a d$_{x^2-y^2}$ (or d$_{xy}$) ground state.[21]

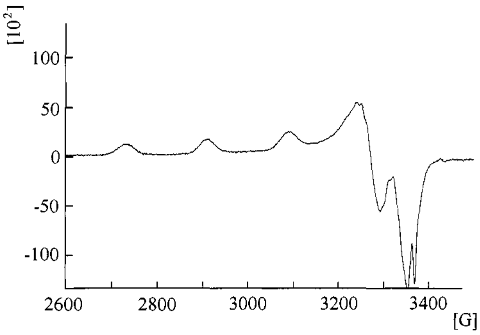
No significant differences are observed between the spectra of **1b−4b** (Table 1). This is expected since the copper centers possess identical local environments in these compounds. The spectrum of **3b** is shown in Figure 2 as an example.

Our data compare well with others reported in the literature for copper(II) complexes with square-pyramidal or elongated octahedral coordination geometries.[22] Particularly relevant examples are several ternary phenanthroline-copper(II) dipeptide complexes ($g_{\parallel} \approx 2.24$, $A_{\parallel} \approx 170 \times 10^{-4}$ cm^{-1}).[23] Slightly lower $g_{\parallel}$ values (< 2.20) were found for square-planar complexes.[22] One or two solvent molecules may thus be coordinated to the copper centers of **1b−4b** in solution. Elemental analysis data confirm the

Table 1. EPR data of complexes **1b**−**4b** (frozen methanol, DPPH as internal reference)

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ [10^{-4} cm^{-1}]
1b	2.271	2.043	177
2b	2.268	2.046	179
3b	2.276	2.046	177
4b	2.274	2.049	179

Figure 2. EPR spectrum of complex **3b** in frozen methanol solution at 77 K (DPPH as internal reference)



presence of at least one water molecule in the solid state. The water contents vary from 1−3.5 equiv. after several days under vacuum at elevated temperatures. We propose the solid-state structures shown in Figure 1 with water occupying the apical positions of square pyramidal coordination environments around the copper centers in our complexes. However, the presence of two weakly bound solvent molecules in solution cannot be ruled out and seems likely.

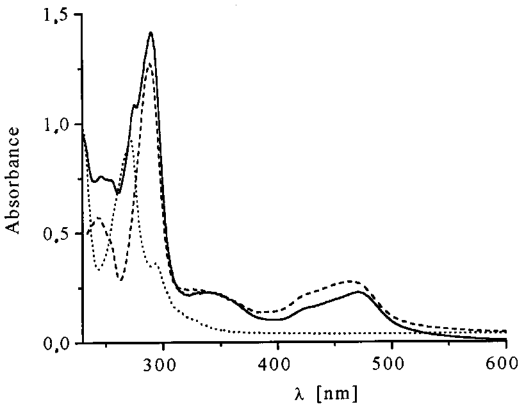
Absorption Spectra

The absorption spectra of **1b**−**4b** in methanol are dominated by the typical features of polypyridineruthenium(II) complexes.[24][25] Most significant is an MLCT band with a maximum at 455 nm and a shoulder at 427 nm. A weak absorption at around 340 nm may be assigned to either an MC[24][25] or an MLCT[26] transition. In the UV region a strong intraligand π-π* band is centered at 288 nm.

The presence of the $[Cu(phen)]^{2+}$ subunit is apparent from a shoulder at 274 nm due to a phenanthroline-based intraligand π-π* transition. A comparison of the absorption spectra in methanol obtained for **3a**, **3b**, and $[Cu(phen)(NO_3)_2]$ is shown in Figure 3. The spectrum of **3b** appears as the sum of the spectra of its constituents, consistent with the absence of any significant ground-state electronic coupling between the two metal centers. In addition, no intervalence charge-transfer absorption bands were observed for **1b**−**4b** in the near-infrared region ($\varepsilon < 10$ for the IT transition). According to the Hush theory[27][28][29] this is further evidence for weak electronic coupling in polynuclear complexes with noninteracting redox centers (class I according to the Robin−Day classification[30][31]).

Similar results were reported in the literature for dinuclear Ru^{II}-Ru^{II} and Ru^{II}-Pt^{II} compounds with bridging alkyl spacers.[32] The amino acid bridges in **1b**−**4b** evidently act as insulators between Ru^{II} and Cu^{II} and thus may be considered to play only a structural role. Each complex fragment is therefore expected to keep its essential individual properties. This condition has been discussed to be important for the definition of supramolecular systems[33] and is crucial for the prediction of properties such as DNA binding and cleavage abilities.

Figure 3. Absorption spectra of 1.5×10^{-5} M solutions of **3a** [------, λ_{max} (lg ε) = 457 nm (4.24), 287 (4.89), 246 (4.53)], **3b** [——, λ_{max} (lg ε) = 455 nm (4.22), 287 (4.94), 256 (4.64)], and $[Cu(phen)(NO_3)_2]$ [········, λ_{max} (lg ε) = 294 (4.38), 272 (4.79)] in methanol



Cyclic Voltammetry

The weak coupling between ruthenium(II) and copper(II) in **1b**−**4b** is also evident from electrochemical data (Table 2). Figure 4 shows the cyclic voltammogram (2nd cycle) of **2b** as an example. Two redox couples are observed. One reversible at a half-wave potential of 1.30 V ($\Delta E_P \approx 80$ mV) is typical for the $Ru^{II/III}$ transition in $[Ru(bipy)_3]^{2+}$ derivatives[24][25] and similar to those observed for the mononuclear precursor complexes **1a**−**4a**. The other couple is irreversible and occurs at $E_{1/2} = 0.1$ V ($\Delta E_P \approx 280$ mV). This value is in good agreement with data reported in the literature for other phenanthrolinecopper complexes.[34][36]

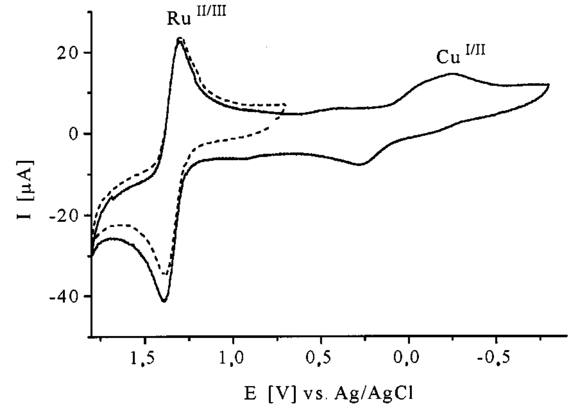
Table 2. Electrochemical data of complexes **1b**−**4b** as measured by cyclic voltammetry[a]

Complex	$E_{1/2}$ [V] (ΔE_P [mV])		
	metal oxidation		ligand reduction
	$Ru^{II/III}$	$Cu^{I/II}$	
1b	1.31 (80)	0.14 (290)	−1.23 (120), −1.45, −1.68 (70)
2b	1.31 (80)	0.10 (280)	−1.23 (100), −1.39, −1.69 (130)
3b	1.30 (90)	0.08 (285)	−1.25 (90), −1.44, −1.66 (130)
4b	1.29 (80)	0.10 (285)	−1.23 (110), −1.44, −1.66 (130)

[a] All measurements were recorded against an Ag/AgCl reference electrode: $E_{1/2,\ Ag/AgCl} = E_{1/2,\ NHE} - 0.222$ V.

The irreversibility of the $Cu^{I/II}$ couple is most likely due to a change in coordination number and stereochemistry upon reduction of Cu^{2+} to Cu^{+}.[22][37][38] This is important since it may impose a kinetic barrier on electron-transfer reactions. It is interesting to note that relatively slow self-exchange rates of 1.5×10^4 M^{-1} s^{-1} have been reported for phenanthrolinecopper complexes.[39] However, an excited-state electron transfer from Ru^{*II} to Cu^{II} in our complexes is possible based on thermodynamic consideration.

Figure 4. Cyclic voltammograms of **2a** (------) and **2b** (——) in CH_3CN



A negative driving force ΔG^0 of -80 kJ mol^{-1} is calculated from the reduction potential E^0_{Red} for $Cu^{I/II}$ (0.10 V), and the excited-state oxidation potential E^{*0}_{Ox} for $Ru^{*II/III}$ (-0.90 V). E^{*0}_{Ox} was obtained according to Equation (1).[40]

$$E^{*0}_{Ox}([M]/[M]^+) = E^0_{Ox}([M]/[M]^+) + E_{0\text{-}0} \qquad (1)$$

$E^0_{Ox}([M]/[M]^+)$ is the oxidation potential of the ground-state molecule and E_{0-0} is the one-electron potential corresponding to the energy of the zero-zero transition (2.26 eV). They were determined from the cyclic voltammograms and the intersection between absorption and emission spectra, respectively.

Another characteristic feature of the $Cu^{I/II}$ redox couple is the broad reduction wave at -0.25 V which appears to consist of two unresolved contributions. This is typical for $[(phen)Cu]^{2+/+}$ complexes and has been ascribed to adsorption processes at the glassy carbon electrode.[36] Similar observations have also been reported for several polynuclear ruthenium complexes.[41]

Cyclic voltammetry and absorption spectroscopy both confirm that the individual properties of the two metal fragments are retained in our Ru^{II}-Cu^{II} complexes. No indication for efficient ground-state electronic coupling between the two metal ions was found. The amino acid bridge acts as an insulator and serves only the purpose of connecting the independent constituents. This observation is important for the following discussion of luminescence properties.

Luminescence Quenching Studies

The $[Ru(bipy)_3]^{2+}$-based emission of **1a−4a** is significantly quenched in the presence of $[Cu(phen)]^{2+}$. This is evident from the emission titration curves shown in Figure 5a. Stern−Volmer plots of the data are found to be non linear (Figure 5b). Saturation is observed at higher copper concentrations. It is therefore concluded that luminescence quenching occurs by intramolecular rather than intermolecular mechanisms.[42][43] This was further supported by titration of $[Ru(bipy)_3]^{2+}$ with $[Cu(phen)(NO_3)_2]$ under similar conditions, where no significant luminescence quenching was detectable. As has been discussed in the previous sections the alkyl bridges in **1b−4b** do not mediate efficient electronic interactions between the metal centers. We therefore propose that a bridged outer-sphere quenching mechanism without direct participation of the bridge in either electron- or energy-transfer processes seems most likely. The alkyl bridge is important for keeping the two metal centers together in a "precursor complex" and is therefore crucial for excited-state interactions even though it does not directly facilitate electronic exchange.

It is obvious from Figure 5a that the titration curves have not reached their minima at a Cu/Ru ratio of 1:1. An excess of copper is necessary to achieve maximum luminescence quenching. Since bimolecular processes have been shown to be negligible this must be a consequence of complex dissociation according to the equilibrium shown below.

$$\mathbf{1a\text{ - }4a} + [Cu(phen)]^{2+} \overset{K}{\rightleftharpoons} \mathbf{1b\text{ - }4b}$$

Luminescence-quenching studies have been employed earlier for the determination of equilibrium constants, K.[44][45][46] Two requirements have to be met for this approach to be valid. The first is that bimolecular processes do not contribute significantly to the observed quenching, as we have already demonstrated for our compounds. The second is a linear dependence of the observed emission intensities on complex concentrations as shown in Equation (2),

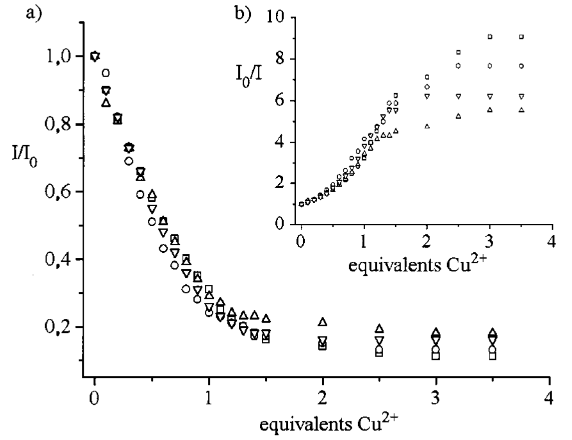
$$I_{obs} = I_{[Ru]} + I_{[Ru\text{-}Cu]} = i_{Ru}\,[Ru] + i_{Ru\text{-}Cu}\,[Ru\text{-}Cu] \qquad (2)$$

where I_{obs} is the observed emission intensity, i_{Ru} and $i_{Ru\text{-}Cu}$ are the molar intensities of the mono- and bimetallic species, respectively, and [Ru] and [Ru-Cu] are the concentrations of the respective complexes in solution. The simple equation (2) generally applies if the absorbance of the solution is smaller than 0.05 at the excitation wavelength, λ_{exc}. This was the case in our studies at ruthenium concentrations of 2.5×10^{-6} M or lower. However, we repeated our experiments at several concentrations ranging from 2.5 $\times 10^{-6}$ M to 1.0×10^{-4} M and found no significant deviations for the obtained K values.

The validity of Equation (2) allows emission intensities to be treated similar to absorbances. Thus, Equation (3) can be derived which relates log K and the equilibrium concentration of free $[Cu(phen)]^{2+}$ to experimentally accessible luminescence data.

I_0 and I_∞ are the luminescence intensities at [Cu] = 0 and [Cu] = ∞, respectively. Computer programs have been developed for the treatment of absorbance data. We have employed the program PSEQUAD[47] for our evaluation of equilibrium constants. Emission intensities have been used instead of absorbances. The results are summarized in Table 3. Most significant is the observed lower stability of the diaminopropionic acid derivative **1b** compared to the three other compounds with increased spacer lengths. The obtained log K values follow the order **1b** < **2b** ≈ **3b** ≈ **4b** and are smaller than those reported in the literature for binary

Figure 5. a)Titrations of **1a** (□), **2a** (○), **3a** (△), and **4a** (▽) (2.5×10^{-6} M, 3 equiv. NaOMe, methanol) with [Cu(phen)(NO_3)$_2$] (2.5×10^{-4} M); intensities are relative to the values obtained at [Cu] = 0. – b) Stern–Volmer plot of the titration curves



$$\log K + \log\,[\mathrm{Cu}]_{eq} = \log\left(\frac{I_{obs} - I_0}{I_\infty - I_{obs}}\right) \qquad (3)$$

copper complexes of amino acids with uncharged side chains such as [Cu(Ala)]$^+$ (log $K = 8.15$) or [Cu(Ile)]$^+$ (log $K = 8.45$).[48]

The electrostatic repulsion between the two positively charged metal ions in our compounds apparently results in a destabilization of the complexes. This explains why **1b** is the least stable derivative in the series since it possesses the shortest alkyl spacer. The differences in stability between the other three compounds are insignificantly small within the experimental errors. This may in part be due to the increased flexibility of the bridges allowing the metal fragments to get closer in space. However, the following discussion of quenching efficiencies in **1b–4b** will support the view that the electrostatic repulsion results in a preference of structures with fully extended alkyl chains.

Table 3. Stability constants of complexes **1b**–**4b** obtained from luminescence spectra in methanol (c[Ru] = 2.5×10^{-6} M) using the program PSEQUAD[47]

Complex	log K
1b	6.76 ± 0.10
2b	7.30 ± 0.15
3b	7.21 ± 0.25
4b	7.32 ± 0.05

Two factors determine the experimentally observed steady-state luminescence intensities at different copper concentrations. The effect of complex stabilities has been discussed in the previous section. The other factor is how efficiently the ruthenium-based emission is quenched in the dinuclear complexes **1b–4b**. Table 4 shows the fraction of **1b–4b**, $x_{\text{Ru-Cu}}$, present in solution at a Ru/Cu ratio of 1:1, together with the corresponding relative luminescence intensities I/I_0 and $(I/I_0)_{100}$ (I = observed steady state emission intensities, I_0 = emission intensity at [Cu] = 0, $(I/I_0)_{100} = I/I_0$ for $x_{\text{Ru-Cu}} = 1$). The relative intensities $(I/I_0)_{100}$ have been calculated from $x_{\text{Ru-Cu}}$ and I/I_0 according to Equation (4).

$$\left(\frac{I}{I_0}\right)_{100} = \frac{\left(\frac{I}{I_0}\right) - (1 - x_{Ru\text{-}Cu})}{x_{Ru\text{-}Cu}} \qquad (4)$$

Table 4. Luminescence quenching data of complexes **1b**–**4b**

Complex	$x_{\text{Ru-Cu}}$[a]	I/I_0[b]	$(I/I_0)_{100}$[c]
1b	0.77	0.31	0.10
2b	0.87	0.24	0.13
3b	0.85	0.29	0.16
4b	0.87	0.26	0.15

[a] Fractions of **1b**–**4b** in solution at [Ru] = [Cu] = 2.5×10^{-6} M. – [b] I = observed emission intensity, I_0 = observed emission intensity at [Cu] = 0. – [c] Calculated value for I/I_0 at $x_{\text{Ru-Cu}} = 1$.

The data shown in Table 4 confirm a dependence of luminescence intensities on the bridge lengths in **1b–4b**. As would be expected intuitively, quenching is most efficient in compound **1b** with the shortest alkyl chain. $(I/I_0)_{100}$ follows the order **1b** < **2b** < **3b** ≈ **4b**. A slightly smaller number is found for **4b** than for **3b**, but the difference is not significant. Interesting in this context are observations made by Osman and Vogler.[49] These authors studied a series of alkyl-bridged naphthalene-Co$^{\text{III}}$ complexes. In contrast to our results, photoinduced electron transfer from naphthalene to Co$^{\text{III}}$ was reported to be most efficient in compounds with longer alkyl chains. This has been explained by an increased flexibility of the bridges resulting in reduced donor-acceptor distances. The opposite bridge-length dependence in our complexes therefore supports the statement made above that electrostatic repulsion between Ru$^{\text{II}}$ and Cu$^{\text{II}}$ forces the alkyl chains in **1b–4b** to adopt a fully extended conformation.

Conclusions

We have designed and synthesized the amino acid bridged heterobimetallic Ru$^{\text{II}}$-Cu$^{\text{II}}$ complexes **1b–4b** as potential photoredox-active DNA-binding and -cleaving reagents. The studies described in this report served to clarify several important questions concerning fundamental structure-function relationships in the complexes.

We were able to demonstrate that **1b–4b** are typical supramolecular systems, i.e. the metal fragments retain their individual ground-state properties. This is important for the prediction of DNA-binding properties since the two functional sites are expected to follow different patterns. Luminescence quenching in our systems was shown to occur only intramolecularly indicating that the bridge efficiently mediates special interactions between the metal centers. A marked dependence of the stability constants and quenching efficiencies on the amino acid bridge structures of **1b–4b** was found. The data suggest that the electrostatic repulsion between Ru$^{\text{II}}$ and Cu$^{\text{II}}$ forces the bridges to adopt a fully extended configuration in solution. These results provide valuable insight into the structural and functional roles of our amino acid ligands in solution.

Further mechanistic investigations will focus on photoinduced electron- or energy-transfer processes, as well as DNA binding and cleavage studies.

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Experimental Section

General Methods: Spectra were recorded with the following instruments: UV/Vis: Shimadzu UV-2101PC. − NIR (acetonitrile solutions): Cary 5G. − IR (KBr pellets): Mattson Polaris FT IR. − Emission: Perkin Elmer LS 50B. − ^{1}H NMR: Bruker Avance DPX 300. All chemical shifts are referenced to residual solvent signals as internal standards previously referenced to TMS, with high-frequency shifts recorded as positive. − ESR: Bruker ESP 300 E. All spectra were recorded at 77 K in frozen methanol. DPPH radical (g = 2.0036) was used to standardize the klystron frequency. − Elemental analysis: Carlo Erba EA 1106. − Cyclic voltammetry was performed with a PAR potentiostat 263 using a three-electrodes cell with glassy carbon working, Ag/AgCl reference and Pt counter electrodes. Acetonitrile solutions of the complexes containing TBAPF$_6$ (10^{-1} M) as supporting electrolyte were used. $E_{1/2}$ values were calculated from half the difference between E_P values for the anodic and cathodic waves from cyclic voltammograms. The ferrocene-ferrocenium couple was observed at 0.45 V (ΔE_P = 88 mV) in acetonitrile under the measurement conditions. − RuCl$_3$ was a donation from Degussa. The synthesis of the $^{\alpha}N$-^{t}Boc-protected (amino acid)ruthenium(II) complexes [{Ru(bipy)$_2$}m-AA-$^{\alpha}N$-^{t}Boc](PF$_6$)$_2$ ($^{\alpha}N$-^{t}Boc-**1a**−**4a**, AA = DAPA, DABA, Orn, Lys) and [{Ru(bipy)$_2$}m-AA] (PF$_6$)$_3$ is described elsewhere.[17] Reagent-grade solvents were obtained from Roth NMR solvents, and all other chemicals, including [Cu(phen)(NO$_3$)$_2$], from Aldrich. Water for preparations was demineralized.

[{Ru(bipy)$_2$}m-AA{Cu(phen)(H$_2$O)}](PF$_6$)$_3$ (AA = DAPA **1b**, DABA **2b**, Orn **3b**, Lys **4b**). − *General Procedure:* A solution of the respective $^{\alpha}N$-protected (amino acid)ruthenium(II) complex [{Ru(bipy)$_2$}m-AA-$^{\alpha}N$-^{t}Boc](PF$_6$)$_2$ in 4 N HCl/dioxane (10 ml) was stirred at 0°C for 1 h. All solvent and excess HCl were removed by rotary evaporation and the residue dried in vacuo overnight. The resulting amine hydrochloride was dissolved in 15 ml of methanol and deprotonated with a solution of NaOMe (1.5 equiv.) in methanol (c = 10^{-1} M). Solid [Cu(phen)(NO$_3$)$_2$] (1.0 equiv.) was added and the suspension stirred at room temperature for 2 h. After the methanol was removed by rotary evaporation, the product was dissolved in 10 ml of water and precipitated with a 1.5-fold excess of NH$_4$PF$_6$ in 1 ml of water. The brown-orange suspension was stirred for 2 h and then the precipitate was isolated by filtration, washed three times with small amounts of water and dried in a desiccator over silica gel. The so obtained products contained varying amounts of water.

[{Ru(bipy)$_2$}m-DAPA{Cu(phen)(H$_2$O)}](PF$_6$)$_3$ (**1b**): Yield: 219 mg (78%). − $C_{47}H_{41}CuF_{18}N_{10}O_4P_3Ru\cdot H_2O$ (1409.4·H$_2$O): calcd. C 39.55, H 3.04, N 9.81; found C 39.66, H 3.17, N 9.53. − ^{1}H NMR (300 MHz, CD$_3$OD, all signals broad): δ = 2.59 (s, 3 H, m4′-CH$_3$); 7.35 (s, 1 H, m5′); 7.47 (s, 4 H, b5); 7.62 (d, 1 H, m5); 7.79−7.94 (m, 6 H, 4 × b6, m6, m6′); 8.09 (m, 4 H, b4); 8.63 (m, 5 H, 4 × b3, m3′). − IR (KBr): ν = 3115 cm^{-1} (m), 3087 (m), 2930 (m), 1650 (s, COO$^-$), 1542 (m), 1465 (m), 1431 (m), 1312 (m), 1270 (m), 1239 (m), 1107 (m), 843 (vs, PF$_6^-$), 766 (s), 727 (m), 558 (s). − UV/Vis (CH$_3$OH): λ_{max} (lg ε) = 455 nm (4.22), 288 (4.96), 256 (4.66).

[{Ru(bipy)$_2$}m-DABA{Cu(phen)(H$_2$O)}](PF$_6$)$_3$ (**2b**): Yield: 225 mg (79%). − $C_{48}H_{43}CuF_{18}N_{10}O_4P_3Ru\cdot 0.5\ H_2O$ (1423.4·0.5 H$_2$O): calcd. C 40.25, H 3.09, N 9.78; found C 40.28, H 2.80, N 9.67. − ^{1}H NMR (300 MHz, CD$_3$OD, all signals broad): δ = 2.59 (s, 3 H, m4′-CH$_3$); 7.36 (s, 1 H, m5′); 7.48 (s, 4 H, b5); 7.62 (s, 1 H, m5); 7.80 (d, 5 H, 4 × b6, m6′); 7.92 (m, 1 H, m6); 8.11 (s, 4 H, b4); 8.64 (t, 5 H, 4 × b3, m3′); 8.97 (d, 1 H, m3). − IR (KBr): ν = 3084 cm^{-1} (m), 2928 (m), 2862 (m), 1650 (s, COO$^-$), 1541 (m), 1463 (m), 1432 (m), 1400 (m), 1313 (m), 1270 (m), 1239 (m), 1107 (m), 842 (vs, PF$_6^-$), 766 (s), 727 (m), 558 (s). − UV/Vis (CH$_3$OH): λ_{max} (lg ε) = 455 nm (4.17), 288 (4.90), 256 (4.61).

[{Ru(bipy)$_2$}m-Orn{Cu(phen)(H$_2$O)}](PF$_6$)$_3$ (**3b**): Yield: 232 mg (81%). − $C_{49}H_{45}CuF_{18}N_{10}O_4P_3Ru$ (1437.5): calcd. C 40.97, H 3.09, N 9.74; found C 41.18, H 3.09, N 9.57. − ^{1}H NMR (300 MHz, CD$_3$OD, all signals broad): δ = 2.59 (s, 3 H, m4′-CH$_3$); 7.35 (d, 1 H, m5′); 7.47 (m, 4 H, b5); 7.61 (m, 1 H, m5); 7.79 (m, 5 H, 4 × b6, m6′); 7.92 (m, 1 H, m6); 8.09 (m, 4 H, b4); 8.64 (t, 5 H, 4 × b3, m3′); 8.95 (s, 1 H, m3). − IR (KBr): ν = 3086 cm^{-1} (m), 2930 (m), 2869 (m), 2862 (m), 1650 (s, COO$^-$), 1542 (m), 1465 (m), 1444 (m), 1431 (m), 1392 (m), 1312 (m), 1270 (m), 1239 (m), 1107 (m), 844 (vs, PF$_6^-$), 766 (s), 727 (m), 558 (s). − UV/Vis (CH$_3$OH): λ_{max} (lg ε) = 455 nm (4.22), 287 (4.94), 256 (4.64).

[{Ru(bipy)$_2$}m-Lys{Cu(phen)(H$_2$O)}](PF$_6$)$_3$ (**4b**): Yield: 296 mg (68%). − $C_{50}H_{47}CuF_{18}N_{10}O_4P_3Ru\cdot 2.5\ H_2O$ (1451.5·2.5 H$_2$O): calcd. C 40.13, H 3.50, N 9.36; found C 40.05, H 3.26, N 9.21. − ^{1}H NMR (300 MHz, CD$_3$OD, all signals broad): δ = 2.59 (s, 3 H, m4′-CH$_3$); 7.34 (s, 1 H, m5′); 7.47 (s, 4 H, b5); 7.60 (s, 1 H, m5); 7.79 (s, 5 H, 4 × b6, m6′); 7.91 (s, 1 H, m6); 8.10 (s, 4 H, b4); 8.66 (s, 5 H, 4 × b3, m3′); 8.95 (d, 1 H, m3). − IR (KBr): ν = 3080 cm^{-1} (m), 2930 (m), 2869 (m), 1650 (s, COO$^-$), 1542 (m), 1465 (m), 1445 (m), 1432 (m), 1312 (m), 1271 (m), 1239 (m), 1107 (m), 842 (vs, PF$_6^-$), 766 (s), 728 (m), 558 (s). − UV/Vis (CH$_3$OH): λ_{max} (lg ε) = 455 nm (4.25), 288 (4.96), 255 (4.64).

Titration Curves: Emission titration curves were followed by uncorrected luminescence spectra obtained with a Perkin Elmer LS 50B spectrophotometer (λ_{exc} = 400 nm, λ_{obs} = 500−690 nm). 25 ml of 2.5−10 × 10^{-6} M solutions of the complexes [{Ru(bipy)$_2$}m-AA](PF$_6$)$_3$ in methanol, containing 3.0 equiv. of NaOMe to yield the deprotonated complex form, were titrated with 2.5−10 × 10^{-4} M solutions of [Cu(phen)(NO$_3$)$_2$] in methanol. The solutions were deaerated by bubbling with dry nitrogen for at least 10 min prior to each measurement. The results were evaluated using the program PSEQUAD.[47]

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