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Synthesis and characterisation of *N*-1,10-phenanthrolin-5-ylalkylamides and their photosensitising heteroleptic Ru(II) complexes

Pedro Ramiro, David García-Fresnadillo and Guillermo Orellana*

Laboratory of Applied Photochemistry, Department of Organic Chemistry, Faculty of Chemistry, Universidad Complutense de Madrid, E-28040 Madrid, Spain

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Abstract—In the context of our studies on ruthenium(II) complexes containing polyazaheterocyclic ligands as functionalised photosensitisers for singlet molecular oxygen generation in heterogeneous phase, we describe the synthesis and spectroscopic characterisation of different amide-functionalised *N*-1,10-phenanthrolin-5-ylalkylamides. These chelators are used to obtain heteroleptic $[Ru(phen)_2\mathbf{L}]^{2+}$ complexes, where **L** stands for 2-iodo-*N*-1,10-phenanthrolin-5-ylacetamide (5-iap), 4-oxo-4-(1,10-phenanthrolin-5-ylamino)butanoic acid (5-suap), 5-oxo-5-(1,10-phenanthrolin-5-ylamino)pentanoic acid (5-glap) and *tert*-butyl 4-oxo-4-(1,10-phenanthrolin-5-ylamino)butylcarbamate (BOC-5-ngap). The spectroscopic data, excited state lifetimes and quenching rate constants with O_2 (ca. 3.7×10^9 L mol^{-1} s^{-1}) of these novel complexes are also reported.

1. Introduction

Ruthenium(II) complexes with polyazaaromatic chelating ligands have been widely studied because of their unique spectroscopic, photochemical and redox properties.[1,2] Since 1959, when the luminescence of tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, was described for the first time,[3] these structures have been used in many areas of chemistry, such as photonic and optoelectronic devices,[4] luminescent probes for micelles and other organised media,[5] artificial photonucleases and photochemical reporters of the rich DNA morphology,[6] development of therapeutic agents,[7] constituents of supramolecular edifices,[8] chemiluminescent analytical reagents[9] and luminescent indicator dyes for optochemical sensing,[10] to name just a few.

The variety of applications for these complexes does not end here: due to their microsecond excited state lifetimes and the diffusion-controlled O_2 quenching rate constants, they display a high quantum yield of singlet (molecular) oxygen, abbreviated $O_2(^1\Delta_g)$, production (Φ_Δ).[11,12] For instance, a Φ_Δ of 1.0 has been measured for tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) in methanol solution.[12] Such reactive oxygen species, typically generated by electronic energy transfer from the triplet excited state of certain dyes (methylene blue, rose bengal, phenalenone, porphyrins,…),[13] are useful for photosensitised oxidation of organic compounds and fine chemicals synthesis,[14,15] molecular probing of microheterogeneous systems,[16] as the 'magic bullet' in photodynamic therapies (PDT)[17] and water disinfection.[18,19] For both synthetic and disinfection purposes, immobilisation of the photosensitising dye onto a solid support allows an easy removal after fulfilling its function.

The spectroscopic, photophysical and photochemical features of Ru(II) polypyridyl complexes may be finely tuned by a judicious molecular design of the heterocyclic chelating ligands in the co-ordination sphere. Moreover, introduction of different ligands around the metal centre (so-called heteroleptic complexes) provides an even finer tuning of their properties and allows introduction of suitable chemical groups for covalent attachment to functionalised solid supports.

In this work, we describe the synthesis of a family of *N*-1,10-phenanthrolin-5-ylalkylamide ligands (**L**) containing a spacer and an electrophilic or nucleophilic end group to tether the corresponding heteroleptic Ru(II) complex to either organic or inorganic polymer supports bearing the opposite chemical function. Phen (1,10-phenanthroline) has

Keywords: 1,10-Phenanthroline; Ruthenium(II) complexes; Polyazaheterocyclic ligands; Singlet oxygen; Photosensitisers.
* Corresponding author. Tel.: +34 913944220; fax: +34 913944103; e-mail: orellana@quim.ucm.es

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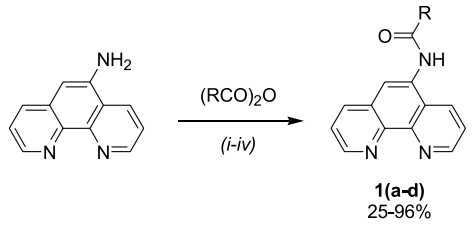
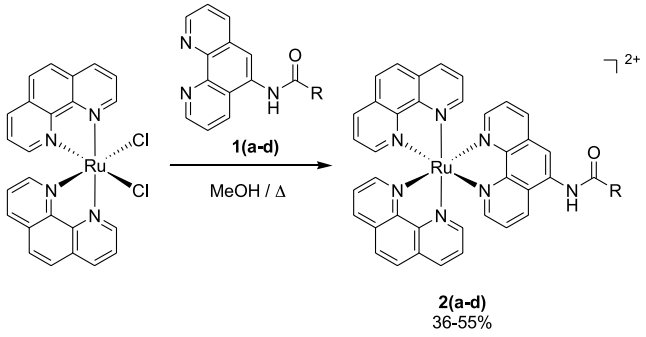
been selected as the ancillary ligand to maximise the emission lifetime and Φ_Δ of the sensitising dye.[11] Such molecular engineering aims to impart the immobilised $[Ru(phen)_2L]^{2+}$ complex the widest compatibility with the solvent (i.e., both aqueous and organic media) for water treatment[20] and synthetic purposes,[14] and to serve as oxygen-sensitive luminescent materials for optosensor development.[10,21,22]

While some work on chemical derivatisation of 1,10-phenanthrolin-5-amine (5-ap) has been reported for introducing long alkyl chains[23] or biomolecular labelling,[24–27] we have developed general procedures for the (difficult) acylation of 5-ap using carboxylic acid anhydrides. In this way, the functionalised phen ligands **1** were prepared (Scheme 1) and fully characterised by NMR, as well as their corresponding heteroleptic Ru(II) complexes **2** (Scheme 2).



Scheme 1. Conditions: (i) **1a**: $(ICH_2CO)_2O/CHCl_3/\Delta$; (ii) **1b**: $(COCH_2CH_2CH_2CO)O/PTSA/CHCl_3$; (iii) **1c**: $(COCH_2CH_2CH_2CO)O/PTSA/CHCl_3$; (iv) **1d**: (1) $ClCO_2Et/Et_3N$, (2) BOC-GABA-OH/$CHCl_3$.



Scheme 2.

In addition to their structural characterisation, the absorption and luminescence spectra, the emission lifetimes and the excited state quenching rate constants with dissolved oxygen have been determined for the novel sensitisers in acetonitrile solution. Proof of singlet oxygen generation in this solvent, using its phosphorescence at 1270 nm, is provided.

2. Results and discussion

The synthesis of the functionalised *N*-1,10-phenanthrolin-5-ylalkylamides (**1a–d**) is carried out by the reaction between 1,10-phenanthrolin-5-amine and different anhydrides either from commercial sources or prepared in situ, modifying some methods described in the literature[26,28,29] (Scheme 1). This reaction takes place with moderate to excellent yields (25–96%) (Table 1) and is a simple way to obtain such ligands in only one step. The usual low yields are related to steric hindrance to the approach of the electrophile due to the peri hydrogen atom in the 4-position. Actually, the highest chemical yield is obtained with the smallest carboxylic acid anhydride (iodoacetic), an improvement over the literature procedure.[24]

Table 1. Chemical yields of the synthesis of *N*-1,10-phenanthrolin-5-ylalkylamides (**1a–d**) and their corresponding heteroleptic Ru(II) complexes (**2a–d**)

R	Ligand	Yield (%)	Complex	Yield (%)
CH_2I	**1a**	96	**2a**	55
$(CH_2)_2CO_2H$	**1b**	25	**2b**	36
$(CH_2)_3CO_2H$	**1c**	43	**2c**	47
$(CH_2)_3NHCO_2C(CH_3)_3$	**1d**	42	**2d**	46

Protection of the ω-amino group with BOC is required to avoid competition in the amide formation step of phenanthroline **1d** (Scheme 1). Facile deprotection of the *tert*-butyloxycarbonyl moiety can be carried out with acetyl chloride in methanol.[30]

Once the functionalised phenanthrolines are prepared, they are used for the synthesis of heteroleptic ruthenium(II) complexes. The reaction of *cis*-dichloro-bis-(1,10-phenanthroline)ruthenium(II), $Ru(phen)_2Cl_2$, and the chelating ligands (**1a–d**) in methanol affords the complexes (**2a–d**) (Scheme 2) in moderate yields (36–55%) after repeated precipitation as PF_6^- salts (Table 1). The chemical composition and structure of these novel complexes has been confirmed by the usual spectroscopic methods (high-field ^1H and ^{13}C NMR, electrospray ionisation MS and elemental analysis).

The ^1H NMR signals are characteristic of the Ru(II) polypyridyl complexes, taking into account the combined effects on the chemical shifts of electronic σ-donation to the metal centre, π-back-bonding to the ligand and magnetic anisotropy of the heterocyclic rings.[31] The α,β and γ protons of the phenanthroline ring appear separately in the aromatic region ($\delta_\gamma > \delta_\alpha > \delta_\beta$).[5] The CH_2 singlet from the amide side chain is duplicated in the case of **2a**, and two signals are observed in 7:3 area ratio. A similar pattern appears in **2c**, where two of the three methylene groups display duplicate signals (3:2 area ratio). The NH proton is also observed twice for **2a** and **2c** in the same ratio described above. Duplication of some signals is observed also in the ^{13}C NMR spectra of those Ru(II) complexes, especially those corresponding to the carbonyl and the side chain methylene groups. As no signal duplication is observed in any of the free ligands, restricted rotation around the $C5_{phen}–N_{amide}$ bond could explain these experimental facts. The strong electron-withdrawing character of the metal complex increases the order of such single bond due to enhanced mesomeric effect of the aminocarbonyl group.

The base peak in the ESI mass spectra of these complexes corresponds to the $[M]^{2+}$ ion. In case of having a carboxylic acid moiety on the side chain, the $[M-H_2O]^{2+}$ ion is observed instead. No abundant fragments are detected together with the molecular ions.

Spectroscopic and photophysical data of the novel Ru(II) complexes (**2a**–**d**) have also been measured (Table 2). Their absorption spectra display bands in two regions, an intense one around 265 nm that may be ascribed to the ligand-centred π–π* transition, and a maximum that corresponds to the metal-to-ligand charge transfer (MLCT) d–π* transition at approximately 450 nm. Regardless the absorption maximum, all the complexes show strong emission peaking around 595 nm. Similar values have been reported for the homoleptic tris-phenanthroline complex.[2]

The excited state lifetimes (τ) of these novel photosensitisers were measured in N_2-saturated, air-equilibrated and O_2-purged acetonitrile solutions (Table 2). In the absence of dioxygen, the emission lifetimes of the heteroleptic Ru(II) complexes (**2a**–**d**) are ca. 700 ns, a value slightly lower than that of $[Ru(phen)_3]^{2+}$. Therefore, introduction of the amide group and functionalised side chain in the 5-position of the phen ligand does not perturb significantly the electronic features of the metal complex and provides a high efficiency of excited state quenching by O_2 (80% of the ^{3}MLCT states produced are deactivated by O_2 in the air-equilibrated solvent, Table 2). The sensitiser quenching rate constants (k_q) in acetonitrile can be determined from the observed (linear) Stern–Volmer relationships ($\tau_0/\tau = 1 + k_q\tau_0[O_2]$).[32] The calculated k_q values (Table 2) are close to 4×10^9 L mol^{-1} s^{-1}, a value near the diffusion control limit at room temperature. These photochemical parameters also make them highly suitable for luminescence oxygen sensing with fibre-optic probes.[10]

Moreover, we have confirmed the production of singlet (molecular) oxygen from the O_2 quenching of the excited state of the novel photosensitisers. Laser-flash illumination in the visible of an aerated acetonitrile solution of any of the Ru(II) complexes (**2a**–**d**) followed by time-resolved detection at 1270 nm (the characteristic $^1O_2$ phosphorescence maximum)[13] affords the typical decay kinetics and emission spectrum of $^1O_2$ (Fig. 1, $^1O_2$ generation by **2d** as a representative member of the family). The emission decay traces have to be fit to a biexponential function due to interference from the wide luminescence band of the photoexcited Ru(II) complex, which is not fully quenched by O_2 under air-saturated conditions.

3. Conclusions

The novel amido-functionalised Ru(II) complexes will allow us to prepare solid-supported photosensitisers containing the covalently bonded dye. Using easy straightforward synthetic procedures, we may attach the efficient $^1O_2$ generators to activated organic and inorganic polymer materials, such as polystyrene, silica gel or glass beads, for water/air disinfection, $^1O_2$-mediated photooxidation reactions or chemical optosensors. These fields are currently being explored in our laboratory.

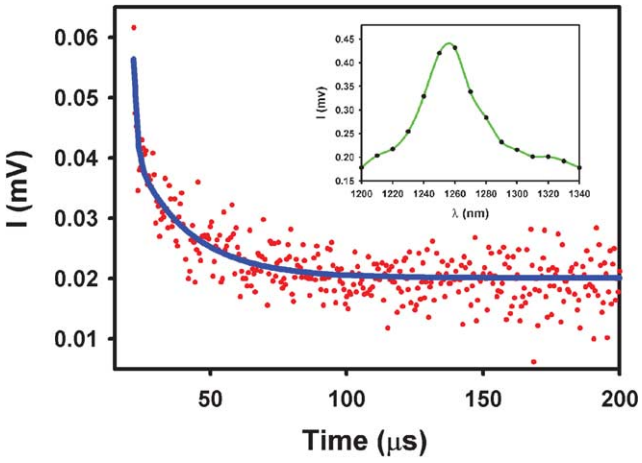


Figure 1. Decay of the emission signal at 1270 nm after laser-flash excitation of an air-equilibrated acetonitrile solution of photosensitising complex **2d**. The solid line through the experimental points represents the best fit to the function $I(t) = 0.02 + 0.0047\exp(-t/4.1) + 0.0148\exp(-t/21)$. Inset: emission spectrum recorded 2.5 μs after the laser pulse.

4. Experimental

4.1. General

All reagents were commercial grade and were used as received unless otherwise stated. 1,10-Phenanthrolin-5-amine (5-ap) was obtained from 5-nitro-1,10-phenanthroline (Aldrich) as previously described by Nasielski-Hinkens et al.[33] $Ru(phen)_2Cl_2$ was prepared according to the procedure reported by Sullivan et al.[34]

Melting points were measured with a Bibby-Sterilin apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at the UCM NMR Central Instrumentation Facilities on a Bruker AC-200 at 200 MHz for ^{1}H and 50 MHz for ^{13}C, or on a Bruker AMX-500 at 500 MHz for ^{1}H and 125 MHz for ^{13}C. $CDCl_3$, CD_3CN, MeOH-d_4 and

Table 2. Wavelengths of the absorption and emission maximums, ^{3}MLCT excited state lifetimes, O_2 quenching constants and fraction of triplets quenched by O_2 for the Ru(II) complexes (**2a**–**d**) in acetonitrile solution at 25 °C

Complex	λ_{abs}^{max} (nm)[a]	λ_{em}^{max} (nm)[a,b]	τ (N_2) (ns)[c]	τ (air) (ns)[c]	$\tau(O_2)$ (ns)[c]	$k_q\times10^{-9}$ (L mol^{-1} s^{-1})[d]	$P_{O_2}^T$ (air)[e]	$P_{O_2}^T$ (O_2)[e]
2a	263, 446	596	716	142	33	3.6	0.80	0.95
2b	262, 446	594	645	144	33	3.6	0.78	0.95
2c	263, 448	593	629	138	31	3.8	0.78	0.95
2d	263, 447	593	696	139	31	3.8	0.80	0.96

[a] Estimated uncertainty ±1 nm.
[b] Uncorrected for the instrument response function.
[c] Estimated uncertainty ±3%.
[d] From the Stern–Volmer lifetime quenching plot (see text); estimated uncertainty ±4%.
[e] Calculated from the equation: $P_{O_2}^T = 1 - (\tau/\tau_0)$.

DMSO-d_6 (Cambridge Isotope Laboratories) were used as solvents. The chemical shifts (δ_H and δ_C) are given from the residual $CHCl_3$ signal (7.26 and 77.0 ppm, respectively). Coupling constants (J) are given in Hz. Electron impact (EI) mass spectra were carried out on a HP 5989A quadrupole instrument at 70 eV with a source temperature of 250 °C. Electrospray ionisation (ESI) mass spectra were obtained on a Bruker Esquire-LC™ apparatus using 3500 V as ionisation voltage, N_2 as nebuliser gas and methanol as solvent. Both instruments belong to the UCM MS Central Instrumentation Facilities. TLC analyses and column chromatography were performed on silica gel $60F_{254}$ plates (Merck) and on silica gel 60 (Merck, 70–230 mesh), respectively.

UV–vis absorption spectra were recorded with a Varian Cary-3Bio spectrophotometer. Emission spectra were obtained with a Perkin-Elmer LS-5 spectrofluorometer at 25 °C and are uncorrected for the instrumental response. Emission lifetimes of the Ru(II) complexes were measured with an Edinburgh Instruments LP-900 laser kinetic spectrometer equipped with a frequency-doubled Nd:YAG laser (Minilite II, Continuum, USA) for excitation at 532 nm (15 mJ per 3 ns pulse) and a red-sensitive Hamamatsu R-928 photomultiplier. Decay traces were recorded at 595 nm through a 550 nm cut-off filter with a Tektronix TDS 340A digital oscilloscope, in N_2-saturated, air-equilibrated and O_2-purged photosensitiser solutions in spectroscopic-grade acetonitrile dried over 3 Å molecular sieves for more than one week. Measurements were carried out after purging the solution with the corresponding gas for at least 30 min. After transmission to a PII computer, the kinetic parameters were extracted by exponential non-linear least squares fitting to the experimental data using the original EI software. $^1O_2$ phosphorescence decay traces were recorded at 1270 nm with an Edinburgh Instruments EI-P N_2-cooled fast Ge diode.

4.2. Preparation of *N*-1,10-phenanthrolin-5-ylalkylamides, 1

4.2.1. Synthesis of phenanthrolines 1a, 1b and 1c. A mixture of 1,10-phenanthrolin-5-amine (195 mg, 1 mmol) and the corresponding anhydride (iodoacetic anhydride: 425 mg, 1.2 mmol; succinic anhydride: 500 mg, 5 mmol; glutaric anhydride: 685 mg, 6 mmol, for **1a**, **1b** and **1c**, respectively), was dissolved in 30 mL of anhydrous $CHCl_3$ at room temperature under argon. In the case of phenanthrolines **1b** and **1c**, *p*-toluensulfonic acid (PTSA, 38 mg, 0.2 mmol) was also added as catalyst.

After refluxing the reaction mixture for 2–3 days, an insoluble precipitate was observed. It was filtered, washed with chloroform and dried. Finally, the product was recristallised in the appropriate solvent.

4.2.1.1. 2-Iodo-*N*-1,10-phenanthrolin-5-ylacetamide, 5-iap, 1a. Filtration of reaction mixture afforded 349 mg (96%) of a yellow solid, mp 180 °C (with decomposition) ($CHCl_3$); δ_H (200 MHz, DMSO-d_6): 4.10 (s, 2H, CH_2), 8.06 (dd, 1H$_\beta$, J=8.2, 4.2 Hz), 8.10 (dd, 1H$_\beta$, J=8.2, 4.2 Hz), 8.42 (s, 1H), 8.88 (d, 1H$_\gamma$, J=8.2 Hz), 8.91 (d, 1H$_\gamma$, J=8.2 Hz), 9.16 (d, 1H$_\alpha$, J=4.2 Hz), 9.27 (d, 1H$_\alpha$, J=4.2 Hz), 10.73 (s, 1H, NH); δ_C (50 MHz, DMSO-d_6): 0.92 (CH_2), 118.93 (CH), 124.51, 124.86 (CH$_\beta$), 128.84, 132.40 (C), 133.53 (CH$_\gamma$), 138.25 (C), 140.56 (CH$_\gamma$), 141.16 (C), 146.73, 149.48 (CH$_\alpha$), 168.21 (CO); *m/z* (EI, 70 eV): 363 ($M^{+\cdot}$, 3), 236 ($M^{+\cdot}-I$, 100), 196 (5-NH_2phen$^{+\cdot}$+H, 83), 168 ($NHCOCH_2I^{+\cdot}$, 83), 127 ($I^{+\cdot}$, 63). Anal. Calcd for $C_{14}H_{10}IN_3O\cdot CHCl_3$: C, 37.34; H, 2.30; N, 8.71%, found: C, 37.13; H, 2.57; N, 9.15%.

4.2.1.2. 4-Oxo-4-(1,10-phenanthrolin-5-ylamino)butanoic acid, 5-suap, 1b. Precipitation of the crude product with methanol afforded 74 mg (25%) of a white solid, mp 188–190 °C (MeOH); δ_H (200 MHz, DMSO-d_6): 2.62 (t, 2H, J=6.2 Hz, CH_2), 2.79 (t, 2H, J=6.2 Hz, CH_2), 7.74 (dd, 1H$_\beta$, J=8.3, 4.3 Hz), 7.81 (dd, 1H$_\beta$, J=8.3, 4.3 Hz), 8.43 (dd, 1H$_\gamma$, J=8.3, 1.5 Hz), 8.65 (dd, 1H$_\gamma$, J=8.3, 1.5 Hz), 9.03 (dd, 1H$_\alpha$, J=4.3, 1.5 Hz), 9.12 (dd, 1H$_\alpha$, J=4.3, 1.5 Hz), 10.22 (s, 1H, NH), 12.25 (br s, 1H, CO_2H); δ_C (50 MHz, DMSO-d_6): 28.92, 30.63 (CH_2), 119.93 (CH), 122.72, 123.49 (CH$_\beta$), 124.69, 128.00 (C), 131.74 (CH$_\gamma$), 131.80 (C), 135.72 (CH$_\gamma$), 143.73, 145.74 (C), 149.23, 149.77 (CH$_\alpha$), 171.38 (CO_2H), 173.87 (NHCO); *m/z* (EI, 70 eV): 295 ($M^{+\cdot}$, 6), 277 ($M^{+\cdot}-H_2O$, 100), 249 ($M^{+\cdot}-HCO_2H$, 23), 195 (5-NH_2phen$^{+\cdot}$, 46). Anal. Calcd for $C_{16}H_{13}N_3O_3\cdot CH_3OH$: C, 62.38; H, 5.38; N, 12.84%, found: C, 62.08; H, 5.63; N, 12.44%.

4.2.1.3. 5-Oxo-5-(1,10-phenanthrolin-5-ylamino)pentanoic acid, 5-glap, 1c. Filtration of reaction mixture afforded 133 mg (43%) of a white solid, mp 233–235 °C ($CHCl_3$); δ_H (200 MHz, DMSO-d_6): 1.92 (q, 2H, J=7.3 Hz, CH_2), 2.38 (t, 2H, J=7.3 Hz, CH_2), 2.60 (t, 2H, J=7.3 Hz, CH_2), 7.75 (dd, 1H$_\beta$, J=8.3, 4.1 Hz), 7.83 (dd, 1H$_\beta$, J=8.3, 4.1 Hz), 8.19 (s, 1H), 8.46 (dd, 1H$_\gamma$, J=8.3, 1.6 Hz), 8.62 (dd, 1H$_\gamma$, J=8.3, 1.6 Hz), 9.04 (dd, 1H$_\alpha$, J=4.1, 1.6 Hz), 9.14 (dd, 1H$_\alpha$, J=4.1, 1.6 Hz), 10.14 (s, 1H, NH), 12.15 (br s, 1H, COOH); δ_C (50 MHz, DMSO-d_6): 20.52, 33.05, 34.98 (CH_2), 119.85 (CH), 122.83, 123.54 (CH$_\beta$), 124.63, 128.10 (C), 131.83, 136.06 (CH$_\gamma$), 143.20, 145.34 (C), 148.91, 149.65 (CH$_\alpha$), 171.96 (CO_2H), 174.15 (NHCO); *m/z* (ESI)=332 $[M+Na]^+$, 310 $[M+H]^+$. Anal. Calcd for $C_{17}H_{15}N_3O_3\cdot CHCl_3$: C, 50.43; H, 3.76; N, 9.80%, found: C, 50.38; H, 4.06; N, 10.04%.

4.2.2. Synthesis of phenanthroline 1d. 1,10-Phenanthrolin-5-amine (195 mg, 1 mmol) was dissolved in 30 mL of $CHCl_3$ and cooled at 0 °C under argon with an ice-water bath. Triethylamine (405 mg, 4 mmol) and ethyl chloroformate (434 mg, 4 mmol) were then added and the reaction mixture was stirred at this temperature for 30 min. Then, 4-(*tert*-butyloxycarbonylamino)butyric acid (BOC-GABA-OH, 406 mg, 2 mmol) was added. The mixture was allowed to reach room temperature and refluxed for 4 days. The reaction progress was monitored by TLC.

The reaction mixture was treated with an aqueous HCl (pH 4) solution (2×25 mL), the organic layer was separated and washed successively with water (2×25 mL), Na_2CO_3-saturated aqueous solution (2×25 mL) and water (2×25 mL). Finally, it was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography using dichloromethane/acetone 1:2 (v/v) as the eluent.

4.2.2.1. *tert*-Butyl 4-oxo-4-(1,10-phenanthrolin-5-ylamino)butylcarbamate, BOC-5-ngap, 1d. Purification of the crude product by column chromatography afforded 160 mg (42%) of a yellow oil; δ_H (500 MHz, $CDCl_3$): 1.51 (s, 9H, $3CH_3$), 2.00 (m, 2H, CH_2), 2.71 (t, 2H, $J=6.4$ Hz, CH_2), 3.36 (c, 2H, $J=6.2$ Hz, CH_2), 5.20 (t, 1H, $J=6.2$ Hz, NH), 7.58 (dd, $1H_\beta$, $J=8.2$, 4.2 Hz), 7.67 (dd, $1H_\beta$, $J=8.2$, 4.2 Hz), 8.26 (dd, $1H_\gamma$, $J=8.2$, 0.9 Hz), 8.45 (s, 1H), 8.89 (dd, $1H_\gamma$, $J=8.2$, 0.9 Hz), 9.00 (dd, $1H_\alpha$, $J=4.2$, 0.9 Hz), 9.10 (dd, $1H_\alpha$, $J=4.2$, 0.9 Hz), 10.31 (s, 1H, NH); δ_C (50 MHz, $CDCl_3$): 26.57 (CH_2), 28.07 (CH_3), 33.87, 39.33 (CH_2), 79.21 (CMe_3), 119.39 (CH), 122.17, 122.91 (CH_β), 124.21, 127.82, 130.87 (C), 131.06, 135.51 (CH_γ), 143.38, 145.39 (C), 148.74, 149.15 (CH_α), 156.81 ($NHCO_2$), 172.98 (NHCO); *m/z* (EI, 70 eV) $=380$ ($M^{+\cdot}$, 6), 324 ([$M^{+\cdot}+H$]–$C(CH_3)_3$, 12), 307 ($M^{+\cdot}-OC(CH_3)_3$, 5), 195 (5-NH_2phen$^{+\cdot}$, 100). Anal. Calcd for $C_{21}H_{24}N_4O_3$: C, 66.30; H, 6.36; N,14.73%, found: C, 65.96; H, 6.31; N, 15.02%.

4.3. Preparation of [bis(1,10-phenanthroline)(*N*-1,10-phenanthrolin-5-ylalkylamide)]ruthenium(II) complexes, $[Ru(phen)_2(5\text{-}(N\text{-}COR)phen)](PF_6)_2$, 2: general procedure

A mixture of the corresponding *N*-1,10-phenanthrolin-5-ylalkylamide **1** (0.450 mmol) and *cis*-dichloro-bis(1,10-phenanthroline)ruthenium(II), $Ru(phen)_2Cl_2$ (200 mg, 0.375 mmol), was dissolved in 30 mL of methanol at room temperature under argon atmosphere. The reaction mixture was refluxed with stirring during 1–2 days. The evolution of the reaction was monitored by TLC. Then the mixture was concentrated at reduced pressure and 1 mL of a saturated ammonium hexafluorophosphate (Fluka) aqueous solution was added. Water was subsequently added to favour precipitation of the product, which was then filtered and washed with plenty of water. The complex was reprecipitated from a methanol/water mixture and finally dried under vacuum (40 °C, 0.1 Torr).

4.3.1. [Bis(1,10-phenanthroline)(2-iodo-*N*-1,10-phenanthrolin-5-ylacetamide)]ruthenium(II) bis(hexafluorophosphate), $[Ru(phen)_2(5\text{-}iap)](PF_6)_2$, 2a. Filtration of the product affords 230 mg (55%) of an orange solid; δ_H (500 MHz, CD_3CN): 4.12 (s, 0.6H, CH_2), 4.47 (s, 1.4H, CH_2), 7.60–7.71 (m, $6H_\beta$), 7.98–8.11 (m, $6H_\alpha$), 8.28 (s, 4H), 8.61–8.64 (m, $4H_\gamma$), 8.65–8.76 (m, $2H_\gamma$), 9.40 (s, 0.3H, NH), 9.45 (s, 0.7H, NH); δ_C (125 MHz, CD_3CN): 0.01, 0.57 (CH_2), 121.13, 121.89, 126.43, 126.88, 127.03, 127.07 (CH), 127.94 (C), 129.03 (CH), 131.53, 131.58, 131.99, 132.00 (C), 132.97, 133.25 (CH), 134.10, 134.40 (C), 137.32, 137.37, 137.78 (CH), 147.00, 148.87, 148.90, 148.92, 148.93, 149.37 (C), 153.23, 153.40, 153.92, 153.95, 154.03, 154.06, 154.08 (CH), 166.85 (CO), 168.69 (CO); *m/z* (ESI) $=412.5$ $[M]^{2+}$. Anal. Calcd for $[C_{38}H_{26}IN_7ORu](PF_6)_2$: C, 40.95; H, 2.35; N, 8.80%, found: C, 40.63; H, 2.41; N, 8.64%.

4.3.2. [Bis(1,10-phenanthroline)(4-oxo-4-(1,10-phenanthrolin-5-ylamino)butanoic acid)]ruthenium(II) bis(hexafluorophosphate), $[Ru(phen)_2(5\text{-}suap)](PF_6)_2$, 2b. Filtration of the product afforded 141 mg (36%) of an orange solid; δ_H (500 MHz, CD_3CN): 2.77 (t, 2H, $J=6.2$ Hz, CH_2), 2.92 (t, 2H, $J=6.2$ Hz, CH_2), 7.59 (dd, $1H_\beta$, $J=8.3$, 5.0 Hz), 7.62–7.69 (m, $5H_\beta$), 7.96 (d, $1H_\alpha$, $J=5.0$ Hz), 8.02–8.08 (m, $5H_\alpha$), 8.27 (s, 4H), 8.55 (d, $1H_\gamma$, $J=8.3$ Hz), 8.61–8.63 (m, $4H_\gamma$, 1H), 8.73 (d, $1H_\gamma$, $J=8.3$ Hz), 8.97 (s, 1H, NH); δ_C (125 MHz, CD_3CN): 29.14, 30.30 (CH_2), 119.70 (C), 125.68, 126.29, 126.36 (CH), 127.24 (C), 128.44 (CH), 131.19, 131.40, 131.42 (C), 132.63 (CH), 134.29 (C), 136.65, 137.18 (CH), 137.26, 146.18, 148.31, 148.34, 148.75 (C), 152.35, 153.32, 153.43, 153.47 (CH), 172.15 (CO), 173.63 (CO); *m/z* (ESI) $=369.5$ $[M-H_2O]^{2+}$. Anal. Calcd for $[C_{40}H_{29}N_7O_3Ru](PF_6)_2$: C, 45.90; H, 2.79; N, 9.37%, found: C, 45.54; H, 2.57; N, 9.23%.

4.3.3. [Bis(1,10-phenanthroline)(5-oxo-5-(1,10-phenanthrolin-5-ylamino)pentanoic acid)]ruthenium(II) bis(hexafluorophosphate), $[Ru(phen)_2(5\text{-}glap)](PF_6)_2$, 2c. Filtration of the product afforded 197 mg (47%) of a dark orange solid; δ_H (500 MHz, CD_3CN): 2.06 (q, 2H, $J=7.3$ Hz, CH_2), 2.47 (t, 0.6H, $J=7.3$ Hz, CH_2), 2.50 (t, 0.4H, $J=7.3$ Hz, CH_2), 2.68 (t, 0.6H, $J=7.3$ Hz, CH_2), 2.69 (t, 0.4H, $J=7.3$ Hz, CH_2), 7.59 (dd, $1H_\beta$, $J=8.3$, 5.2 Hz), 7.62–7.68 (m, $5H_\beta$), 7.96 (d, $1H_\alpha$, $J=5.2$ Hz), 8.02–8.09 (m, $5H_\alpha$), 8.28 (s, 4H), 8.54 (d, $1H_\gamma$, $J=8.3$ Hz), 8.61–8.64 (m, $4H_\gamma$, 1H), 8.74 (d, $1H_\gamma$, $J=8.3$ Hz), 8.95 (s, 0.6H, NH), 8.97 (s, 0.4H, NH); δ_C (125 MHz, CD_3CN): 20.84, 20.90 (CH_2), 32.98, 33.24 (CH_2), 35.99, 36.02 (CH_2), 119.86, 125.81, 126.34, 126.37 (CH), 126.45, 127.28 (C), 128.49 (CH), 131.18, 131.43, 131.44 (C), 132.89, 132.92 (CH), 134.34 (C), 136.64, 137.25 (CH), 146.15, 148.29, 148.33, 148.37, 148.71, 148.75, 152.32 (C), 152.36, 153.36, 153.40, 153.44, 153.49, 153.52 (CH), 172.86, 172.93 (CO), 173.87, 174.25 (CO); *m/z* (ESI) $=376.5$ $[M-H_2O]^{2+}$. Anal. Calcd for $[C_{41}H_{31}N_7O_3Ru](PF_6)_2$: C, 46.42; H, 2.95; N, 9.24%, found: C, 46.17; H, 3.23; N, 9.10%.

4.3.4. [Bis(1,10-phenanthroline)(*tert*-butyl 4-oxo-4-(1,10-phenanthrolin-5-ylamino)butylcarbamate)]ruthenium(II) bis(hexafluorophosphate), $[Ru(phen)_2(BOC\text{-}5\text{-}ngap)](PF_6)_2$, 2d. Filtration of the product afforded 195 mg (46%) of an orange-red solid; δ_H (500 MHz, CD_3CN): 1.91 (q, 2H, $J=7.1$ Hz, CH_2), 2.63 (t, 2H, $J=7.1$ Hz, CH_2), 3.21 (c, 2H, $J=6.4$ Hz, CH_2), 5.53 (br s, 1H, NH), 7.59 (dd, $1H_\beta$, $J=8.1$, 5.1 Hz), 7.62–7.67 (m, $5H_\beta$), 7.95 (dd, $1H_\alpha$, $J=5.1$, 0.7 Hz), 8.01–8.07 (m, $5H_\alpha$), 8.27 (s, 4H), 8.54 (d, $1H_\gamma$, $J=8.0$ Hz), 8.60–8.62 (m, $4H_\gamma$), 8.70 (s, 1H), 8.82 (d, $1H_\gamma$, $J=8.0$ Hz), 9.25 (broad s, 1H, NH); δ_C (125 MHz, CD_3CN): 26.53 (CH_2), 28.07 (CH_3), 34.23, 39.74 (CH_2), 78.92 (CMe_3), 117.72 (C), 125.61 (CH), 126.27 (C), 126.29 (CH), 126.37, 127.16 (C), 128.44 (CH), 131.23, 131.40 (C), 132.68 (CH), 134.48 (C), 136.58, 137.18 (CH), 146.05, 148.31, 148.34, 148.71 (C), 152.25, 153.32, 153.36, 153.40, 153.45 (CH), 157.08 ($NHCO_2$), 173.14 (NHCO); *m/z* (ESI) $=421$ $[M]^{2+}$. Anal. Calcd for $[C_{45}H_{40}N_8O_3Ru](PF_6)_2$: C 47.75, H 3.56, N 9.90%, found: C, 47.68; H, 3.90; N, 9.87%.

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