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Synthesis and Properties of Tetrasubstituted 1,10-Phenanthrolines and Their Ruthenium Complexes

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The synthesis and the photophysical properties of a series of tetrasubstituted phenanthroline (phen) ruthenium complexes of the type $[Ru(tbbpy)_2(phen\text{-}R_4)]^{2+}$ (tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; phen = 1,10-phenanthroline; R represents the substitution at 3-, 5-, 6- and 8-positions with phenyl, 4-*tert*-butylphenyl and *para*-biphenyl) and of a homoleptic $[Ru(phen\text{-}R'_4)_3]^{2+}$ (R′ = 4-*tert*-butylphenyl) are described. The phen-R_4 ligands were obtained in high yields using Suzuki-type coupling reactions. The solid-state structure of 3,5,6,8-tetraphenylphenanthroline is reported. The investigation of the photophysical properties of the free ligands reveals a pronounced effect of the aryl substitution on absorption and emission properties. These properties are mirrored in the corresponding complexes, which possess room-temperature emission lifetimes of up to 2833 ns.

Introduction

Luminescent polypyridyl–metal complexes, especially of ruthenium and osmium, have received considerable attention due to their favourable combination of interesting photophysical properties such as long-lived excited triplet states (^{3}MLCT) and high chemical stability.[1] This has also allowed them to play an important role in artificial photosynthesis,[2] dye sensitised solar cells[3] or luminescent sensors, for instance, for oxygen.[4] The photophysical properties of the ruthenium and osmium complexes can be easily tuned by variation of the ligand π-system.[5] Modification of the topology of the ligand structure allows the construction of elaborate supramolecular architectures containing multiple metal centres.[6] Within this context it is essential to be able to introduce substituents at a potential ligand at a predefined position and in variable numbers. Beside bipydines and terpyridines, derivatives of 1,10-phenanthroline (Figure 1) have received increasing attention since they can be easily transformed into various bridging ligands such as tetrapyridophenazins[7] or ligands which form the basis for luminescent DNA sensors.[8]

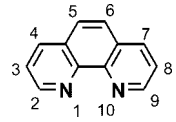

Figure 1. 1,10-Phenanthroline and the numbering scheme employed.

Strong effects on the electronic transitions of the 1,10-phenanthroline ligand and its Ru^{II} complexes have been observed, which depend on the nature and position of the substituents of the phenanthroline scaffold.[9–11] In general, 1,10-phenanthroline ligands substituted at the 2,9- and the 4,7-positions are accessible using various synthetic pathways.[12–15]

However, access to phenanthrolines substituted in the 3- and 3,8-positions is rather limited and often requires tedious work up.[16–19] Tor and co-workers have shown that a multitude of different phenanthrolines can be synthesised by organometallic reactions starting from 3-bromo- and 3,8-dibromo-1,10-phenanthrolines.[20] Using this methodology, Br-phen ligands and the corresponding complexes have been employed in the construction of luminescent sensors for metal ions,[10] multinuclear metal complexes possessing interesting photophysical properties[10,11,16–22] and nucleotide labelled luminescent complexes.[23–25]

Substitutions at the 5,6-positions of the phenanthroline are very rarely reported.[26] 5,6-Bis-thiophenyl-1,10-phenanthrolines, which were obtained by a Suzuki coupling, were employed for the construction of light-driven switches.[27]

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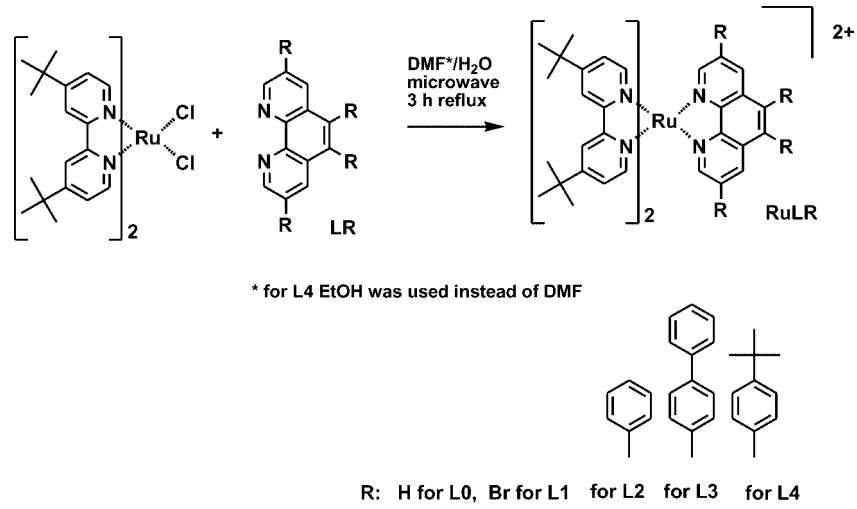

Figure 2. Naming of ruthenium complexes and corresponding ligands.

Recently we reported a bromination reaction of 1,10-phenanthroline which allowed the selective formation of 3,5,6,8-tetrabromophenanthroline (phen-Br_4) in an one-step multigram reaction.[28] There we showed that the regioselective nucleophilic substitution of phen-Br_4 in the $[Ru(tbbpy)_2(phen\text{-}Br_4)]^{2+}$ complex in the 3,8-position was possible under mild conditions and at room temperature. Furthermore, the synthesis of tetraalkynyl-substituted phenanthrolines based on phen-Br_4 was observed using Negishi-type conditions. Preliminary investigations showed that the tetraalkynyl-substituted phenanthrolines may serve as ligands for ruthenium(II) centres.[29]

It is noteworthy that the introduction of alkynyl functional groups in bipyridine or phenanthroline frames leads to the expansion of the conjugated π-system which will have a dramatic impact on the metal-to-ligand charge-transfer excited state of ruthenium complexes. The introduction of aryl substituents, however, does not necessarily lead to the expansion of the conjugated π-system since the torsion angle of these substituents relative to the phenanthroline main frame can be substantial, thus limiting delocalisation.[30] The extremely long lifetimes of the tris-(4,7-diphenylphenanthroline)ruthenium(II) complex of up to 9640 ns which is extensively used in oxygen sensing is, however, worth noting.[31]

In this contribution we present a series of tetraaryl-substituted 1,10-phenanthroline ligands, which were prepared by Suzuki reactions, and their corresponding ruthenium–polypyridyl complexes (see Figure 2).

To avoid solubility problems we utilised the bis(4,4′-di-*tert*-butyl-2,2′-bipyridine)Ru^{II} core, $(tbbpy)_2Ru^{2+}$, since this ensures high solubility in organic solvents.[32] The novel ligands L**2** to L**4** were prepared to illustrate the potential of the building-block approach utilising organometallic C–C coupling reactions. We will focus this investigation on the synthetic accessibility of differently substituted ruthenium complexes with tetrasubstituted phenanthrolines and the preliminary characterisations of their photophysical properties.

Results and Discussion

Synthesis

All prepared complexes contain 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbbpy) to increase the solubility of the ruthenium complexes in less polar organic solvents. The new ligands L**2** to L**4** rely on the accessibility of 3,5,6,8-tetrabromophenanthroline (L**1**, phen-Br_4) which was conveniently prepared using literature methods.[28] All four bromine functionalities in L**1** were easily substituted by aromatics using conventional Suzuki reactions utilising $Pd(PPh_3)_4$ as catalyst, yielding L**2**–L**4** in good yields (see Figure 3).

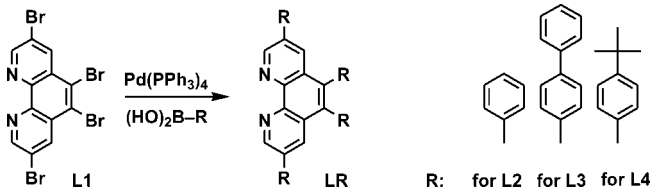

Figure 3. Synthetic route to tetraaryl-substituted phen ligands.

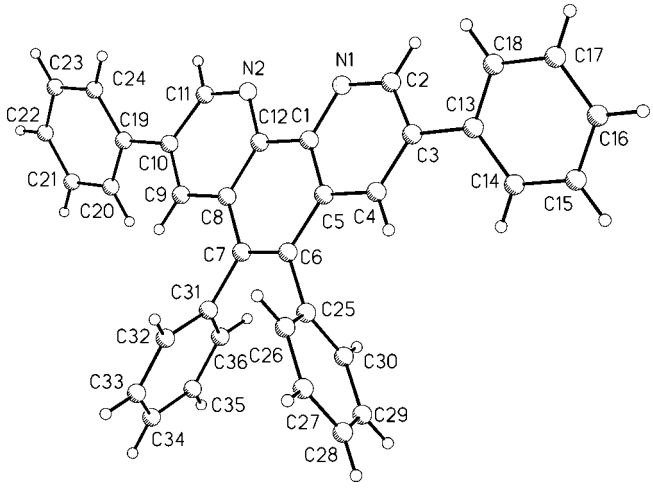

Figure 4. Solid-state structure of L**2**.

The nature of the products was unambiguously identified using multidimensional NMR spectroscopic methods, MS and UV-Vis/emission spectroscopy. The nature of the reaction products and the interaction between the hydrogen substituents of the phenanthroline frame and the aryl substituents was confirmed by the solid-state structure obtained for **L2** shown in Figure 4.

The phenanthroline frame is nearly ideally planar (deviation from planarity is 0.015 Å), whereas the two phenyl substituents in the 3,8-positions of the phenanthroline are twisted out of the plane by 29° (C4, C3, C13, C14) and 33° (C9, C10, C19, C20). The two other phenyl substituents in the 5- and 6-positions of the phenanthroline are twisted even more relative to the plane by 82° (C5, C6, C25, C26) and 71° (C7, C8, C31, C32). The strong twisting of the 5,6-substituents is a consequence of the repulsion imposed by the two neighbouring phenyl rings on each other. The smaller steric pressure for the phenyl substituents in the 3,8-positions is a consequence of the interaction of the hydrogen atoms of the phenanthroline pyridine ring with the

Table 1. Photophysical properties of **L2**–**L4**, $[Ru(tbbpy)_2(LR)]^{2+}$ (R = 0, 1, 2, 3, 4) and $[Ru(\mathbf{L4})_3]^{2+}$.

Compound	Solvent	Absorption	Emission	τ [ns]	τ [ns]
		λ_{max} [nm] (ε [1000 L mol^{-1} cm^{-1}])	λ_{max} [nm]	aerated	deaerated
L0[a]	DCM	sh[b] 280 (14), 265 (30), 233 (40)	359	–	–
L2	DCM	sh 330 (27), 290 (53), sh 271 (43)	400	–	–
L3	DCM	sh 340 (48), 308 (62), 279 (60)	406	–	–
L4	DCM	sh 335 (29), 300 (47), 265 (37)	408	–	–
Ru**L0**	ACN	454 (16), sh 431 (15), 287 (63), 265 (53), 214 (60)	610	211	1423
Ru**L1**	ACN	sh 486 (12), 441 (15), 340 (9), 288 (101), 250 (48), 210 (84), 193 (74)	672	100	1336
Ru**L2**	ACN	442 (13), sh 347 (22), 288 (80), 248 (46)	633	189	2833
	DCM	445 (14), 347 (28), 289 (74), 259 (41), 252 (41)	618	529	1448
Ru**L3**	ACN	444 (18), 355 (53), sh 316 (62), 286 (117), 258 (105)	640	201	1477
	DCM	448 (18), 362 (53), sh 318 (54), 286 (113), 261 (100)	625	550	1308
Ru**L4**	ACN	444 (15), 351 (36), sh 313 (46), 288 (80), 243 (53)	628	153	1551
	DCM	462 (15), sh 428 (13), 352 (34), sh 310 (38), 289 (74), 251 (44)	613	468	823
$Ru(\mathbf{L4})_3$	ACN	465 (19), sh 435 (16), sh 348 (83), 315 (111), 268 (93), 242 (126)	604	151	1017
	DCM	462 (19), 430 (17), 329 (92), 274 (82), 246 (110)	594	198	283
$Ru(\mathbf{L0})_3$	ACN	445 (16), sh 417 (15), 313 (5), sh 291 (22), 263 (105), 223 (81)	593	460[a]	–
	DCM	448 (17), 422 (15), 314 (5), sh 290 (21), 264 (100)	578	150[a]	–

[a] The data for **L0** and $Ru(\mathbf{L0})_3$ is given for comparison, see ref.[34] [b] Shoulder = sh.

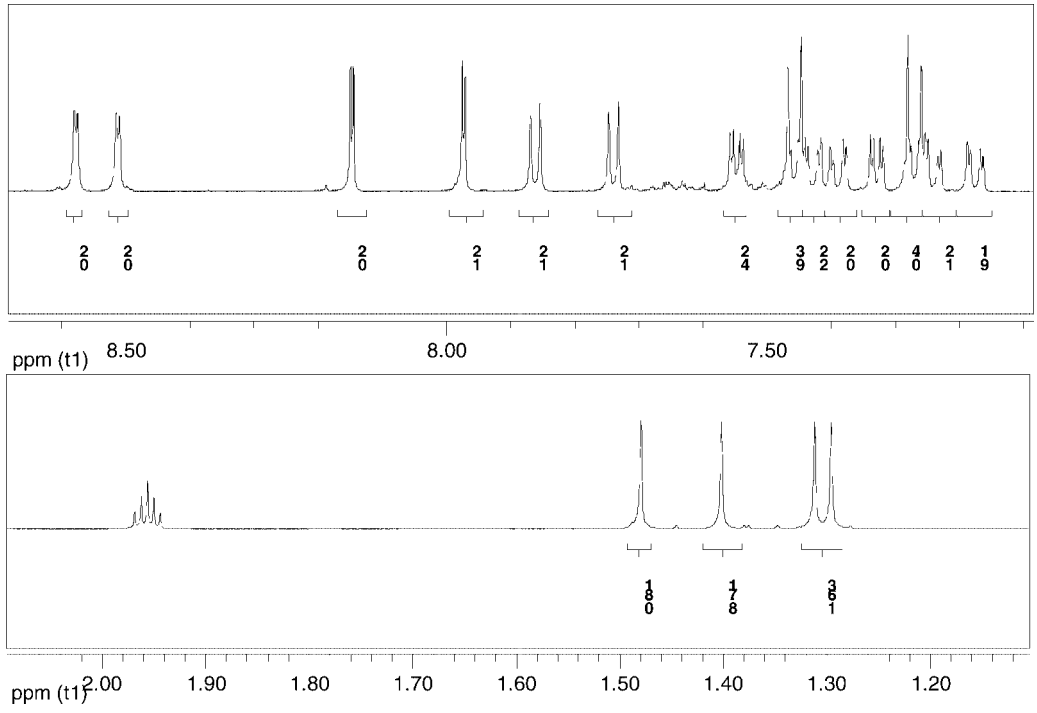

Figure 5. ^{1}H NMR spectrum of Ru**L4**.

neighbouring phenyl ring which results in significantly smaller torsion angles.

Complexation of **L0**–**L4** to $(tbbpy)_2Ru^{2+}$ fragments [Ru] was achieved using microwave irradiation.[33] Because of the poor solubility of **L2** and **L3**, DMF had to be used. The short reaction times made possible by the use of the microwave ensured that no significant formation of ruthenium–carbonyl complexes from the decomposition of the DMF occurred. The full characterisation of all complexes by multidimensional NMR spectroscopic methods, MS and UV-Vis/emission spectroscopy is outlined in the Experimental Section and in Table 1. The ^1H NMR spectrum of the heteroleptic complex Ru**L4** is depicted in Figure 5, and it shows four *tert*-butyl signals between 1.2 and 1.6 ppm. Two *tert*-butyl signals are tbbpy-based, with the third and the fourth stem from the *tert*-butyl groups of the substituents in the 3,8- and 5,6-positions, respectively. The signals in the aromatic region could be assigned to the two *tert*-butyl bipyridine ligands and to the phenanthroline ligand **L4** by H,H COSY NMR spectroscopy.

The compositions of the complexes Ru**L0**–Ru**L4** were additionally confirmed by ESI mass spectroscopy. The spectra always contained the $[M - PF_6]^+$ and $[M - 2PF_6]^{2+}$ peaks. These peaks were assigned to the corresponding molecular ion with the aid of a matching isotopic pattern as depicted for $[RuL4 - PF_6]^+$ in Figure 6.

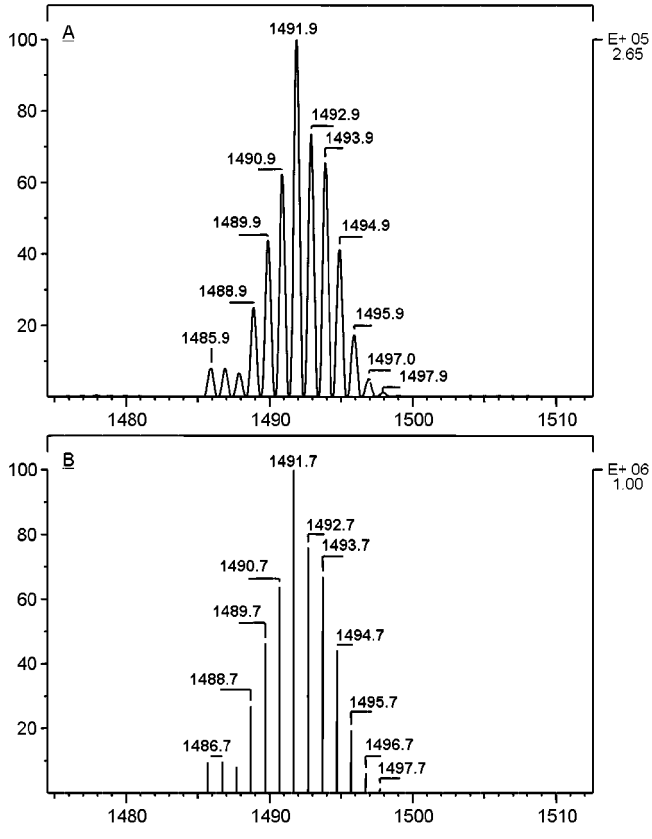

Figure 6. $[RuL4 - PF_6]^+$ peak of the ESI-MS of Ru**L4** in MeOH (A) and the corresponding isotopic pattern (B) of $C_{88}H_{104}N_6RuPF_6$.

We obtained the homoleptic complex $Ru(L4)_3$ using standard microwave-assisted reaction conditions. Attempts to synthesise $Ru(L1)_3$ did not yield any product that could be characterised but rather a mixture of different decomposition products.

Electronic Spectra

All three new ligands **L2**–**L4** display redshifted absorption maxima relative to that of 1,10-phenanthroline, **L0**, at around 300 nm and a shoulder at around 340 nm and for **L3** up to 370 nm. A clear influence of the peripheral substitution pattern on the shape of the long wavelength maxima is observed (Figure 7). The absorption spectrum of **L0** features two distinct maxima at 265 and 233 nm.[34] All three aromatically substituted ligands (**L2** to **L4**) show relatively strong emission between 400 nm (**L2**) and 408 nm (**L4**) in dichloromethane (DCM). The influence of the aromatic substitution on the emission is obvious by a pronounced redshift of about 40 nm between **L0** and **L2** to **L4**.

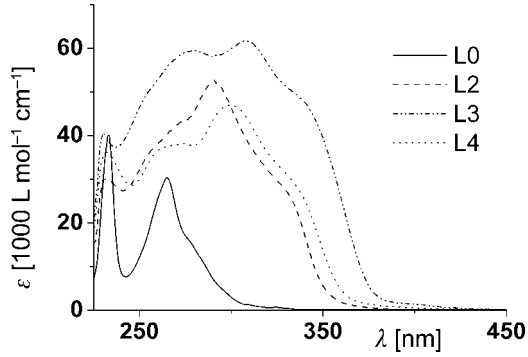

Figure 7. Absorption spectra of LR (R = 0, 2, 3, 4) in CH_2Cl_2 (DCM).

The absorption and emission data of **L2** to **L4** indicate that the substitution of the phenanthroline frame with aromatic moieties results in significant changes in the electronic properties of the ligands. A similar observation was previously made for substituted dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligands.[35]

All four complexes Ru**L1** to Ru**L4** show absorption properties which are common for this class of ruthenium–polypyridyl compounds. The absorption spectra in acetonitrile (ACN) of the new complex Ru**L3** and Ru**L0** (for comparison) are depicted in Figure 8. The shape of the long wavelength maxima of the new complexes show an influence of the peripheral substitution pattern since shoulders of these MLCT bands appear slightly redshifted with regard to that of the related compound $[Ru(tbbpy)_2(phen)]^{2+}$ (Ru**L0**). The intensity of the phenanthroline-based transitions at ca. 286 nm increases from Ru**L0** (63×10^3 M^{-1} cm^{-1}) to Ru**L3** (117×10^3 M^{-1} cm^{-1}). The introduction of more extensive aromatic substituents leads to a new π–π* transition around 350 nm which decreases in energy and increases in intensity from Ru**L2** (347 nm, 22×10^3 M^{-1} cm^{-1}) to Ru**L4** (351 nm, 36×10^3 M^{-1} cm^{-1}) to Ru**L3** (355 nm, 53×10^3 M^{-1} cm^{-1}).

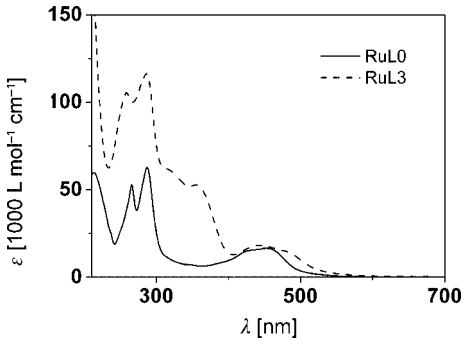

Figure 8. Absorption spectra of Ru**L0** and Ru**L3** in CH_3CN.

The homoleptic complex Ru(**L4**)$_3$ has a bathochromically shifted absorption maximum of 465 nm. The next highest energy transition is observed at 348 nm, similar to that of Ru**L4**, but with a higher extinction coefficient as expected. This allows the assignment of this band to a π–π* transition in the tetra(*tert*-butylphenyl)-substituted phenanthroline ligand **L4**. The absorption intensity of the band at 243 nm of the bisheteroleptic Ru**L4** is almost half of the homoleptic Ru(**L4**)$_3$ complexes which can also be considered as a **L4**-based transition. The investigation in dichloromethane shows that no significant changes in the absorption characteristics are observed except for Ru**L4** which displays a redshift of the long wavelength absorption maximum of 18 nm.

The luminescence data for all four complexes were obtained in acetonitrile and dichloromethane. The influence of the solvent on emission wavelength is evident by the ca. 15 nm redshift of the emission maxima upon going from dichloromethane to acetonitrile, which correlates to the increased polarity of the solvent and the nature of the MLCT transition. Similar effects of solvent polarity on the emission wavelength in substituted phenanthroline–ruthenium complexes have been observed.[36] The impact of the substitution at the phen core is observed for the phosphorescence maxima in CH_3CN that shifts from 610 nm for Ru**L0** to 640 nm for Ru**L3** (see Table 1). The emission of the homoleptic Ru(**L4**)$_3$ slightly redshifts to 604 nm relative to the emission of Ru(**L0**)$_3$ (Table 1). Currently it is not possible to give a conclusive explanation for the observed effects of solvent polarity and substitution at the phenanthroline ligand; more detailed investigations using spectroscopic techniques such as resonance Raman and time-resolved spectroscopy in combination with theoretical methods might aid in the interpretation and characterisation of the nature of the emitting state. The information obtained so far indicates that the expansion of the 1,10-phenanthroline frame by aryl substituents does lead to a moderate change in the energies of the excited states which might be caused by limited delocalisation of the resulting aromatic frame due to the twisting of the aryl substituents caused by steric hindrance by neighbouring hydrogen atoms. A higher degree of delocalisation could be obtained by introduction of alkyne substituents like tri(isopropyl)silylacetylene.[29] In this case, the MLCT absorption of $[Ru(tbbpy)_2(L^*)]^{2+}$ {L* = 3,5,6,8-tetrakis[tri(isopropylsilyl)acetylene]phenanthroline} has a maximum at 439 nm with a shoulder at 505 nm and an emission maximum at 692 nm in acetonitrile.

The lifetimes of the excited states of all complexes in aerated solution lie in the expected range. Generally, longer lifetimes are identified in aerated dichloromethane solutions if compared with those in aerated acetonitrile solutions. Deaeration leads in both solvents to increasing lifetimes of the excited triplet MLCT as expected. However, this effect is more pronounced for acetonitrile solutions. In acetonitrile solution a nearly 15-fold increase from 189 to 2833 ns is detected for Ru**L2** upon removal of oxygen. This significant increase in lifetime renders the tetraaryl-substituted phenanthroline complexes potential candidates for applications as oxygen sensors.[4] In contrast to the data obtained for the heteroleptic complexes, the homoleptic complex Ru(**L4**)$_3$ shows relatively short lifetimes of 150 ns, especially if compared with the parent phenanthroline complex Ru(**L0**)$_3$ with 460 ns.

Photometric investigation of a solution of Ru**L2** which had been irradiated in acetonitrile for 72 hours with visible light $\lambda > 450$ nm showed that no significant photobleaching was detected.

Electrochemistry

The electrochemical behaviour of the complexes was studied in acetonitrile and in DMF (Table 2). The reductions of complexes Ru**L3** and Ru(**L4**)$_3$ are not well-behaved in acetonitrile solution, probably due to the adsorption of the reduced species onto the surface of the electrode, and show abrupt and sharp adsorption and desorption spikes. In DMF this phenomenon disappears in the case of Ru**L3**. The behaviour of Ru(**L4**)$_3$ will be the subject of further investigations. A representative cyclic voltammogram for Ru**L2** is depicted in Figure 9.

Table 2. Electrochemical data for the complexes $[Ru(LR)]^{2+}$ (R = 0, 2, 3, 4).

Complex	*Solvent*	$E_{1/2}$ox [V]; (Ru^{II}/Ru^{III} vs. Fc/Fc^+)	$E_{1/2}$red [V] vs. Fc/Fc^+			
Ru**L0**	ACN	0.74	–1.77	–1.98	–2.25	–
Ru**L1**	ACN	0.92[a]	–	–	–	–
Ru**L2**	ACN	0.82	–1.63	–1.96	–2.18	–2.47
Ru**L3**	ACN	0.82	–	–	–	–
Ru**L4**	ACN	0.80	–1.65	–1.96	–2.19	–2.56
Ru**L0**	DMF	0.76	–1.78	–1.99	–2.24	–
Ru**L2**	DMF	0.77	–1.60	–1.94	–2.18	–
Ru**L3**	DMF	0.78	–1.58	–1.95	–2.18	–2.43
Ru**L4**	DMF	0.76	–1.62	–1.95	–2.19	–2.57

[a] Data taken from ref.[28]

The oxidation potentials of the ruthenium complexes Ru**L2**–Ru**L4** are only slightly affected by the peripheral substitution at the phen ligand (Table 2). This can be observed by the increase in the oxidation potential of Ru**L0** (0.74 V) over Ru**L4** (0.80 V) followed by Ru**L2** (0.82 V) and Ru**L3** (0.82 V) vs. Fc/Fc^+. The presence of four bromo sub-

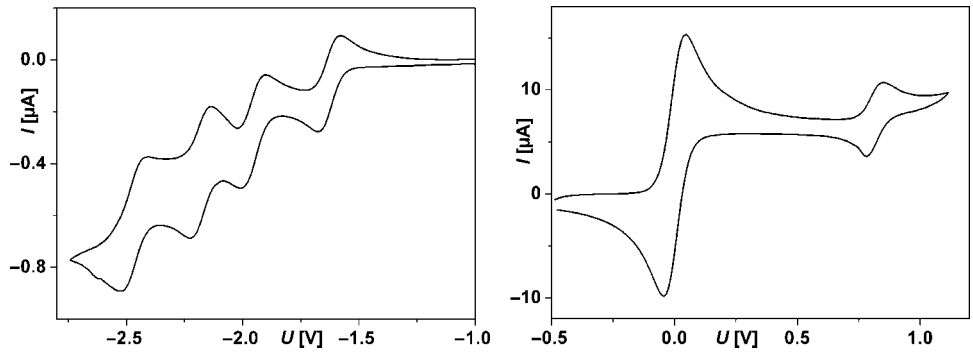

Figure 9. Cyclic voltammograms of RuL**2** (1 mM) in CH_3CN containing Bu_4NBF_4 (0.1 M) vs. Fc/Fc^+ at 0.0 V (scan rate 0.05 Vs^{-1}, step potential 0.01 V).

stituents in RuL**1** shifts the oxidation potential of the ruthenium centre by 0.18 to 0.92 V. This suggests that the introduction of the aryl substituents has a relatively small influence on the metal-based ground state. The value observed for the first reduction potential suggests that L**2**–L**4** are easier to reduce than L**0**.

The reduction events of the complexes RuL**2**–RuL**4** in DMF show only small differences in their potentials of maximal 40 mV for the first reduction and ca. 10 mV for the second and third reduction processes. In contrast to this, the potentials of the ligand reduction of the unsubstituted RuL**0** show a cathodic shift with regard to the potentials of RuL**2**–RuL**4**. The differences of these shifts are 180 mV for the first, 40 mV for the second and 60 mV for the third reduction process.

Conclusions

In conclusion we have shown that it is possible to introduce four substituents into a phenanthroline frame using Suzuki coupling reactions starting from the free ligand phen-Br_4, L**1**. The absorption spectra of the free ligands are highly dependent on the substitution pattern. Importantly, with increasing aryl character the ligand-centred π–π* transition of the LR ligand moves to lower energy. The substituted ligands form heteroleptic complexes in high yields. It is also possible to form a homoleptic complex with a *tert*-butyl-substituted 3,5,6,8-tetraphenylphenanthroline, Ru(L**4**)$_3$. The UV/Vis spectra of the complexes RuL**2**–RuL**4** show a redshift of the MLCT bands and the appearance of intensive π–π* transitions between 300 and 400 nm. The excited-state lifetimes of tetrasubstituted Ru–phenanthroline complexes are very sensitive to oxygen; the lifetime is almost 3 µs for RuL**2**. If compared with that of the unsubstituted phenanthroline complex RuL**0**, this represents an increase of 100% in the lifetime of the excited state. The synthetic accessibility of various tetrasubstituted phenanthrolines makes them ideal targets for further developments as building blocks for the construction of tuneable luminescent sensors or oligonuclear complexes.

Experimental Section

Unless otherwise noted, all Pd-catalysed cross-coupling reactions were conducted under dry, deoxygenated argon using standard Schlenk techniques. Ru(tbbpy)$_2Cl_2$[33] and 3,5,6,8-tetrabromo-1,10-phenanthroline[28] were prepared using literature methods. Toluene was distilled from sodium benzophenone ketyl under argon prior to use. All other solvents were used as received. Boronic acids were purchased from Fluka, Aldrich and Lancaster.

^{1}H NMR spectra were recorded with a Bruker 400 MHz/200 MHz spectrophotometer. The mass spectra were obtained using a SSQ 170, Finnigan MAT at the Friedrich Schiller University, Jena. Electrospray mass spectra were recorded with a Finnigan MAT, MAT 95 XL. The positive ES mass spectra were obtained with voltages of 3–4 kV applied to the electrospray needle. The microwave-assisted reactions were carried out using the Microwave Laboratory Systems MLS EM-2 microwave system.

Typical Procedure for Preparation of LR (R = 2, 3, 4) from phen-Br_4 (L1): A Schlenk vessel was charged with phen-Br_4 (0.3 g, 0.61 mmol) and the corresponding boronic acid (2.54 mmol), $Pd(PPh_3)_4$ [0.044 g, $n = 3.81 \times 10^{-5}$ mol (1.5 mol-%)] in dry toluene (60 mL) and oxygen-free solution of 2 M aqueous Na_2CO_3 (20 mL). The suspension was refluxed under argon for 3 d. After cooling to room temp., the reaction mixture was taken up in water (100 mL) followed by extraction with chloroform. The solvent of the combined organic layers was removed, and the crude product was dried under vacuum. Column chromatography was performed using silica and a gradient eluent system starting with $CHCl_3$ and changing to $CHCl_3$/MeOH (99:1 and later to 9:1). The main fluorescent band was collected and yielded the pure ligand.

3,5,6,8-Tetraphenylphenanthroline (L2): Yield: 71%. ^{1}H NMR (CD_2Cl_2): δ = 7.24–7.65 (m, 20 H, phenyl), 8.07 [s, long-range coupling (lc), ^4J = 2 Hz, 2 H, H4,H7-phen], 9.41 [s(lc), ^4J = 2 Hz, 2 H, H2,H9-phen] ppm. MS (DEI, EI+Q1MS): *m*/*z* (%) = 484 (100) [M^+]. $C_{36}H_{24}N_2 \cdot 1CH_3OH$ (516.61): calcd. C 86.02, H 5.46, N 5.42; found C 85.93, H 5.25, N 5.14.

3,5,6,8-Tetra(*para*-biphenyl)phenanthroline (L3): Yield: 82%. ^{1}H NMR ($CDCl_3$): δ = 7.30–7.75 (m, 36 H, phenyl), 8.36 (s, 2 H, H4,H7-phen), 9.68 [s(lc), 2 H, H2,H9-phen] ppm. MS (DEI, EI+Q1MS): *m*/*z* (%) = 788 (28) [M^+]. Recrystallisation from CH_2Cl_2. $C_{60}H_{40}N_2 \cdot 0.5CH_2Cl_2$ (831.43): calcd. C 87.4, H 4.97, N 3.37; found C 87.8, H 5.32, N 2.99.

3,5,6,8-Tetra(4-*tert*-butylphenyl)phenanthroline (L4): Yield: 76%. ^{1}H NMR ($CDCl_3$): δ = 1.28 (s, 18 H, CH_3 *tert*-butyl), 1.35 (s, 18

H, CH_3 *tert*-butyl), 7.05 (d, ^3J = 8 Hz, 4 H, phenylA), 7.25 (d, ^3J = 8 Hz, 4 H, phenylA), 7.51 (d, ^3J = 8.4 Hz, 4 H, phenylB), 7.57 (d, ^3J = 8.4 Hz, 4 H, phenylB), 8.34 (s, 2 H, H4,H7-phen), 9.57 (s, 2 H, H2,H9-phen) ppm. MS (DEI, EI+Q1MS): *m*/*z* (%) = 709 (4) [M^+]. $C_{52}H_{56}N_2{\cdot}1CH_3OH$ (741.05): calcd. C 85.9, H 8.16, N 3.78; found C 85.81, H 7.72, N 3.33.

Preparation of RuL2 and RuL3: $Ru(tbbpy)_2Cl_2$ (0.1 g, 0.14 mmol) and the corresponding ligand (0.14 mmol) were suspended in DMF/H_2O (80 mL/10 mL) and heated at reflux for 3 h using microwave irradiation (150 W). Afterwards the reaction mixture was filtered, and the solvent was removed under reduced pressure. The complexes were recrystallised from a mixture of ethanol and aqueous NH_4PF_6, and further purified by column chromatography using a stationary silica phase and a gradient changing from EtOH to EtOH/H_2O/KNO_3. The novel ruthenium complexes based on the aryl-substituted phenanthroline ligands did not yield satisfactory elemental analysis results, which might be due to the presence of multiple flexible substituents retaining varying amounts of solvents.

$[Ru(tbbpy)_2(L2)](PF_6)_2$ (RuL2): Yield 84%. ^{1}H NMR (CD_3CN, 400 MHz): δ = 1.38 (s, 18 H, CH_3 *tert*-butyl), 1.45 (s, 18 H, CH_3 *tert*-butyl), 7.25–7.45 (m, 22 H, phenyl, H5-bpy), 7.52 (d, ^3J = 6 Hz, ^4J = 2 Hz, 2 H, H5′-bpy), 7.73 (d, ^3J = 6 Hz, 2 H, H6-bpy), 7.83 (d, ^3J = 6 Hz, 2 H, H6′-bpy), 8.00 (s, ^4J = 1.6 Hz, 2 H, phen), 8.11 (s, ^4J = 2 Hz, 2 H, phen), 8.49 (s, ^4J = 2 Hz, 2 H, H3-bpy), 8.56 (s, ^4J = 1.6 Hz, 2 H, H3′-bpy) ppm. MS (ESI, MeOH): *m*/*z* = 1267.5 ($[M - PF_6]^+$, 100% with matching isotopic pattern).

$[Ru(tbbpy)_2(L3)](PF_6)_2$ (RuL3): Yield: 70%. ^{1}H NMR (CD_3CN, 400 MHz): δ = 1.39 (s, 18 H, CH_3 *tert*-butyl), 1.47 (s, 18 H, CH_3 *tert*-butyl), 7.3–7.5 (m, 18 H, phenyl, H5-bpy), 7.55 [d(lc), ^3J = 5.8, ^4J = 1.8 Hz, 2 H, H5′-bpy], 7.58–7.70 (m, 20 H, phenyl), 7.77 (d, ^3J = 6 Hz, 2 H, H6-bpy), 7.86 (d, ^3J = 5.6 Hz, 2 H, H6′-bpy), 8.09 [s(lc), ^4J = 2 Hz, 2 H, phen], 8.26 [s(lc), ^4J = 2 Hz, 2 H, phen], 8.517 [s(lc), ^4J = 2 Hz, 2 H, H3-bpy], 8.58 [s(lc), ^4J = 2 Hz, 2 H, H3′-bpy] ppm. MS (ESI, MeOH): *m*/*z* = 1571.5 ($[M - PF_6]^+$, 74%), 713.3 ($[M - 2PF_6]^{2+}$, 100% with matching isotopic pattern).

Preparation of $[Ru(tbbpy)_2(L4)](PF_6)_2$ (RuL4): $Ru(tbbpy)_2Cl_2$ (0.2 g, 0.282 mmol) and the corresponding ligand (0.282 mmol) were suspended in EtOH/H_2O (60 mL/20 mL) and heated at reflux for 1 h using microwave irradiation (150 W). Afterwards the reaction mixture was filtered. The work-up procedure used was the same as that for Ru**L2** and Ru**L3**. Yield: 89%. Silica and chloroform were used for column chromatography. ^{1}H NMR (CD_3CN, 400 MHz): δ = 1.27 (s, 18 H, CH_3 *tert*-butyl), 1.28 (s, 18 H, CH_3 *tert*-butyl), 1.38 (s, 18 H, CH_3 *tert*-butyl), 1.46 (s, 18 H, CH_3 *tert*-butyl), 7.15 (d, ^3J = 8 Hz, ^4J = 1.8 Hz, 2 H, phenylA), 7.22 (d, ^3J = 8 Hz, ^4J = 1.6 Hz, 2 H, phenylA), 7.25 (d, ^3J = 8.4 Hz, 4 H, phenylB), 7.31 (d, ^3J = 6.4 Hz, ^4J = 2 Hz, 2 H, H5-bpy), 7.36 (d, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 2 H, phenylA), 7.40 (d, ^3J = 8 Hz, ^4J = 2.2 Hz, 2 H, phenylA), 7.44 (d, ^3J = 8.8 Hz, 4 H, phenylB), 7.53 (d, ^3J = 6, ^4J = 2 Hz, 2 H, H5′-bpy), 7.72 (d, ^3J = 6 Hz, 2 H, H6-bpy), 7.84 (d, ^3J = 6 Hz, 2 H, H6′-bpy), 7.95 (s, ^4J = 2 Hz, 2 H, H4,H7-phen), 8.12 (s, ^4J = 1.6 Hz, 2 H, H2,H9-phen), 8.49 (s, ^4J = 1.6 Hz, 2 H, H3-bpy), 8.55 (s, ^4J = 1.6 Hz, 2 H, H3′-bpy) ppm. MS (ESI, MeOH): *m*/*z* = 1491.5 ($[M - PF_6]^+$, 100% with matching isotopic pattern), 673.3 ($[M - 2PF_6]^{2+}$, 55% with matching isotopic pattern).

Synthesis of the Homoleptic Complex of L4, $[Ru(L4)_3](PF_6)_2$ $[Ru(L4)_3]$: A mixture of $RuCl_3{\cdot}3H_2O$ (0.012 g, 45.9 μmol) and L**4** (0.101 g, 0.143 mmol) was suspended in ethanol (30 mL), methanol (20 mL), DMF (15 mL) and water (15 mL). The reaction mixture was refluxed in a microwave oven for 3 h at 200 W and cooled down. Afterwards the solution was filtered, and the solvent was removed by rotary evaporation. The crude product was purified using column chromatography [silica, $CHCl_3$/heptane (v/v = 2)]. While the amount of heptane in the gradient was decreased, a violet band and a red main band were gathered from the column. Switching the eluent to $CHCl_3$/MeOH led to the collection of a brown band. The red band was recrystallised from acetone and aqueous NH_4PF_6 solution. Yield: 46%. ^{1}H NMR (CD_3CN, 400 MHz): δ = 1.24 (s, 54 H, CH_3 *tert*-butyl), 1.29 (s, 54 H, CH_3 *tert*-butyl), 7.23 (d, ^3J = 8.4 Hz, 12 H, phenyl), 7.39 (d, ^3J = 8.4 Hz, 12 H, phenyl), 8.20 [s(lc), ^4J = 2 Hz, 6 H, phen], 8.47 [s(lc), ^4J = 2 Hz, 6 H, phen] ppm. MS (ESI, MeOH): *m*/*z* = 2372 ($[M - PF_6]^+$, 26% with matching isotopic pattern), 1114.4 ($[M - 2PF_6]^{2+}$, 100% with matching isotopic pattern).

Crystal Structure Determination: The intensity data for the compound were collected with a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarisation effects but not for absorption.[37,38] The structures were solved by direct methods (SHELRS[39]) and refined by full-matrix least-squares techniques against F_o^2 (SHELRL-97[40]). The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[40] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. CCDC-617531 (L**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for L2: $C_{36}H_{24}N_2{\cdot}2CHCl_3$, M_r = 723.31 g mol^{-1}, colourless prism, size 0.05 × 0.05 × 0.04 mm^3, triclinic, space group $P\bar{1}$, *a* = 12.8649(8), *b* = 12.9330(6), *c* = 12.9950(7) Å, *α* = 64.525(3), *β* = 64.591(3), *γ* = 68.457(3)°, *V* = 1718.31(16) Å^3, *T* = –90 °C, *Z* = 2, $\rho_{calcd.}$ = 1.398 g cm^{-3}, μ(Mo-K_α) = 5.31 cm^{-1}, *F*(000) = 740, 12260 reflections in *h*(–16/16), *k*(–15/16), *l*(–14/16), measured in the range 2.02° ≤ *Θ* ≤ 27.46°, completeness Θ_{max} = 98.7%, 7758 independent reflections, R_{int} = 0.0281, 5185 reflections with $F_o > 4\sigma(F_o)$, 415 parameters, 0 restraints, R_1(obs) = 0.0527, wR_2(obs) = 0.1134, R_1(all) = 0.0933, wR_2(all) = 0.1338, GOOF = 1.003, largest difference peak and hole = 0.462/–0.492 e Å^{-3}.

Electronic Spectroscopy: UV/Vis absorption spectra (accuracy ±2 nm) were recorded with an Analytikjena Specord S 600 spectrometer with standard software-based tools. Emission spectra (accuracy ±5 nm) were recorded at 298 K using a Perkin–Elmer LS50B luminescence spectrophotometer, which was equipped with a red-sensitive Hamamatsu R298 PMT detector and interfaced with an Elonex PC466 employing Perkin–Elmer FlWinLab custom-built software. Emission spectra are uncorrected for photomultiplier response. 10-mm path length quartz cells were used for recording spectra.

Emission Lifetime Measurements: Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) time-correlated single photon counting apparatus (TCSPC) comprised of two model J-yA monochromators (emission and excitation), a single photon photomultiplier detection system model 5300 and a F900 nanosecond flashlamp (nitrogen filled at 1.1 atm pressure, 40 kHz or 0.3 atm pressure, 20 kHz) interfaced with a personal computer by a NorlandMCA card. A 410 nm cut-off filter was used in emission to attenuate scatter of the excitation light (337 nm); luminescence was monitored at the k_{max} of the emission. Data correlation and manipulation was carried out using EAI F900 software version 6.24. Samples were de-aerated using argon for 30 min prior to measurements, followed by repeated purging to en-

sure complete oxygen exclusion. Emission lifetimes were calculated using a single-exponential fitting function, Levenberg–Marquardt algorithm with iterative deconvolution (Edinburgh instruments F900 software). The reduced $v2$ and residual plots were used to judge the quality of the fits. Lifetimes are ±5%.

Electrochemistry: The electrochemical measurements were executed with a PGSTAT booth (manufacturer: Autolab) with the aid of the appropriate GPES software. The experiments were carried out by means of a three-electrode technique in degassed acetonitrile with tetrabutylammoniumtetrafluoroborate (0.1 mol L^{-1}) as the conducting salt. A Hg-dropping electrode or a rotating-disc platinum electrode was used as the working electrode. The reference electrode was a Ag/AgCl electrode. The electrode's calibration took place according to the ferrocene standard potential in acetonitrile for which a value of +0.827 V was assumed. The concentration of the complexes measured was 1 mmol L^{-1}.

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