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FULL PAPER

Acetylene-substituted pyrazino[2,3-*f*][1,10]phenanthrolines and their Ru(II) complexes: syntheses, electronic properties and an exploration of their suitability as building blocks for metal-coordinated dehydroannulenes

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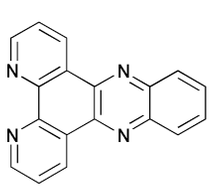
Aryl- and silyl-terminated 6,7-dialkynylpyrazino[2,3-*f*][1,10]phenanthrolines (pyzphen) have been prepared by the condensation of [1,10]phenanthroline-5,6-diamine with appropriately functionalised dialkynyl-1,2-diones. These new ligands were used as chelators in the formation of the corresponding $[Ru(bpy)_2(pyzphen)]\cdot 2PF_6$ and $[Ru(phen)_2(pyzphen)]\cdot 2PF_6$ complexes. The terminally free diethynyl $[Ru(bpy)_2(pyzphen)]$ complex, obtained by protodesilylation of a silyl-protected precursor, was shown to be amenable to oxidative acetylene hetero-coupling reactions with arylacetylenes and allowed the preparation of the corresponding butadiynyl-substituted derivatives. Homo-coupling reactions of the terminally free diethynyl $[Ru(bpy)_2(pyzphen)]$ complex to produce cyclic dehydroannulene-arrays were successful, but furnished an inseparable mixture of compounds of at least two different ring sizes. The photophysical and electrochemical properties of both the free ligands and their Ru(II)-complexes are clearly modified by the presence of the alkynyl substituents. In comparison with non-acetylenic model compounds it was established that acetylene substitution induces bathochromically shifted electronic absorptions and emissions to various degrees in ligands and complexes, leads to increased luminescence lifetimes and quantum yields of the ruthenium pyzphen complexes, and renders the acetylenic ligands and their complexes more susceptible to electrochemical reduction.

Introduction

Ruthenium(II)-diimine complexes have emerged over the years as key players in the design of light-harvesting devices,[1] as photonic nanowires[2] and as luminescent probes for the study of biomolecules such as DNA[3,4] and lipid vesicles.[5] Much effort has focussed on the design of appropriately functionalised chelating ligands to enable a specific application of the metal coordination compound. A prominent example[6] of such a complex is $[Ru(bpy)_2(dppz)]^{2+}$ where the chelating dppz (dipyrido[3,2-*a*:2′,3′-*c*]phenazine) ligand **1** serves, for example, as a direct probe for the microenvironment (*e.g.* as a DNA intercalator) and as an acceptor of electron density in light-induced metal-to-ligand charge transfers. Other phenanthroline-based ligands have been equipped with multiple binding sites for the formation of polynuclear metal complexes.[7] More recently, electronically modifying substituents have been implemented on a naphthophenanthroline ligand that is structurally related to the dppz system.[8,9]



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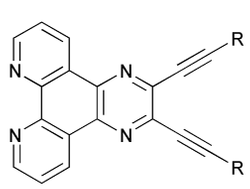

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We wish to present here the dialkynyl-substituted pyrazino-[2,3-*f*][1,10]phenanthrolines (pyzphen) **2** as a new structural motif for chelating diimine ligands. Our interest in these compounds is twofold: On the one hand, the alkynyl substituents of **2** are an integral part of the ligand's delocalised π-electron system and will therefore lead to modified electron acceptor properties of the metal-complexed diimine that could be put to use in fine-tuning metal–ligand interactions according to the requirements of a given application. The first part of this hypothesis is corroborated by semiempirical MO calculations on **2** (R = H, Fig. 1) that show both its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO) to have large contributions from the alkynyl subunits.

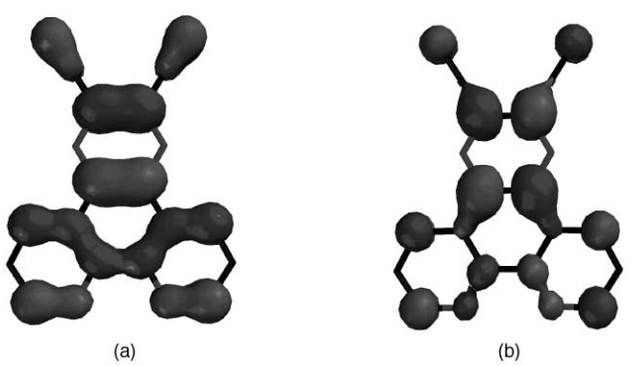

Fig. 1 Shape of the HOMO (a) and the LUMO (b) of 6,7-diethynyl-pyzphen as calculated with the PM3 parameter set.

Secondly, the acetylenes provide a flexible synthetic handle for further functionalisations[10–12] and may enable the assembly of dehydroannulene scaffolds with a cyclic array of exotopic metal coordination sites by oxidative acetylene coupling reactions.[13] First examples for architectures of this type have sporadically emerged in the recent literature,[14–16] but in no case has **2** been exploited as a building block.

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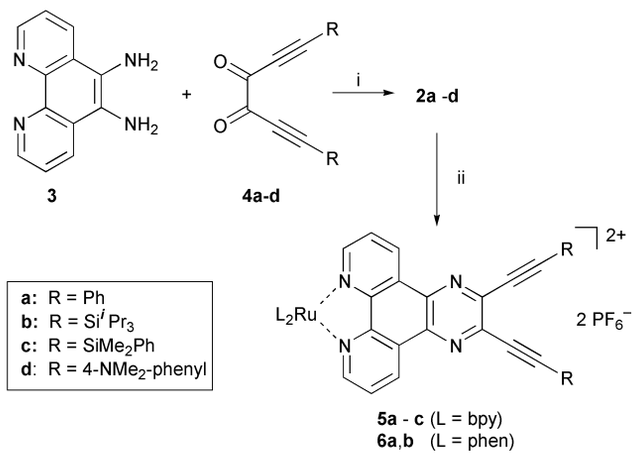
Outlined herein are the syntheses of the acetylenic pyzphen ligands, their conversion into $[Ru(bpy)_2(pyzphen)]^{2+}$ and $[Ru(phen)_2(pyzphen)]^{2+}$ complexes, a discussion of some of their photophysical and electrochemical properties, and a preliminary study of the suitability of these complexes for metal-ligated dehydroannulene frameworks.

Results and discussion

Syntheses

The condensation of 5,6-diamino[1,10]phenanthroline **3**[17] (Scheme 1) with vicinal diones was thought to be a facile



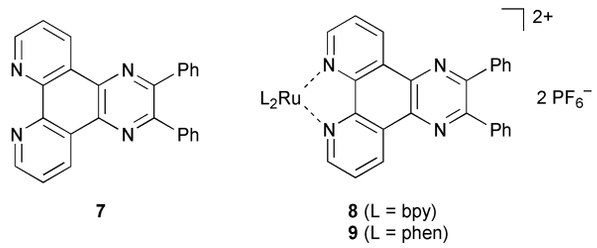
Scheme 1 Reagents and conditions: i, AcOH, rt, 1 h, **2a**: 79%, **2b**: 72%, **2c**: 57%, **2d**: 87%; ii, $[Ru(bpy)_2Cl_2]\cdot 2H_2O$, or $[Ru(phen)_2Cl_2]\cdot 2H_2O$, EtOH, reflux, 16 h, **5a**: 78%, **5b**: 81%, **5c**: 85%, **6a**: 84%, **6b**: 73%.

method to establish the pyzphen backbone and to study the effects of varying the substituents in the 6,7-positions. This strategy was made possible by the availability of the acetylenic diones **4**, a class of compounds which we have recently introduced and which is easily prepared by copper-mediated alkynylations of oxalyl chloride.[18] Of the dialkynyldiones discussed here, **4a**[19] and **4b**[18] have been described previously, whereas **4c** and **4d** are new. The dimethylphenylsilyl-terminated dialkynyldione **4c** is particularly noteworthy since it is the first stabilised dialkynyldione from which teminal free acetylenes can be obtained under the mild conditions of potassium carbonate mediated protodesilylation.[18] We will make use of this beneficial aspect in the course of this study (*vide infra*).

In accordance with our projections, the acetylenic pyzphen ligands **2a**–**d** were smoothly obtained by separately stirring **3** and **4a**–**d** in acetic acid at room temperature. The functionalised heterocycles are colourless or orange (**2d**) hygroscopic solids that rapidly turn yellow or brown upon exposure to the atmosphere. Refluxing solutions of **2a**–**c** with $[Ru(bpy)_2Cl_2]\cdot 2H_2O$[20] in ethanol for several hours furnished, after anion-exchange with aqueous NH_4PF_6, the corresponding metal complexes **5a**–**c** as amorphous, deep orange or red solids. For comparison, the corresponding $[Ru(phen)_2]$ complexes **6a** and **6b** were prepared in a similar fashion starting from $[Ru(phen)_2Cl_2]\cdot 2H_2O$[21] and **4a**,**b** respectively.

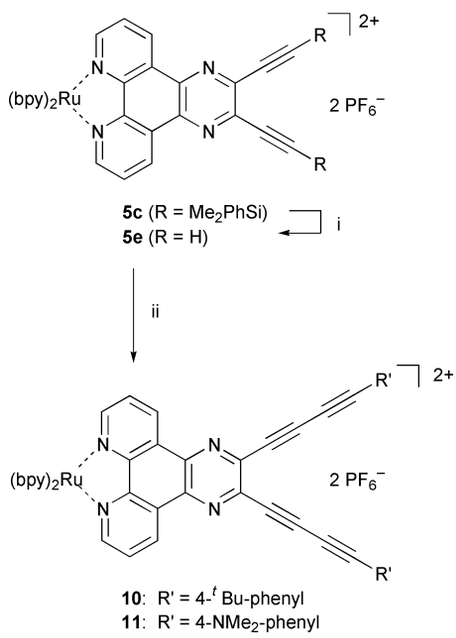
The non-acetylenic reference complexes **8** and **9** were synthesised along similar routes by the condensation of **3** with benzil and subsequent coordination of the intermediate 6,7-diphenyl-pyzphen **7** to the $[Ru(bpy)_2]$ or $[Ru(phen)_2]$ fragments, respectively.

In an effort to investigate the suitability of the newly generated acetylenic structures to partake in oxidative acetylene coupling reactions, we initially attempted to protodesilylate the triisopropylsilyl-terminated pyzphen ligand **2b** with tetrabutylammonium fluoride in THF. However, these experiments furnished a grey precipitate, whose constitution was established



by mass spectrometry and ^{1}H-NMR spectroscopy, but which was found to be almost insoluble in common organic solvents, most disappointingly also in those traditionally used for oxidative acetylene coupling reactions (MeOH, $CHCl_3$, acetone, pyridine, 1,2-dichlorobenzene). The pyzphen system **2c**, which is equipped with the more labile dimethylphenylsilyl groups at the alkyne termini, led to the same compound when protodesilylated by K_2CO_3 in THF at 0 °C. Much to our chagrin, the triisopropylsilyl-protected ruthenium pyzphen complex **5b** did not prove to be a viable starting point for the generation of terminally free acetylenic pyzphen systems, as it decomposed rapidly upon attempted removal of the silyl groups with fluoride.

Finally, our efforts to generate free terminal acetylene groups on the pyzphen moiety were met with success when a combination of cationic Ru(II) solubilising fragment and labile silyl terminus was used to balance reactivity and solubility. Thus, complex **5c** was smoothly protodesilylated to **5e** by stirring the former together with K_2CO_3 in MeCN for 15 min (Scheme 2).

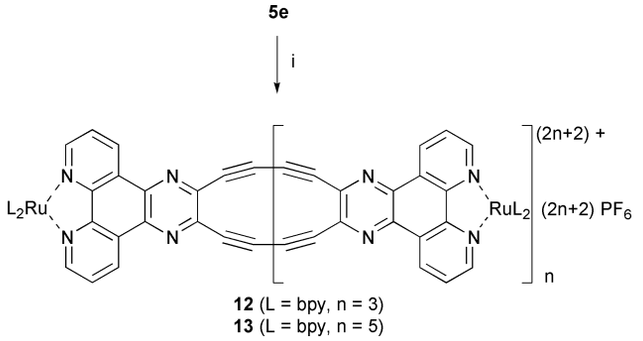


Scheme 2 Reagents and conditions: i, K_2CO_3, MeCN, rt, 15 min, 95%; ii, 4-*tert*-butylphenylacetylene (for **10**) or 4-*N*,*N*-dimethylaminophenylacetylene (for **11**), CuCl, TMEDA, O_2, acetone, rt, 4 h, **10**: 74%, **11**: 72%.

Compound **5e** was isolated as an orange, air-stable solid that is soluble in dichloromethane, acetonitrile, acetone and DMSO.

Much to our satisfaction, **5e** turned out to be amenable to oxidative acetylene coupling reactions: Hence, subjecting an acetone solution of **5e** to an excess of the respective arylacetylene in the presence of TMEDA, CuCl and air[22] furnished the butadiynyl-substituted Ru(II) pyzphen complexes **10** and **11** in yields over 70% (Scheme 2).

The successful preparations of the butadiynyl compounds **10** and **11** by oxidative acetylene *hetero*-coupling suggest that it should also be feasible to employ **5e** for the assembly of cyclic polynuclear metal arrays by similar *homo*-coupling reactions (Scheme 3). Accordingly, when **5e** alone was subjected to the



Scheme 3 Reagents and conditions: i, CuCl, TMEDA, O_2, acetone, rt, 4 h.

Hay-coupling conditions, all starting material was rapidly consumed. Mass spectrometric analysis, using MALDI-TOF techniques, of the products obtained after chromatographic purification on alumina confirmed that indeed metal-coordinated dehydroannulene structures had been formed. Distinct peaks were observed at *m*/*z* ratios of 3919 and 6012, respectively, corresponding to the molecular ions of tetrameric dehydro[24]annulene **12** (n = 3) and hexameric dehydro[36]-annulene **13** (n = 5). Unfortunately, all attempts to isolate individual [Ru(bpy)$_2$]-coordinated dehydroannulenes from this mixture by either fractional crystallisation or by size-exclusion chromatography on Sephadex columns failed. As we did not succeed in controlling the stoichiometry of the homo-coupling of **5e** to unambiguously prepare just one dehydroannulene ring size, we are currently exploring alternative synthetic strategies[23] to obtain molecular architectures of this type.

Electron absorption and emission data

In agreement with our preliminary PM3-MO calculation on the electronic structure of the pyzphen ligands (*vide supra*), the influence of the acetylene substituents on the electronic properties of the heterocycles is clearly observable in their respective electronic absorption spectra (Fig. 2). The longest

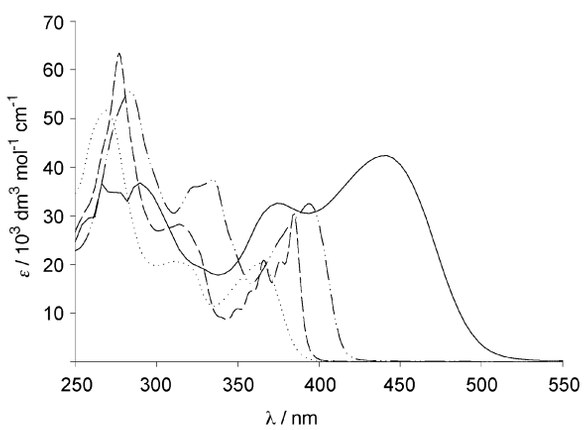


Fig. 2 Electronic absorption spectra of **2a** (–··–), **2b** (---), **2d** (——) and **7** (···) at room temperature in dichloromethane.

wavelength absorptions of **2a**,**b**,**d** are substantially bathochromically shifted (by up to 90 nm in the order **2d** > **2a** > **2b**) relative to that of the non-acetylenic reference compound **7** and are more intense than that of the latter. Further fine-tuning of the absorption properties of the alkynyl pyzphen systems can be achieved by substituting the terminal aryl group, suggesting that electron delocalisation is operational throughout the heterocyclic π-system. Hence, dimethylamino-substituted **2d** displays a significantly red-shifted longest wavelength absorption relative to that of unsubstituted **2a**. The observed red shift could be further enhanced by the possibility of an intramolecular charge-transfer between the terminal amine donor and the pyzphen acceptor unit. The effect of alkynyl-substitution is subdued, however, in the emission spectra of the pyzphen heterocycles, where excitation at wavelengths of the respective absorption maximum around 320 nm results in emissions ranging between 408 (**2b**, **2c**) and 415 nm (**2a**) relative to 403 nm in **7** (data not shown).

The presence of alkyne substituents is also apparent from an inspection of the photophysical data of the Ru(pyzphen)-complexes (Tables 1 and 2, Fig. 3), albeit to varying degrees. In

Table 1 Electronic absorption data of [Ru(II)(pyzphen)]-complexes[a]

	Absorption λ_{max}/nm (ε/10^{-4} dm^3 mol^{-1} cm^{-1})				
5a	288 (87)	315 (sh)	391 (33)		453 (19)
5b	288 (84)	360 (sh)	377 (23)	424 (sh)	453 (15)
5c	287 (107)	358 (21)	374 (26)	424 (sh)	453 (18)
5e	282 (100)	346 (21)	362 (25)	423 (sh)	451 (21)
6a	265 (112)	295 (sh)	317 (sh)	393 (45)	450 (sh)
6b	265 (108)	290 (sh)	361 (sh)	377 (45)	449 (21)
8	288 (98)		362 (25)	421 (sh)	453 (21)
9	265 (119)	290 (sh)	367 (25)	420 (sh)	450 (22)
10	288 (93)			414 (40)	465 (sh)
11	288 (90)		326 (59)	389 (sh)	489 (47)

[a] All spectra were recorded at room temperature in CH_2Cl_2.

Table 2 Electronic emission data of [Ru(II)(pyzphen)]-complexes[a]

	λ_{em}/nm[b]	τ_f/ns[c]	τ_f/ns[c,d]	Φ_f[e]
5a	602	350	570	0.041
5b	604	320	490	0.036
5c	605			
5e	610			
6a	598	250	330	0.029
6b	598	240	300	0.022
8	595	270	420	0.028
9	593	150	190	0.015
10	606[f]			
11	612			

[a] All measurements in CH_2Cl_2 at rt. [b] Emission upon excitation at 450 nm. [c] Luminescence lifetimes ±10%. [d] Dearated solution. [e] Luminescence quantum yields (±20%) relative to [Ru(bpy)$_3$Cl$_2$] in aerated H_2O (Φ = 0.028). [f] λ_{ex} = 465nm.

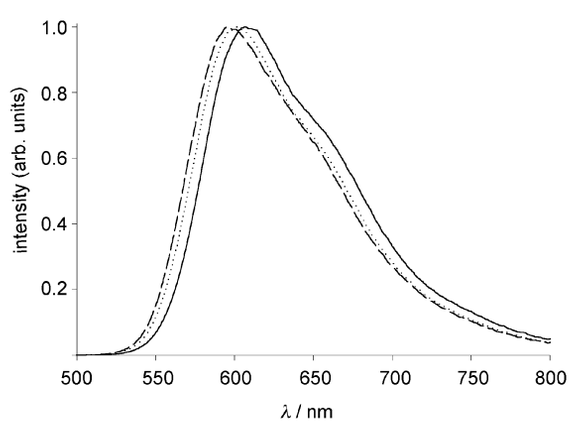


Fig. 3 Emission spectra of **5a** (···), **8** (---), and **10** (——) in dichloromethane at room temperature upon excitation at 450 nm.

all cases, the absorption spectra of the complexes are dominated by intense absorptions at relatively short wavelengths around 265 nm (series **6** and **9**) and 290 nm (series **5** and **8**, **10**, **11**). The longest wavelength absorption maxima in ethynyl-substituted pyzphen complexes of series **5** and **6**, usually assigned as metal-to-ligand charge transfer bands,[24] remain largely invariant around 450 nm and do not differ significantly from those of the non-acetylenic reference complexes **8** and **9**.

The differences are more marked when comparing the absorptions of **8** and those of the butadiynyl pyzphen complexes **10** and **11**, which show red-shifted longest wavelength absorptions at 465 nm and 489 nm, respectively.

Alkynyl-substitution of the chelating pyzphen ligands also effects the luminescence properties of the corresponding Ru(II) coordination compounds (Table 2, Fig. 3). For example, the emissions of the $[Ru(bpy)_2(pyzphen)]$ complexes **5a**–**c**, **5e**, **10** and **11** are slightly bathochromically shifted (up to 17 nm) with respect to that of non-acetylenic **8**. A similar, although less pronounced trend can be noted when the auxiliary chelating ligands of the ruthenium complexes are changed from bpy to phen. Thus, when comparing the stimulated emissions of complexes **6a**,**b** and **9**, a bathochromic shift of *ca.* 5 nm is observed in the case of the acetylenic pyzphen complexes **6a**,**b**. As the emissions in Ru-diimine complexes are thought to arise from excited MLCT states[24] it therefore appears that the nature of the distal pyzphen ligand substituents does have a small, but non-negligible, influence on the electronic interaction between metal and ligand. This is in agreement with the behaviour of $[Ru(bpy)_2(dppz)]^{2+}$ whose MLTC transitions were shown to be vectorial and involve the more readily electron-accepting dppz ligand.[6] The emission observed in this complex at 610 nm therefore arises from excited states localised on the dppz moiety, although the exact nature of these states (a singlet MLCT dppz radical anion or a triplet ππ* state) is still a contentious issue.[25–28]

The notion that alkynyl-substitution does impinge on the electronic properties of [Ru(pyzphen)]-complexes is further corroborated upon inspection of their luminescence lifetimes and quantum yields (Table 2). In the compounds investigated here, alkynyl-substitution generally results in extended luminescence lifetimes and increased luminescence quantum yields in both the bpy and the phen series. Thus, whereas τ of acetylenic **5a**,**b** in air-equilibrated solutions are 350 ns and 320 ns respectively, the corresponding value for **8** is, with τ = 270 ns, considerably shorter. A similar trend is observed in the series of $[Ru(phen)_2(pyzphen)]$-complexes, where the luminescence lifetime differences between **6a**,**b** and **9** amount to 100 ns and 90 ns, respectively. The differences in the luminescence lifetimes between acetylenic and non-acetylenic systems becomes equally apparent in the absence of oxygen, where the lifetimes of **5a** and **5b** are increased by 63% and 53% to 570 ns and 490 ns, respectively, whereas that of **8** increases by 56% to 420 ns with respect to those measured in aerated solutions. The extended luminescence lifetimes of dialkynyl-pyzphen complexes are accompanied by increased luminescence quantum yields, most prominently so within the series of the phen complexes, in which ϕ almost doubles on going from non-acetylenic **9** (ϕ = 0.015) to acetylenic **6a** (ϕ = 0.029). Again, the highest value is observed in case of phenylethynyl-substituted **5a** (ϕ = 0.041). Clearly, all alkynyl-pyzphen bearing ruthenium-complexes presented here are more efficient fluorophores than $[Ru(bpy)_2(dppz)]^{2+}$ (τ = 270 ns, ϕ = 0.021 in EtOH),[6] a conclusion which suggests an evaluation of the suitability of the new systems in biological applications similar to those of the latter.

Electrochemical data

The electrochemical data (Table 3) also reflect a marked influence of the alkynyl substituents on the electronic properties of the pyzphen ligands and their ruthenium complexes. Due to their expanded π-systems,[29] reduction of the acetylenic compounds **2a**,**b** and **2d** occurs at potentials that are *ca.* 300 mV less negative than that of **7**. Not unexpectedly, the most facile reduction along the series occurs at the extended π-system of phenyl-terminated **2a**. Electron-donor substituted **2d**, on the other hand, exhibits a first reduction potential that is 70 mV lower, thereby reemphasising the fact that a fine-tuning of the ligand's electronic properties by variation of the aryl substitution pattern is possible. Coordination of these ligands to the $[Ru(bpy)_2]^{2+}$-fragment leads to less negative first reduction potentials, although the differences in the case of the acetylenic ligands are relatively small (*cf.* −1.49 V for **2a** and −1.13 V for **5a**). It is more pronounced for the non-acetylenic reference compounds **7** and **8** (ΔE = 0.54 V). A potential difference of ΔE = 0.32 V was observed for the dppz/$[Ru(bpy)_2(dppz)]^{2+}$ system and was interpreted as a reflection of the limited electronic coupling between the ruthenium cation and the dppz ligand.[6] Apparently, the electrochemical behaviour of acetylenic [Ru(pyzphen)]-complexes seems to mirror that of the $[Ru(bpy)_2(dppz)]^{2+}$ system, and it is perhaps not surprising, therefore, that the redox potential of the Ru(II)/Ru(III)-couple remains largely unaffected by the nature of the pyzphen ligands.

Table 3 Electrochemical data of pyzphen ligands and their Ru(II)-complexes [a]

	$E_{1/2}(Ru^{II/III})$/V	E_{red}/V	
2a		−1.49 [b]	
2b		−1.53 [b]	
2d	[c]	−1.56 [b]	
7		−1.81 [b]	
5a	1.24	−1.13 [d]	−1.56 [d]
5b	1.25	−1.16	−1.53
5e	1.24	−1.11 [d]	−1.57 [d]
6a	1.25	−1.14 [d]	−1.50 [d]
6b	1.25	−1.17 [d]	−1.49 [d]
8	1.23	−1.36	−1.59
9	1.23	−1.38 [d]	−1.53 [d]
10	1.24	−0.95 [d]	
11	1.24 [e]	−1.00 [d]	

[a] Potentials were determined by cyclovoltammetry with a scan rate of 0.05 V s^{-1} on a Pt working electrode *vs.* Fc/Fc^+ at rt in deaerated MeCN (Ru-complexes) or CH_2Cl_2 (ligands) using 0.1 M NBu_4BF_4 as supporting electrolyte. [b] Redox potentials $E_{1/2}$. [c] Irreversible oxidation at 0.83 V. [d] Irreversible. [e] Additional oxidation at 0.87 V.

There is little variation between the reduction potentials of bpy- and phen-ligated [Ru(pyzphen)]-complexes, suggesting that in all cases the pyzphen ligand serves as the initial electron acceptor. In agreement with the electrochemical behaviour of the uncoordinated pyzphen heterocycles, the complexes are more easily reduced if the pyzphen ligands are acetylene substituted (*cf.* −1.13 V for **5a** *vs.* −1.36 V for **8**). The introduction of a second acetylene unit further facilitates electron uptake, as can be observed from the reduction potential of the butadiynyl-system **10** (−0.95 V) and **11** (−1.00 V). However, while secondary, presumably bpy- and phen-centred reductions are found around potentials of *ca.* −1.5 V for the ethynyl-complexes of series **5** and **6**, the radical-anions of **10** and **11** rapidly decompose and a subsequent reduction of their bpy ligands is not observed even at scan rates of up to 300 mV s^{-1}.

Conclusions

This work has established a convenient route to acetylene-substituted pyzphen heterocycles and their corresponding $[Ru(bpy)_2]$- and $[Ru(phen)_2]$-complexes. The condensation between phen-diamine and the functionalised dialkynyl-1,2-diones, which lies at the core of the pyzphen construction, can be readily adapted to provide a variety of substituted dialkynyl pyzphen ligand systems. While oxidative acetylene coupling reactions are feasible with terminally free acetylenic Ru-pyzphen complexes and lead to the corresponding butadiynyl derivatives, the absence of stoichiometry control during analogous homo-coupling reactions prevented the isolation of discrete metal-coordinated dehydroannulenes, pointing at the need for a different synthetic strategy to access these complex architectures.

The presence of alkynyl substituents on the pyzphen core clearly manifests itself in the optical and electrochemical

properties of both the free ligands and their corresponding ruthenium complexes. Alkynyl substitution leads to bathochromically shifted absorptions and emissions, increased luminescence lifetimes and luminescence quantum yields as well as to more readily reducible systems. In particular the luminescence and the electrochemical behaviour of the ruthenium dialkynyl-pyzphen complexes resemble those of $[Ru(bpy)_2(dppz)]^{2+}$, a compound widely used as a luminescent probe. Compared to related peripherally substituted dppz-ligands that have been employed for this purpose,[4] the ease with which the new pyzphen systems can be structurally varied renders them a valuable alternative for this type of application.

Experimental

General details

Cyclic voltammetry was carried out on an Autolab PGStat 100 (Ecochimie, Netherlands), controlled by GPES software (version 4.8). A platinum disc electrode BAS (diameter 1.6 mm) was used as the working electrode and was polished prior to each experiment using a suspension of alumina powder in water. A platinum wire (diameter 0.5 mm) served as a counter and a silver wire (diameter 0.5 mm) as a quasi reference electrode. All potentials are given *vs.* the Fc/Fc^+ couple as internal standard at 0.31 V *vs.* SCE.[30] Melting points were determined on a Reichert hotstage and are uncorrected. Microanalyses were carried out on a Perkin-Elmer 2400 CHN machine. UV/Vis–absorption spectra were taken on a Perkin-Elmer Lambda 40 instrument in dichloromethane. Luminescence spectra were recorded on a Perkin-Elmer LS50B spectrometer fitted with a red-sensitive R928 photomultiplier tube. Emission spectra are corrected for photomultiplier response using calibration curves provided by the manufacturer. Luminescence quantum yields were determined on a SPEX Fluorolog 2 spectrofluorimeter (equipped with an RCA C31034 Peltier-cooled GaAs photomultiplier) by excitation at 450 nm. The emission spectra are corrected for photomultiplier response. Luminescence quantum yields were calculated according to eqn. (1), where s and r stand for sample and

$$\Phi_s/\Phi_r = A_r n_s^2 (\text{area})_s / A_s n_r^2 (\text{area})_r \quad (1)$$

reference standard, respectively, A is the absorbance adjusted to be ≤ 0.1 at the selected excitation wavelength and n is the refractive index of the solvent. $[Ru(bpy)_3Cl_2]$ was chosen as the reference standard ($\phi_s = 0.028$ in air-equilibrated water).[31]

Time-resolved emission experiments were performed using a 450 nm pump light delivered by a tunable nanosecond pulsed solid-state laser (Coherent Infinity XPO and frequency doubling). The width of the pulse was approximately 2 ns (fwhm), and its energy was less than 2 mJ/pulse. The emission was recorded with a streak camera (Hamamatsu C5680–21) equipped with a M 5677 sweep unit. Infrared spectra were taken on a Perkin-Elmer 1600 FT-IR instrument either as KBr discs or in dichloromethane solution. NMR-spectra were recorded on Bruker AMX400 and Bruker DRX500 machines in $CDCl_3$ or DMSO-d_6. Residual protic solvent signals of $CHCl_3$ (δ_H = 7.24 ppm, δ_C = 77.0 ppm) and DMSO (δ_H = 2.49 ppm, δ_C = 39.5 ppm) were used as internal reference. Signal assignments in the ^{1}H-NMR were assisted by correlation spectroscopy (COSY). Mass spectra were recorded on a VG ZAB SE machine (EI, FAB).

All reactions were conducted in oven-dried glassware under an atmosphere of argon. Solvents were purified and dried according to standard procedures[32] and were freshly distilled prior to use. Amines were freshly distilled from KOH. Lithium bromide was dried at 160 °C at 0.1 mmHg for two hours immediately prior to usage. Known compounds (**4a**,**b**,[18] dimethylphenylsilylacetylene,[33] **3**,[17] *p*-ethynyl-*N*,*N*-dimethylaniline,[34] *p*-*tert*-butylphenyl-acetylene,[35] $[Ru(bpy)_2Cl_2]\cdot 2H_2O$,[20] and $[Ru(phen)_2Cl_2]\cdot 2H_2O$[21]) were synthesised according to the literature procedures. All other reagents are available from commercial suppliers and were used without further purification.

1,6-Bis(dimethylphenylsilyl)hexa-1,5-diyne-3,4-dione (4c)

To a cooled (0 °C) solution of dimethylphenylsilylacetylene[33] (1.334 g, 8.33 mmol) in THF (10 ml) was added BuLi (5.2 ml of a 1.6 M solution in hexane, 8.33 mmol). After stirring for 15 min at 0 °C this solution was added to a solution of pre-dried LiBr (1.45 g, 16.67 mmol) and CuBr (1.195 g, 8.33 mmol) in THF (50 ml) at 0 °C *via* cannula. After stirring for a further 15 min at 0 °C an ice-cold solution of oxalyl chloride (480 mg, 3.78 mmol) in THF (10 ml) was added *via* cannula. Stirring was continued for one hour before the reaction mixture was hydrolysed by the addition of a mixture of saturated aqueous ammonium chloride solution (40 ml) and 1 M HCl (10 ml). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 50 ml). The combined organic layers were washed with brine (50 ml) and dried over Na_2SO_4. After evaporation of the solvent, the resulting yellow–red oil was filtered through a plug of silica (eluted with 10% ethyl acetate in hexane) to furnish an orange oil, yield 633 mg (1.69 mmol, 45%). The compound decomposed slowly even when stored under argon at −20 °C. (Found: 375.1230. $C_{22}H_{23}O_2Si_2$ requires 375.1237); λ_{max}/nm (CH_2Cl_2) 260 (ε/dm^3 mol^{-1} cm^{-1} 9000); ν_{max}/cm^{-1} (CH_2Cl_2) (CH) 2965 (s), (C≡C) 2150 (s), (C=O) 1680 (s); δ_H (400 MHz, $CDCl_3$) 7.60 (2 H, m, Ph), 7.40 (3 H, m, Ph), 0.51 (6 H, s, CH_3); δ_C (100 MHz, $CDCl_3$) (C=O) 171.6, (aromatic C) 133.9, 133.8, 130.2, 128.2, (C≡C) 107.1, 99.8, (CH_3) −1.9; *m*/*z* (EI-MS) 374 (11%, M^+), 187 (36%, $M^+/2$), 159 (100%, $M^+/2$ − CO).

1,6-Bis(4-*N*,*N*-dimethylaminophenyl)hexa-1,5-diyne-3,4-dione (4d)

The synthesis was performed in analogy to that of **4c**. The reaction was quenched by the addition of a saturated aqueous ammonium chloride solution (50 ml). The organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 50 ml). After removal of the solvents the black residue was dissolved in dichloromethane (200 ml), washed with water (3 × 100 ml), brine (50 ml) and dried over Na_2SO_4. The crude product, obtained by evaporation of the solvent, was triturated with boiling ethyl acetate to yield **4d** as a deep red solid, yield 703 mg (2.04 mmol, 54%), mp 221–223 °C (decomp.) (Found: C, 76.8; H, 5.9; N, 8.0. $C_{22}H_{20}N_2O_2$ requires C, 76.7; H, 5.9; N, 8.1%); λ_{max}/nm (CH_2Cl_2) 321 (ε/dm^3 mol^{-1} cm^{-1} 36500), 457 (40000); ν_{max}/cm^{-1} (KBr disc) (C=C) 2165 (s), (C=O) 1662 (s); δ_H (400 MHz, $CDCl_3$) 7.56 (4 H, d, J = 9.1 Hz, Ph), 6.62 (4 H, d, J = 9.1 Hz, Ph), 3.04 (12 H, s, CH_3); δ_C (100 MHz, $CDCl_3$) (C=O) 172.9, (aromatic C) 152.3, 136.2, 111.5, (C≡C) 105.0, (aromatic C) 104.7, (C≡C) 89.2, (CH_3) 40.0; *m*/*z* (EI-MS) 344 (2%, M^+), 172 (100%, $M^+/2$).

General procedure for the synthesis of the pyrazino[2,3-*f*][1,10]-phenanthroline ligands

To a deaerated solution of the respective 1,2-diketone **4** or benzil (0.5 mmol) in acetic acid (15 ml) was added phenanthroline-5,6-diamine **3**[17] (0.5 mmol) in one portion. The reaction mixture was stirred for one hour during which time the colour changed from deep brown to red. The solvent was removed *in vacuo* and the red residue was recrystallised from methanol unless otherwise stated. α, β and γ ^{1}H-NMR signals refer to protons in the 2, 3 and 4 positions relative to the phenanthroline nitrogen.

6,7-Bis(phenylethynyl)pyrazino[2,3-*f*][1,10]phenanthroline (2a)

Yellow solid, yield 171 mg (0.395 mmol, 79%), mp 281–283 °C (decomp.) (Found: C, 83.3; H, 3.6; N, 12.9. $C_{30}H_{16}N_4$ requires C, 83.3; H, 3.7; N, 13.0%); λ_{max}/nm (CH_2Cl_2) 284 (ε/dm^3 mol^{-1} cm^{-1} 55500), 322 (sh), 335 (37000), 394 (32000); ν_{max}/cm^{-1} (CH_2Cl_2) (CH) 3050 (s), 2983 (m), (C≡C) 2207 (s); δ_H (400 MHz, $CDCl_3$) 9.49 (2 H, dd, *J* = 8.2, 1.7 Hz, γ CH), 9.25 (2 H, dd, *J* = 4.4, 1.7 Hz, α CH), 7.75 (2 H, dd, *J* = 8.2, 4.4 Hz, β CH), 7.70 (4 H, m, Ph), 7.40 (6 H, m, Ph); δ_C (100 MHz, $CDCl_3$) (aromatic C) 152.5, 147.7, 141.0, 138.0, 133.7, 132.3, 129.9, 128.6, 126.3, 124.0, 121.6, (C≡C) 96.8, 86.8; *m*/*z* (EI-MS) 432 (100%, M^+).

6,7-Bis(triisopropylsilylethynyl)pyrazino[2,3-*f*][1,10]phenanthroline (2b). The red residue obtained after standard workup was subjected to column chromatography (neutral aluminium oxide, hexane–dichloromethane–triethylamine = 65 : 30 : 5). After recrystallisation from methanol, **2b** was isolated as white, hygroscopic needles, which turned yellow upon exposure to the ambient conditions, yield 214 mg (0.36 mmol, 72%), mp 175–177 °C (Found: C, 72.4: H, 8.2; N, 9.3. $C_{36}H_{48}N_4Si_2$ requires C, 72.9; H, 8.2; N, 9.5%); (Found: 593.3495. $C_{36}H_{49}N_4Si_2$ requires 593.3496); λ_{max}/nm (CH_2Cl_2) 277 (ε/dm^3 mol^{-1} cm^{-1} 62000), 315 (27000), 350 (sh), 358 (sh), 366 (19000), 376 (20000), 385 (28000); ν_{max}/cm^{-1} (CH_2Cl_2) (CH) 2946 (s), 2867 (s), (C≡C) 2159 (w); δ_H (400 MHz, $CDCl_3$) 9.42 (2 H, dd, *J* = 8.2, 1.6 Hz, γ CH), 9.23 (2 H, dd, *J* = 4.5, 1.6 Hz, α CH), 7.75 (2 H, dd, *J* = 8.2, 4.5 Hz, β CH), 1.28–1.05 (42 H, m, *i*-Pr); δ_C (100 MHz, $CDCl_3$) (aromatic C) 152.5, 147.7, 138.8, 138.0, 133.7, 126.3, 124.0, (C≡C) 103.4, 100.2, (CH_3) 18.7, (Si–CH) 11.3; *m*/*z* (EI-MS) 592 (7%, M^+), 549 (23%, $M^+ - i$-Pr), 507 (100%, $M^+ - 2\ i$-Pr].

6,7-Bis(dimethylphenylsilylethynyl)pyrazino[2,3-*f*][1,10]phenanthroline (2c). The red residue obtained after standard workup was subjected to column chromatography (silica, 5% methanol in dichloromethane) and recrystallised from methanol to give **2c** as a white, hygroscopic solid, which turned yellow upon exposure to the ambient conditions, yield 156 mg (0.285 mmol, 57%), mp 157–160 °C (decomp.) (Found: C, 74.4; H, 5.0; N, 10.2. $C_{34}H_{28}N_4Si_2$ requires C, 74.4; H, 5.1; N, 10.2%); (λ_{max}/nm (CH_2Cl_2) 276 (ε/dm^3 mol^{-1} cm^{-1} 60000), 315 (21000), 349 (sh), 357 (sh), 365 (14000), 376 (15000), 384 (21000); (ν_{max}/cm^{-1} (CH_2Cl_2) (CH) 2975 (s), 2967 (s), (C≡C) 2158 (w); δ_H (400 MHz, $CDCl_3$) 9.44 (2 H, dd, *J* = 8.2, 1.8 Hz, γ CH), 9.24 (2 H, dd, *J* = 4.4, 1.8 Hz, α CH), 7.74 (2 H, dd, *J* = 8.2, 4.4 Hz, β CH), 7.71 (4 H, m, Ph), 7.40–7.35 (6 H, m, Ph), 0.54 (12 H, s, CH_3); δ_C (100 MHz, $CDCl_3$) (aromatic C) 152.7, 147.7, 140.2, 138.2, 135.5, 133.9, 133.8, 129.8, 128.0, 126.1, 124.1, (C≡C) 102.2, 101.4, (CH_3) −1.2; *m*/*z* (EI-MS) 448 (100%, M^+), 433 (42%, $M^+ - CH_3$).

6,7-Bis(4-*N*,*N*-dimethylaminophenylethynyl)pyrazino[2,3-*f*]-[1,10]phenanthroline (2d). The red residue obtained after standard workup was dissolved in dichloromethane, the solution was washed with water and dried (Na_2SO_4). After removal of the solvent *in vacuo* the remaining brown residue was filtered through a short plug of silica gel. Eluting first with 1% methanol in dichloromethane afforded unreacted diketone, changing the eluent to 5% methanol in dichloromethane afforded **2d** as an orange solid, yield 225 mg (0.43 mmol, 87%), mp 252–254 °C (decomp.) (Found: C, 78.2: H, 5.0; N, 16.0. $C_{34}H_{26}N_6$ requires C, 78.7; H, 5.1; N, 16.7%); (Found: 519.2285. $C_{34}H_{27}N_6$ requires 519.2297); λ_{max}/nm (CH_2Cl_2) 272 (ε/dm^3 mol^{-1} cm^{-1} 38000), 281 (sh), 294 (sh), 327 (sh), 375 (32000), 439 (41000);); ν_{max}/cm^{-1} (KBr disc) (CH) 3034 (s), 2891 (m), (C≡C) 2183 (s); δ_H (400 MHz, $CDCl_3$) 9.48 (2 H, d, *J* = 8.1 Hz, γ CH), 9.22 (2 H, d, *J* = 4.2 Hz, α CH), 7.74 (2 H, dd, *J* = 8.1, 4.2 Hz, β CH), 7.61 (4 H, d, *J* = 8.7 Hz, Ph), 6.67 (4 H, d, *J* = 8.7 Hz, Ph), 3.03 (12 H, s, CH_3); δ_C (100 MHz, $CDCl_3$) (aromatic C) 152.0, 151.0, 147.5, 141.5, 137.3, 133.9, 133.5, 126.7, 123.8, 111.7, 108.2, (C≡C) 99.3, 86.5, (CH_3) 40.1; *m*/*z* (EI-MS) 519 (100%, M^+).

6,7-Diethynylpyrazino[2,3-*f*][1,10]phenanthroline. Tetrabutylammonium fluoride (1.04 ml of a 1 M solution in THF, 1.04 mmol) was added to a deaerated solution of **2b** (310 mg, 0.52 mmol) in THF (10 ml) at 0 °C. The grey solid, formed instantly during the addition, was filtered and washed with CH_2Cl_2 (3 × 30 ml), yield 105 mg (0.38 mmol, 72%). The compound was found to be very hygroscopic and almost insoluble in common organic solvents. It was characterised by ^{1}H-NMR and EI-MS. δ_H (400 MHz, $CDCl_3$) 9.46 (2 H, dd, *J* = 8.2, 1.8 Hz, γ CH), 9.29 (2 H, dd, *J* = 4.5, 1.8 Hz, α CH), 7.79 (2 H, dd, *J* = 8.2, 4.5 Hz, β CH), 3.70 (2 H, s, acetylenic H); *m*/*z* (EI-MS) 280 (100%, M^+).

6,7-Diphenylpyrazino[2,3-*f*][1,10]phenanthroline (7). White solid, yield 131 mg (0.34 mmol, 68%), mp > 300 °C (Found: C, 80.9; H, 4.1; N, 14.6. $C_{26}H_{16}N_4$ requires C, 81.2; H, 4.2; N, 14.6%); λ_{max}/nm (CH_2Cl_2) 269 (ε/dm^3 mol^{-1} cm^{-1} 52000), 311 (21000), 364 (20000); ν_{max}/cm^{-1} (CH_2Cl_2) (CH) 3060 (s); δ_H (400 MHz, $CDCl_3$) 9.54 (2 H, dd, *J* = 8.1, 1.7 Hz, γ CH), 9.26 (2 H, dd, *J* = 4.4, 1.7 Hz, α CH), 7.76 (2 H, dd, *J* = 8.1, 4.4 Hz, β CH), 7.67 (4 H, m, Ph); 7.40 (6 H, m, Ph); δ_C (100 MHz, $CDCl_3$) (aromatic C) 152.5, 152.0, 147.6, 138.7, 137.8, 133.3, 130.0, 129.1, 128.3, 127.0, 123.9; *m*/*z* (EI-MS) 384 (100%, M^+).

General procedure for the preparation of [Ru(bpy)$_2$(pyzphen)] and [Ru(phen)$_2$(pyzphen)] complexes

To a stirred, deaerated solution of pyzphen ligands **2** or **7** (0.2 mmol) in ethanol (20 ml) was added either $[Ru(bpy)_2Cl_2]\cdot 2H_2O$[20] (97 mg, 0.2 mmol) or $[Ru(phen)_2Cl_2]\cdot 2H_2O$[21] (113 mg, 0.2 mmol). The reaction mixture was heated under reflux for 16 hours in an argon atmosphere. After cooling to 0 °C an aqueous solution of NH_4PF_6 was added until no further precipitate was formed. The suspension was stored for 2 hours at −20 °C before the precipitate was filtered, washed successively with H_2O (10 ml), ethanol (10 ml) and diethyl ether (20 ml) to furnish the metal complexes as analytically pure orange to red solids.

[Ru(bpy)$_2$(6,7-bis(phenylethynyl)pyzphen)]·2PF$_6$ (5a). Red solid, yield 177 mg (0.16 mmol, 78%), mp 265–268 °C (decomp.) (Found: C, 52.0; H, 2.8; N, 9.6. $RuC_{50}H_{32}N_8(PF_6)_2\cdot H_2O$ requires C, 52.1; H, 2.8; N, 9.7%); λ_{max}/nm (CH_2Cl_2) 288 (ε/dm^3 mol^{-1} cm^{-1} 87000), 315 (sh), 391 (33000), 453 (19000); ν_{max}/cm^{-1} (KBr disc) (CH) 3074 (s), (C≡C) 2209 (s); δ_H (500 MHz, DMSO-d$_6$) 9.49 (2 H, dd, *J* = 8.3, 1.3 Hz, lig), 8.87 (2 H, d, *J* = 8.3 Hz, bpy), 8.84 (2 H, d, *J* = 8.3 Hz, bpy), 8.27 (2 H, dd, *J* = 5.3, 1.3 Hz, lig), 8.22 (2 H, m, bpy), 8.13 (2 H, m, bpy), 8.02 (2 H, dd, *J* = 8.3, 5.3 Hz, lig), 7.81 (2 H, m, bpy), 7.77 (4 H, m, Ph), 7.70 (2 H, m, bpy), 7.61–7.40 (8 H, m, Ph, bpy), 7.38 (2 H, m, bpy); δ_C (100 MHz, DMSO-d$_6$) (aromatic C) 156.8, 156.5, 153.8, 151.9, 151.4, 149.3, 141.2, 138.1, 138.0, 137.6, 133.2, 132.1, 131.0, 129.3, 128.7, 127.9, 127.8, 127.7, 124.5, 124.4, 120.1, (C≡C) 97.7, 86.4; *m*/*z* (FAB-MS) 846 (34%, $M^+ - 2\ PF_6$).

[Ru(bpy)$_2$(6,7-bis(triisopropylsilylethynyl)pyzphen)]·2PF$_6$ (5b). Orange solid, yield 210 mg (0.16 mmol, 81%), mp > 300 °C (Found: C, 51.1; H, 4.9; N, 8.6. $RuC_{56}H_{64}N_8Si_2(PF_6)_2\cdot H_2O$ requires C, 51.2; H, 4.9, N, 8.5%); λ_{max}/nm (CH_2Cl_2) 288 (ε/dm^3 mol^{-1} cm^{-1} 84000), 360 (sh), 377 (23000), 424 (sh), 453 (15000); ν_{max}/cm^{-1} (KBr disc) (CH) 2945 (s), 2866 (s), (C≡C) 2156 (w); δ_H (500 MHz, DMSO-d$_6$) 9.37 (2 H, dd, *J* = 8.3, 1.2 Hz, lig), 8.88 (2 H, d, *J* = 8.3 Hz, bpy), 8.85 (2 H, d, *J* = 8.3 Hz, bpy), 8.27 (2 H, dd, *J* = 5.3, 1.2 Hz, lig), 8.23 (2 H, m, bpy), 8.14 (2 H, m, bpy), 8.03 (2 H, dd, *J* = 8.3, 5.3 Hz, lig), 7.83 (2 H, m, bpy), 7.68 (2 H, m, bpy), 7.60 (2 H, m, bpy), 7.37 (2 H, m, bpy), 1.30–1.19 (42 H, m, *i*-Pr); δ_C (100 MHz, DMSO-d$_6$) (aromatic C) 156.8,

156.5, 153.9, 151.7, 151.5, 149.3, 139.5, 138.1, 138.0, 137.9, 133.2, 128.5, 127.9, 127.8, 127.7, 124.5, 124.4, (C≡C) 103.0, 101.1, (CH_3) 18.5, (Si–CH) 10.7; *m*/*z* (FAB-MS) 1151 (73%, $M^+ - PF_6$), 1005 (38%, $M^+ - 2\ PF_6$).

[Ru(bpy)$_2$(6,7-bis(dimethylphenylsilylethynyl)pyzphen)]·2PF$_6$ (5c). Orange solid, yield 213 mg (0.17 mmol, 85%), mp 213–215 °C (decomp.) (Found: C, 51.1; H, 3.5; N, 9.0. $RuC_{54}H_{44}N_8Si_2(PF_6)_2\cdot H_2O$ requires C, 51.1; H, 3.5; N, 8.8%); λ_{max}/nm (CH_2Cl_2) 287 (ε/dm^3 mol^{-1} cm^{-1} 107000), 358 (21000), 374 (26000), 424 (sh), 453 (18000); ν_{max}/cm^{-1} (KBr disc) (CH) 3088 (s), 2862 (s), (C≡C) 2160 (w); δ_H (400 MHz, DMSO-d$_6$) 9.44 (2 H, dd, *J* = 8.3, 1.3 Hz, lig), 8.88 (2 H, d, *J* = 8.3 Hz, bpy), 8.85 (2 H, d, *J* = 8.3 Hz, bpy), 8.26 (2 H, dd, *J* = 5.4, 1.3 Hz, lig), 8.23 (2 H, m, bpy), 8.14 (2 H, m, bpy), 7.99 (2 H, dd, *J* = 8.3, 5.4 Hz, lig), 7.81 (2 H, m, bpy), 7.73 (4 H, m, Ph), 7.69 (2 H, m, bpy), 7.50–7.43 (8 H, m, Ph, bpy), 7.39 (2 H, m, bpy), 0.54 (12 H, s, CH_3); δ_C (100 MHz, DMSO-d$_6$) (aromatic C) 156.7, 156.5, 153.9, 151.8, 151.4, 149.4, 140.3, 138.1, 138.0, 137.8, 134.6, 133.7, 133.5, 130.1, 128.5, 128.2, 127.9, 127.7 (2C), 124.5, 124.4, (C≡C) 102.7, 101.7, (CH_3) −1.6; *m*/*z* (FAB-MS) 1107 (14%, $M^+ - PF_6$), 962 (14%, $M^+ - 2\ PF_6$), 135 (100%, $PDMS^+$).

[Ru(bpy)$_2$(6,7-diethynylpyzphen)]·2PF$_6$ (5e). Potassium carbonate (83 mg, 0.6 mmol) was added to a solution of **5c** (250 mg, 0.2 mmol) in acetonitrile (25 ml). After stirring for 15 minutes at rt, the reaction was hydrolysed with water (25 ml). The resulting solution was extracted with dichloromethane (3 × 50 ml). Drying over Na_2SO_4, filtration and removal of the solvent *in vacuo* afforded a red solid, which was recrystallised from a mixture of acetonitrile, dichloromethane and diethyl ether. The orange solid was collected and dried, yield 187 mg (0.19 mmol, 95%), mp > 300 °C (Found: C, 45.2; H, 2.5; N, 10.8. $RuC_{38}H_{24}N_8(PF_6)_2\cdot H_2O$ requires C, 45.5; H, 2.4; N, 11.2%); λ_{max}/nm (CH_2Cl_2) 282 (ε/dm^3 mol^{-1} cm^{-1} 100000), 346 (21000), 362 (25000), 423 (sh), 451 (21000); ν_{max}/cm^{-1} (KBr disc) (C≡CH) 3275 (s), (CH) 3086 (m), (C≡C) 2113 (s); δ_H (400 MHz, DMSO-d$_6$) 9.42 (2 H, dd, *J* = 8.2, 1.0 Hz, lig), 8.87 (2 H, d, *J* = 8.3 Hz, bpy), 8.83 (2 H, d, *J* = 8.3 Hz, bpy), 8.26 (2 H, dd, *J* = 5.3, 1.0 Hz, lig), 8.21 (2 H, m, bpy), 8.12 (2 H, m, bpy), 8.00 (2 H, dd, *J* = 8.2, 5.3 Hz, lig), 7.80 (2 H, m, bpy), 7.66 (2 H, m, bpy), 7.58 (2 H, m, bpy), 7.35 (2 H, m, bpy), 5.28 (2 H, s, acetylenic H); δ_C (100 MHz, DMSO-d$_6$) (aromatic C) 156.7, 156.4, 153.8, 151.7, 151.3, 149.3, 140.4, 138.0, 137.9, 137.8, 133.2, 128.4, 127.8, 127.6 (2C), 124.4, 124.3, (C≡C) 89.6, 79.7; *m*/*z* (FAB-MS) 839 (66%, $M^+ - PF_6$), 694 (56%, $M^+ - 2\ PF_6$).

[Ru(phen)$_2$(6,7-bis(phenylethynyl)pyzphen)]·2PF$_6$ (6a). Red solid, yield 200 mg (0.17 mmol, 84%), mp > 250 °C (decomp.) (Found: C, 54.2; H, 2.7; N, 9.3. $RuC_{54}H_{32}N_8(PF_6)_2\cdot H_2O$ requires C, 54.0; H, 2.7; N, 9.3%); λ_{max}/nm (CH_2Cl_2) 265 (ε/dm^3 mol^{-1} cm^{-1} 112000), 295 (sh), 317 (sh), 393 (45000), 450 (sh); ν_{max}/cm^{-1} (KBr disc) (CH) 3085 (m), (C≡C) 2205 (s); δ_H (400 MHz, DMSO-d$_6$) 9.46 (2 H, dd, *J* = 8.3, 1.2 Hz, lig), 8.79 (2 H, dd, *J* = 8.3, 1.2 Hz, phen), 8.77 (2 H, dd, *J* = 8.3, 1.2 Hz, phen), 8.39 (4 H, s, phen), 8.23 (2 H, dd, *J* = 5.3, 1.2 Hz, phen), 8.21 (2 H, dd, *J* = 5.3, 1.2 Hz, lig), 8.05 (2 H, dd, *J* = 5.3, 1.2 Hz, phen), 7.89 (2 H, dd, *J* = 8.3, 5.3 Hz, lig), 7.81 (2 H, dd, *J* = 8.3, 5.3 Hz, phen), 7.78–7.75 (6 H, m, phen, Ph), 7.60–7.54 (6 H, m, Ph); δ_C (100 MHz, DMSO-d$_6$) (aromatic C) 154.2, 153.1, 152.5, 149.6, 147.1 (2C), 141.1, 137.5, 136.9, 133.1, 132.0 (2C), 130.8, 130.4 (2C), 129.2, 128.5, 128.0, 127.9, 127.4, 126.2, 126.1, 120.1, (C≡C) 97.6, 86.3; *m*/*z* (FAB-MS) 894 (3%, $M^+ - 2\ PF_6$).

[Ru(phen)$_2$(6,7-bis(triisopropylsilylethynyl)pyzphen)]·2PF$_6$ (6b). Red solid (196 mg, 73%), mp 245–247 °C (Found: C, 53.1; H, 4.8; N, 8.2. $RuC_{60}H_{64}N_8Si_2(PF_6)_2\cdot H_2O$ requires C, 52.9; H, 4.7; N, 8.2%); λ_{max}/nm (CH_2Cl_2) 265 (ε/dm^3 mol^{-1} cm^{-1} 108000), 290 (sh), 361 (sh), 377 (45000), 449 (21000); ν_{max}/cm^{-1} (KBr disc) (CH) 2943 (s), 2865 (s), (C≡C) 2155 (w); δ_H (400 MHz, DMSO-d$_6$) 9.32 (2 H, dd, *J* = 8.3, 1.2 Hz, lig), 8.78 (2 H, dd, *J* = 8.3, 1.2 Hz, phen), 8.76 (2 H, dd, *J* = 8.3, 1.2 Hz, phen), 8.38 (4 H, s, phen), 8.20 (2 H, dd, *J* = 5.4, 1.2 Hz, lig), 8.17 (2 H, dd, *J* = 5.2, 1.2 Hz, phen), 8.04 (2 H, dd, *J* = 5.2, 1.1 Hz, phen), 7.90 (2 H, dd, *J* = 8.3, 5.4 Hz, lig), 7.77 (4 H, m, phen), 1.28–1.08 (42 H, m, *i*-Pr); δ_C (100 MHz, DMSO-d$_6$) (aromatic C) 154.3, 152.9, 152.6, 149.6, 147.1, 147.0, 139.4, 137.8, 136.9 (2 C), 133.1, 130.4 (2 C), 128.3, 128.0 (2 C), 127.5, 126.2, 126.1, (C≡C) 102.9, 101.1, (*i*-Pr) 18.4, 10.7; *m*/*z* (FAB-MS) 1199 (12%, $M^+ - PF_6$), 1054 (9%, $M^+ - 2\ PF_6$).

[Ru(bpy)$_2$(6,7-diphenylpyzphen)]·2PF$_6$ (8). Orange solid, yield 155 mg (0.14 mmol, 71%), mp 258–260 °C (Found: C, 50.0; H, 2.7; N, 9.9. $RuC_{46}H_{32}N_8(PF_6)_2\cdot H_2O$ requires C, 50.0; H, 2.9; N, 10.1%); λ_{max}/nm (CH_2Cl_2) 288 (ε/dm^3 mol^{-1} cm^{-1} 98000), 362 (25000), 421, (sh), 453 (21000); ν_{max}/cm^{-1} (KBr disc) (CH) 3087 (s); δ_H (500 MHz, DMSO-d$_6$) 9.59 (2 H, dd, *J* = 8.2, 1.3 Hz, lig), 8.89 (2 H, d, *J* = 8.2 Hz, bpy), 8.86 (2 H, d, *J* = 8.2 Hz, bpy), 8.27 (2 H, dd, *J* = 5.3, 1.3 Hz, CH), 8.24 (2 H, m, bpy), 8.14 (2 H, m, bpy), 8.03 (2 H, dd, *J* = 8.2, 5.3 Hz, lig), 7.86 (2 H, m, bpy), 7.73 (2 H, m, bpy), 7.70 (4 H, m, Ph), 7.62 (2 H, m, bpy), 7.54–7.47 (6 H, m, Ph), 7.38 (2 H, m, bpy); δ_C (100 MHz, DMSO-d$_6$) (aromatic C) 156.6, 156.3, 153.4, 153.1, 151.6, 151.2, 148.8, 137.9, 137.8 (2C), 136.9, 132.9, 129.6, 129.4, 129.1, 128.3, 127.7, 127.5, 127.2, 125.3, 125.2; *m*/*z* (FAB-MS) 1088 (1%, M^+), 944 (100%, $M^+ - PF_6$), 798 (32%, $M^+ - 2\ PF_6$).

[Ru(phen)$_2$(6,7-diphenylpyzphen)]·2PF$_6$ (9). Orange solid, yield 178 mg (0.16 mmol, 78%), mp > 250 °C (Found: C, 52.2; H, 2.8; N, 9.6. $RuC_{50}H_{32}N_8(PF_6)_2\cdot H_2O$ requires C, 52.0; H, 2.8; N, 9.7%); λ_{max}/nm (CH_2Cl_2) 265 (ε/dm^3 mol^{-1} cm^{-1} 119000), 290 (sh), 367 (25000), 420 (sh), 450 (22000); ν_{max}/cm^{-1} (KBr disc) (CH) 3086 (s); δ_H (500 MHz, DMSO-d$_6$) 9.54 (2 H, dd, *J* = 8.2, 1.1 Hz, lig), 8.78 (2 H, dd, *J* = 8.2, 1.0 Hz, phen), 8.77 (2 H, dd, *J* = 8.2, 1.0 Hz, phen), 8.39 (4 H, s, phen), 8.23 (2 H, dd, *J* = 5.2, 1.0 Hz, phen), 8.20 (2 H, dd, *J* = 5.3, 1.1 Hz, lig), 8.07 (2 H, dd, *J* = 5.2, 1.0 Hz, phen), 7.89 (2 H, dd, *J* = 8.2, 5.3 Hz, lig), 7.78 (4 H, m, phen), 7.67 (4 H, m, Ph,), 7.46 (6 H, m, Ph); δ_C (100 MHz, DMSO-d$_6$) (aromatic C) 153.7, 153.5, 153.0, 152.6, 149.4, 147.1 (2C), 137.8, 137.0, 136.9 (2C), 133.0, 130.4 (2C), 129.7, 129.5, 129.1, 128.4, 128.2, 128.0, 127.2, 126.2, 126.1; *m*/*z* (FAB-MS) 991 (10%, $M^+ - PF_6$), 846 (34%, $M^+ - 2\ PF_6$).

General procedure for oxidative acetylene coupling reactions of 5e and arylacetylenes

Copper(I) chloride (124 mg 1.25 mmol) was added to a solution of tetramethylethylenediamine (148 mg, 1.25 mmol) in dry acetone (5 ml) and the mixture was stirred for 30 minutes. The resulting deep green solution was added to a solution of **5e** (50 mg, 0.05 mmol) and the respective arylacetylene (1.25 mmol) in dry acetone (150 ml). While stirring, a constant stream of dry air was bubbled through the reaction mixture. After 4 hours, the reaction mixture was concentrated *in vacuo* and filtered through a plug of alumina. Eluting the plug with dichloromethane furnished the 1,4-diarylbutadiyne, changing the eluent to a 10 mM solution of NH_4PF_6 in acetonitrile afforded the product.

[Ru(bpy)$_2$(6,7-bis(4-*tert*-butylphenylbutadiynyl)pyzphen)]·2PF$_6$ (10). Orange solid, yield 49 mg (0.038 mmol, 74%), mp 198–200 °C (decomp.) (Found: C, 56.2; H, 3.8; N, 8.4. $RuC_{62}H_{48}N_8(PF_6)_2\cdot H_2O$ requires C, 56.6; H, 3.6; N, 8.5%); λ_{max}/nm (CH_2Cl_2) 288 (ε/dm^3 mol^{-1} cm^{-1} 93000), 414 (40000), 465 (sh); ν_{max}/cm^{-1} (KBr disc) (CH) 2961 (s), (C≡C) 2202 (s); δ_H (500 MHz, DMSO-d$_6$) 9.44 (2 H, dd, *J* = 8.2, 0.9 Hz, lig), 8.87 (2 H, d, *J* = 8.3 Hz, bpy), 8.83 (2 H, d, *J* = 8.3 Hz, bpy), 8.27 (2 H, dd, *J* = 5.2, 0.9 Hz, lig), 8.22 (2 H, m, bpy), 8.13 (2 H, m, bpy), 8.01 (2 H, dd, *J* = 8.2, 5.2 Hz, lig), 7.81 (2 H, m, bpy), 7.68 (2 H, m, bpy), 7.68 (4 H, d, *J* = 8.4 Hz, Ph), 7.58 (2 H, m, bpy), 7.51 (4 H, d, *J* = 8.4 Hz, Ph), 7.36 (2 H, m, bpy), 1.29 (18 H, s, *t*-Bu); δ_C (100 MHz, DMSO-

d_6) (aromatic C) 156.7, 156.4, 154.3, 154.1, 151.8, 151.4, 149.5, 140.3, 138.1, 137.9, 137.6, 133.3, 132.9, 128.4, 127.9, 127.7 (2C), 126.0, 124.5, 124.4, 116.1, (C≡C) 87.5, 81.3, 77.2, 72.0, (CCH_3) 34.8, (CCH_3) 30.7; *m/z* (FAB-MS) 1151 (81%, $M^+ - PF_6$), 1006 (100%, $M^+ - 2\ PF_6$).

[Ru(bpy)$_2$(6,7-bis(4-*N*,*N*-dimethylaminophenylbutadiynyl)-pyzphen)]·2PF$_6$ (11). The product was found to be hygroscopic. Red solid, yield 47 mg (0.037 mmol, 72%), mp > 300 °C (Found: C, 52.3; H, 3.1; N, 10.4. $RuC_{58}H_{42}N_{10}(PF_6)_2 \cdot 3\ H_2O$ requires C, 52.6; H, 3.2; N, 10.6%); λ_{max}/nm (CH_2Cl_2) 288 (ε/dm^3 mol^{-1} cm^{-1} 90000), 326 (59000), 349 (sh), 489 (47000); ν_{max}/cm^{-1} (KBr disc) (CH) 3080 (w), (C≡C) 2180 (s); δ_H (400 MHz, DMSO-d_6) 9.43 (2 H, dd, J = 8.2, 1.0 Hz, lig), 8.87 (2 H, d, J = 8.2 Hz, bpy), 8.84 (2 H, d, J = 8.2 Hz, bpy), 8.25 (2 H, dd, J = 5.4, 1.0 Hz, lig), 8.21 (2 H, m, bpy), 8.13 (2 H, m, bpy), 7.99 (2 H, dd, J = 8.2, 5.4 Hz, lig), 7.80 (2 H, m, bpy), 7.68 (2 H, m, bpy), 7.58 (2 H, m, bpy), 7.53 (4 H, d, J = 8.9 Hz, Ph), 7.37 (2 H, m, bpy), 6.73 (4 H, d, J = 8.9 Hz, Ph), 3.00 (12 H, s, CH_3); δ_C (100 MHz, DMSO-d_6) (aromatic C) 156.7, 156.4, 153.8, 151.8, 151.5, 151.4, 149.3, 140.5, 138.1, 138.0, 137.6, 134.5, 134.3, 133.3, 128.5, 127.9, 127.7, 124.5, 124.4, 111.8, 103.8, (C≡C) 90.7, 83.0, 77.9, 71.8, (CH_3) 41.3; *m/z* (FAB-MS) 980 (4% $M^+ - 2\ PF_6$).

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