

# Pyrene-Bridged Bis(phenanthroline) Ligands and Their Dinuclear Ruthenium(II) Complexes

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The Friedländer condensation of 8-amino-7-quinolinecarbaldehyde with a series of four isomeric diacetylpyrenes provides the corresponding 1,3-, 1,6-, 1,8-, and 2,7-bis(2'-[1',10']phenanthrolinyl)pyrenes. These ligands, along with the tetrahydro analogue to the 2,7-pyrene-bridged isomer, have been treated with  $[\text{Ru}(\text{D}_8\text{bpy})_2\text{Cl}_2]$ , where  $[\text{D}_8]\text{bpy} = [\text{D}_8]2,2'$ -bipyridine, to afford the dinuclear  $\text{Ru}^{\text{II}}$  complexes,  $^1\text{H}$  NMR and X-ray crystallographic analysis of which indic-

ate that the bridging pyrene is layered between a  $[\text{D}_8]\text{bpy}$  auxiliary ligand coordinated to each metal atom. Although well situated for  $\pi$ - $\pi$  interactions, little such effect is seen on the photophysical and electrochemical properties of these complexes.

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## Introduction

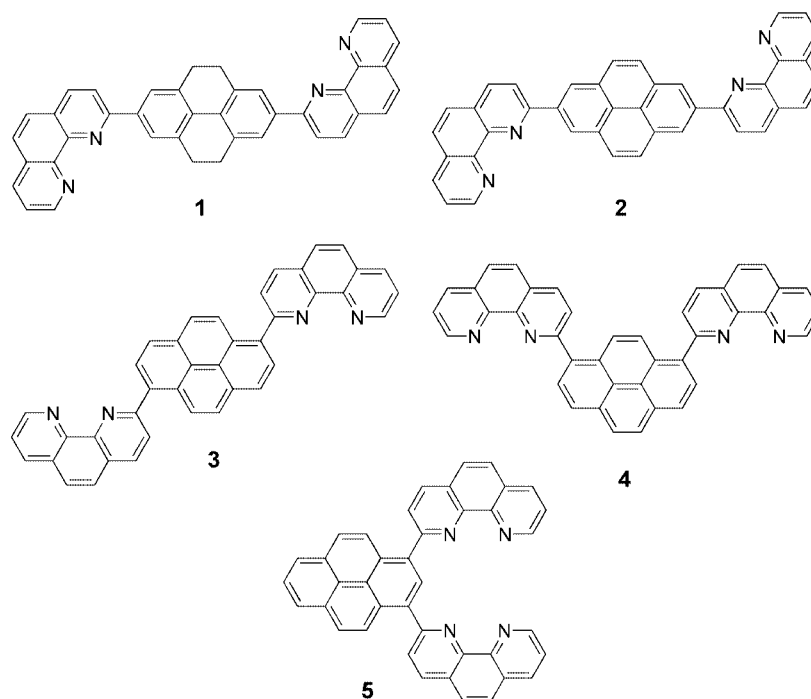
Polynuclear transition metal complexes are of considerable current interest due to their potential for metal-metal cooperativity, an important design aspect in constructing molecular devices.<sup>[1]</sup> A critical component in such polynuclear complexes is the bridging ligand, which typically consists of two or more metal chelation sites connected by an appropriate linker. The most common chelators are 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2';6',2''-terpyridine (tpy), or closely related derivatives. These binding sites have been connected by linkers designed to control both the distance between the metal centers and the electronic communication between the sites. Distance control can be effected by using rigid linkers of known dimensions.<sup>[2]</sup> Spatial control will also depend on the point of attachment of the linker to the bpy, phen, or tpy end groups.

To attain better electronic communication between linked metal centers, substantial attention has been paid to the conjugating ability of the linker. Linkers with one or more  $\pi$ -bonds are common, while the inclusion of a tetrahedral center such as an  $\text{sp}^3$ -carbon atom can serve as an insulating junction.<sup>[3]</sup> Conjugated  $\pi$ -systems as linkers pose further problems, the most important of which is the potential for orthogonality between any two adjacent  $\pi$ -links. Such an orthogonal junction can also behave as an insulator, as has been noted with polyene and polyphenylene linkers.<sup>[4]</sup> Polyalkynyl linkers seem to avoid the problem and have come into use.<sup>[5]</sup>

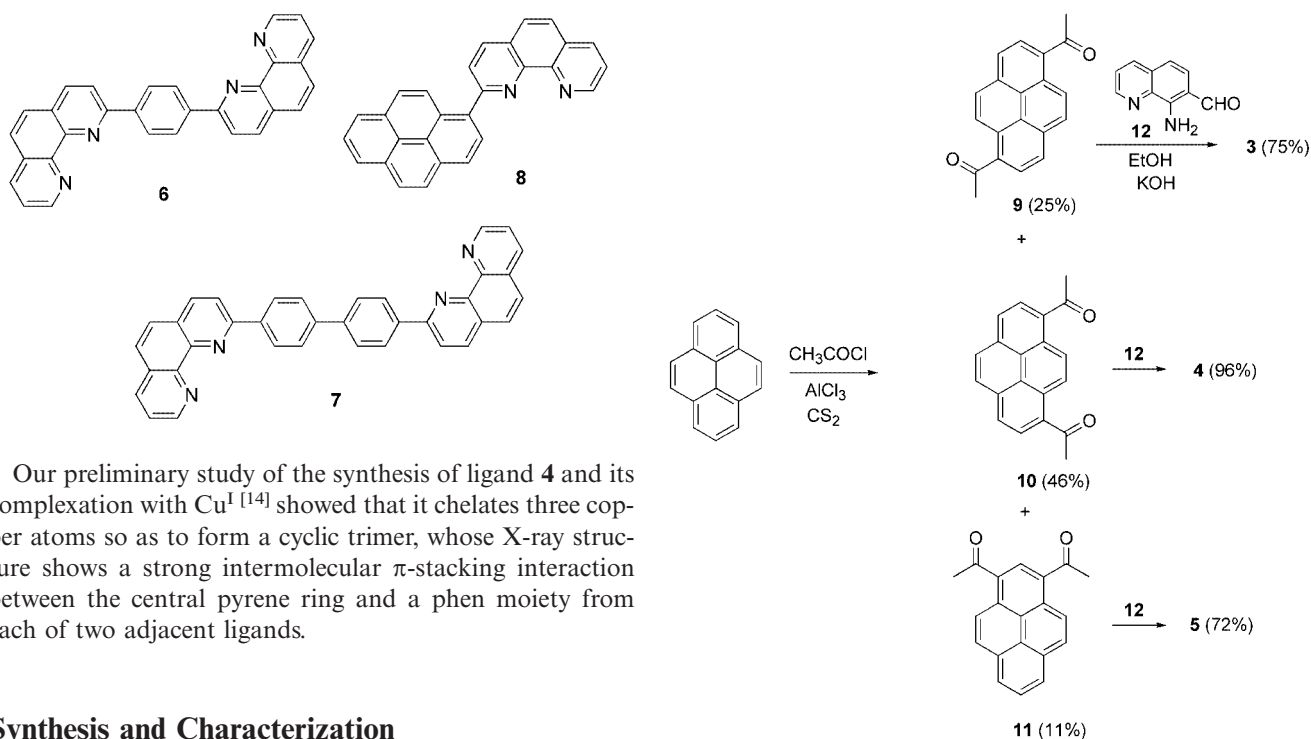
Our interest in pyrene as part of a ligand system is due to the promising symmetry and electronic structure of this polynuclear aromatic compound. Firstly, the pyrene nucleus has three twofold axes which allow some symmetry to be retained in various mono- and disubstituted derivatives. Secondly, the pyrene nucleus is electroactive, having an oxidation potential of +1.28 V and a reduction potential of -2.09 V.<sup>[6]</sup> Thirdly, pyrene has a strong chromophore that extends over the entire molecule. It also has a reasonable excited-state lifetime (650 ns) and shows a strong emission at 372 nm.<sup>[7]</sup> Pyrene fluorescence has led to its being utilized in various sensor applications where fluorescence quenching is a useful reporter characteristic.<sup>[8]</sup> Finally the large  $\pi$ -surface of pyrene gives it some organizational qualities. The  $\pi$ -stacking of two pyrene molecules is concentration dependent, leading to the formation of an excimer which emits at lower intensity and longer wavelength than the monomer.<sup>[9]</sup>

Consequently, we sought to use pyrene as a linker in bridging ligand design. The availability of several isomers of diacetylpyrene<sup>[10]</sup> and our ability to elaborate an acetyl into a 2-phen group<sup>[11]</sup> led us to prepare and study the family of bridging ligands **1–5** reported here. Previously we have prepared 1,4-bis(2'-phen)benzene (**6**) and its dinuclear  $\text{Ru}^{\text{II}}$  complex,<sup>[12]</sup> and have studied the 4,4'-disubstituted biphenyl analogue **7**. Although the ligands experience free rotation about the bond connecting phen to the linker, the incorporation of an  $[\text{Ru}(\text{bpy})_2]^{2+}$  unit rigidifies the system by inhibiting this rotation. Nevertheless, the dinuclear complex of **7** can still rotate freely about the central biphenyl linkage. In addition to complexes of **6** and **7**, we have also studied the  $\text{Ru}^{\text{II}}$  complex of 1-(2'-phen)pyrene (**8**), the mononuclear analogue of the complexes derived from **3–5**.<sup>[13]</sup>

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Scheme 1. Bridging pyrene-based ligands



Our preliminary study of the synthesis of ligand **4** and its complexation with  $\text{Cu}^{\text{I}}$  [14] showed that it chelates three copper atoms so as to form a cyclic trimer, whose X-ray structure shows a strong intermolecular  $\pi$ -stacking interaction between the central pyrene ring and a phen moiety from each of two adjacent ligands.

## Synthesis and Characterization

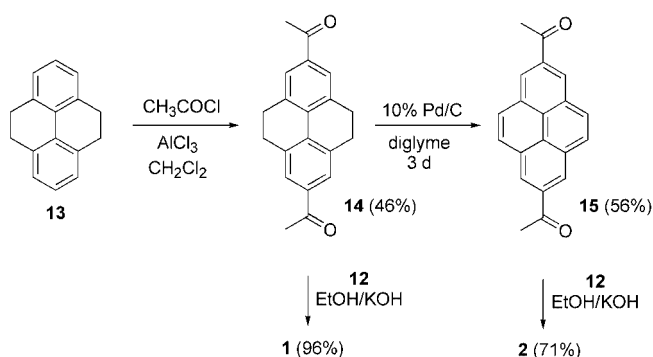
The strategic and selective introduction of acetyl groups onto the pyrene nucleus is key to the synthesis of **1–5**. Friedel–Crafts monoacetylation of pyrene is specific to the 1-position. Under normal conditions the 2-isomer cannot be isolated. If excess acetyl chloride is employed, a second acetyl group may be introduced at the 3-, 6-, or 8-position. Further acetylation is not readily accomplished. According to a published procedure, we produced a mixture of the

three diacetyl isomers **9–11**, which may be separated by a combination of chromatography and crystallization.<sup>[10]</sup>

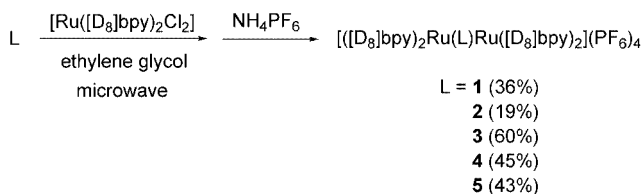
We have demonstrated that the Friedländer condensation of 8-amino-7-quinolinecarbaldehyde (**12**) with acetyl-substituted aromatic compounds is a convenient way to prepare 2-arylphen derivatives.<sup>[11]</sup> In this manner 2 equiv. of **12** were condensed with each of the diacetylpyrenes to provide the corresponding bis(phen)pyrenes **3–5** in yields of 72–96%.

Each of these ligands possesses a  $C_2$  symmetry axis so that in the  $^1\text{H}$  NMR spectrum only four (**3** and **4**) or five (**5**) pyrene signals appeared along with the characteristic seven signals for the phen ring.

The more problematic substitution at the 2-position of pyrene was achieved by Harvey and co-workers by carefully controlled hydrogenation of purified pyrene to afford the 4,5,9,10-tetrahydro derivative **13**.<sup>[15]</sup> This material is actually a bis(dimethylene)-bridged derivative of biphenyl which can be specifically monoacetylated at the 2-position or diacetylated at the 2,7-positions. The reaction of 2 equiv. of **12** with the diacetyl derivative **14** provides the bis(phen)-tetrahydropyrene **1**. Alternatively, **14** may be dehydrogenated to provide the diacetylpyrene **15** which can then be converted into the bis(phen) species **2**.



These five bis(phen)pyrenes were then treated with 2 equiv. of  $[\text{Ru}(\text{D}_8\text{bpy})_2\text{Cl}_2]$  to incorporate two  $\text{Ru}^{\text{II}}$  centers at the vacant phen binding sites. This reaction was sluggish under the normal conditions of reflux in aqueous ethanol, due partially to poor solubility of the ligands, but when carried out in ethylene glycol under microwave irradiation<sup>[16]</sup> (30–40 min) yields of 19–60% of the purified complexes as their hexafluorophosphate salts were obtained.



The use of  $\text{D}_8\text{bpy}$  greatly facilitates NMR characterization of the complexes by eliminating all signals from the bpy auxiliary ligands (Figure 1).<sup>[17]</sup> The phen protons could be readily identified by their characteristic coupling patterns and chemical shifts. The H-4' to H-9' protons were narrowly grouped in ranges spanning about 0.1 ppm. The H-3' resonance was most affected by the adjacent linker. For the complexes of **2–4** the signal of this proton appeared in the range  $\delta = 8.02\text{--}8.11$  ppm. For the complex of the tetrahydropyrene ligand **1**, the H-3' signal appeared

at  $\delta = 7.70$  ppm, very similar to the  $\delta = 7.72$  ppm recorded for the analogous complex of **7**.<sup>[12]</sup>

It should be noted that each  $\text{Ru}^{\text{II}}$  center is chiral and thus may exist in either the  $\Delta$  or  $\Lambda$  configuration. For dinuclear complexes such as those under study, this would lead to two sets of diastereomers, a  $d,l$  form ( $\Delta\Delta$  and  $\Lambda\Lambda$ ) and a *meso* form ( $\Delta\Lambda$ ). For the dinuclear  $\text{Ru}^{\text{II}}$  complex of **6** the metal centers were sufficiently interacting that two clear sets of NMR signals were visible and could, in fact, be assigned to specific stereoisomers which were present in an approximate 1:1 ratio.<sup>[12]</sup> For the dinuclear complexes of **2–4**, a mixture of diastereomers was similarly evidenced by the NMR spectra. Although some enrichment may have occurred during chromatographic purification, no attempt was made to separate these diastereomers and so they were further evaluated as a mixture.

Figure 1 shows the 600 MHz  $^1\text{H}$  NMR spectrum of the dinuclear complex of ligand **2**. All the peaks are clearly resolved and 2D analysis allowed their complete assignment. The phen subunits are sufficiently non-interacting that they only show one set of signals for both diastereomers. The H4' to H7' protons are remote from the complexation site and their signals appear in the downfield region. The H3', H8', and H9' proton signals are shifted upfield due to shielding by the auxiliary  $[\text{D}_8]\text{bpy}$  ligands or the central pyrene ring. The multiplicities and chemical shifts of the pyrene proton signals may be explained by symmetry effects associated with the  $d,l$  or *meso* diastereoisomer. For the *meso* isomer  $\text{H3} = \text{H8}$  and the signal of this proton appears as a singlet at  $\delta = 6.81$  ppm, strongly shielded by an auxiliary  $[\text{D}_8]\text{bpy}$  ligand. For this isomer  $\text{H1} = \text{H6}$  and this atom is deshielded, its signal appearing at  $\delta = 8.18$  ppm. For the *meso* isomer  $\text{H4} = \text{H9} \neq \text{H5}$  and thus H4 and H9 (as well as H5 and H10) appear as doublets at  $\delta = 7.97$  and 7.56, respectively. For the  $d,l$  isomer the symmetry plane lies along the short axis of the pyrene bridge so that  $\text{H3} = \text{H6}$  (singlet at  $\delta = 6.89$  ppm). Likewise H4 and H5 as well as H9 and H10 are equivalent, giving the singlets at  $\delta = 7.63$  and 7.89 ppm.

## Structure and Properties

We have previously described the dinuclear  $\text{Ru}^{\text{II}}$  complexes of **6** and **7**.<sup>[12]</sup> With  $[(\text{bpy})_2\text{Ru}(\text{6})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$  we had expected that  $\pi$ -stacking between the central benzene ring and a pyridine ring of an auxiliary bpy associated with each metal center would provide some communication between the metal atoms. Both photophysical and electrochemical data suggested that no such communication existed and the two metal centers behaved quite independently. A crystal structure analysis of this system indicated that the two  $\pi$ -stacked pyridine rings were bent out of a parallel arrangement and thus  $\pi$ - $\pi$  interaction might well be diminished.

The pyrene-bridged systems might be less congested, resulting in better  $\pi$ -overlap. Furthermore, the  $16\pi$ -electron central pyrene ring would provide better delocalization of

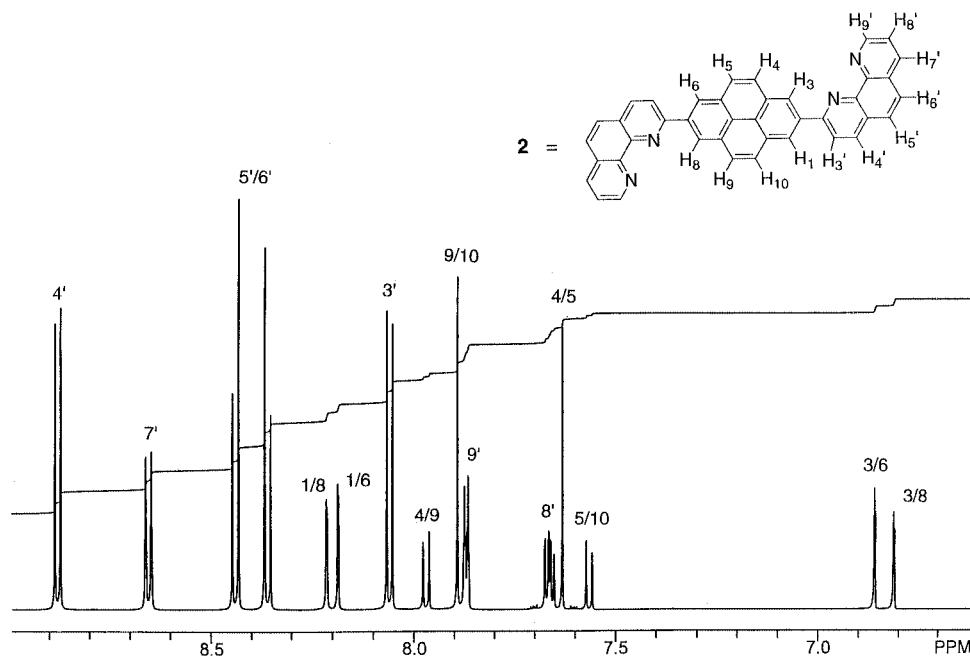


Figure 1. Downfield region of the 600 MHz  $^1\text{H}$  NMR spectrum of  $[(\text{D}_8\text{bpy})_2\text{Ru}(\mathbf{2})\text{Ru}(\text{D}_8\text{bpy})_2](\text{PF}_6)_4$  in  $\text{CD}_3\text{CN}$  at 25  $^\circ\text{C}$

the excited state. A structural comparison between the two dinuclear complexes was made by determining the crystal structure of  $[(\text{D}_8\text{bpy})_2\text{Ru}(\mathbf{3})\text{Ru}(\text{D}_8\text{bpy})_2](\text{PF}_6)_4$  (Figure 2 illustrates an ORTEP drawing of the cation). Figure 3 shows a side view of the same cation as well as the analogous dinuclear  $[\text{Ru}(\text{bpy})_2]$  complex of ligand **6**.

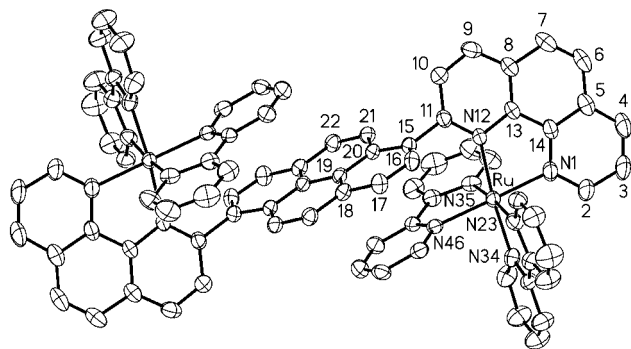


Figure 2. ORTEP drawing of the cation of  $[(\text{D}_8\text{bpy})_2\text{Ru}(\mathbf{3})\text{Ru}(\text{D}_8\text{bpy})_2](\text{PF}_6)_4$  showing the atom-numbering scheme

The larger pyrene, as compared with benzene, leads to a greater separation of the two  $[(\text{phen})\text{Ru}(\text{bpy})_2]$  halves of the molecule. All the Ru–N bond lengths fall in the range 2.05–2.07 Å, except for Ru–N12 which is 2.13 Å. This elongation is caused by interaction of pyrene with one of the auxiliary bpy groups. The bpy groups are less distorted than in the complex of **6**, and two bpy groups that form the outer layers of the central  $\pi$ -sandwich are more planar, with a dihedral angle between the two bpy pyridine rings of 6.6 $^\circ$  as compared with 21.6 $^\circ$  in the benzene-bridged complex. The other bpy is even more planar with a dihedral angle of only 1.8 $^\circ$ , which compares to 7.5 $^\circ$  in the benzene-bridged complex. The phen and pyrene are also more orthogonal

with a dihedral angle of 76.4 $^\circ$ , some 16 $^\circ$  greater than for the benzene-bridged system.

The decreased congestion is due mainly to the increased distance between the inner bpy on one Ru and the phen complexed to the other Ru. In the complex of **6**, this C26'–C10 distance is 3.73 Å, pushing the pyridine out of a plane that would be parallel with the central benzene. This distortion is illustrated in Figure 2 where the C26–C26' distance is 8.76 Å. For the pyrene complex, the bpy–phen interaction is relieved and the C43'–C10 distance lengthens to 5.19 Å while C43–C43', at 6.73 Å, is over 2 Å less than the corresponding distance for the benzene-bridged complex. The atoms in the pyridines that form the  $\pi$ -sandwich and the central benzene of **6** are between 2.91 and 4.21 Å apart, while for the pyrene-bridged complex these distances are 3.09–3.39 Å. The average distance between these planes is 3.24 Å, indicating possible strong  $\pi$ – $\pi$  interaction.

Surprisingly, the photophysical properties of the pyrene-bridged complexes do not evidence any strong coupling between the metal centers. Table 1 lists the absorption and emission data for the ligands and complexes as well as for **8** and the mononuclear model compounds  $[\text{Ru}(\mathbf{8})(\text{bpy})_2]^{2+}$  and  $[\text{Ru}(\text{phen})(\text{D}_8\text{bpy})_2]^{2+}$ . The 1,3-, 1,6-, and 1,8-diphenylpyrenes **3**–**5** all show quite similar absorption and emission spectra. The 2,7-diphen isomer absorbs at slightly higher energy, very similar to the 2-phenpyrene **8**. This is consistent with electronic decoupling of the 2,7-positions as reported by Müllen and co-workers.<sup>[18]</sup> The emission maxima for the pyrene systems appear in the range 432–488 nm and are all lower in energy than the corresponding bridged biphenyl system **1**.

Fages and co-workers have carried out a detailed photophysical study on two systems related to **3** and **8** in which a 4-(2,2'-bpy) group is attached to pyrene in place of phen.<sup>[20]</sup>

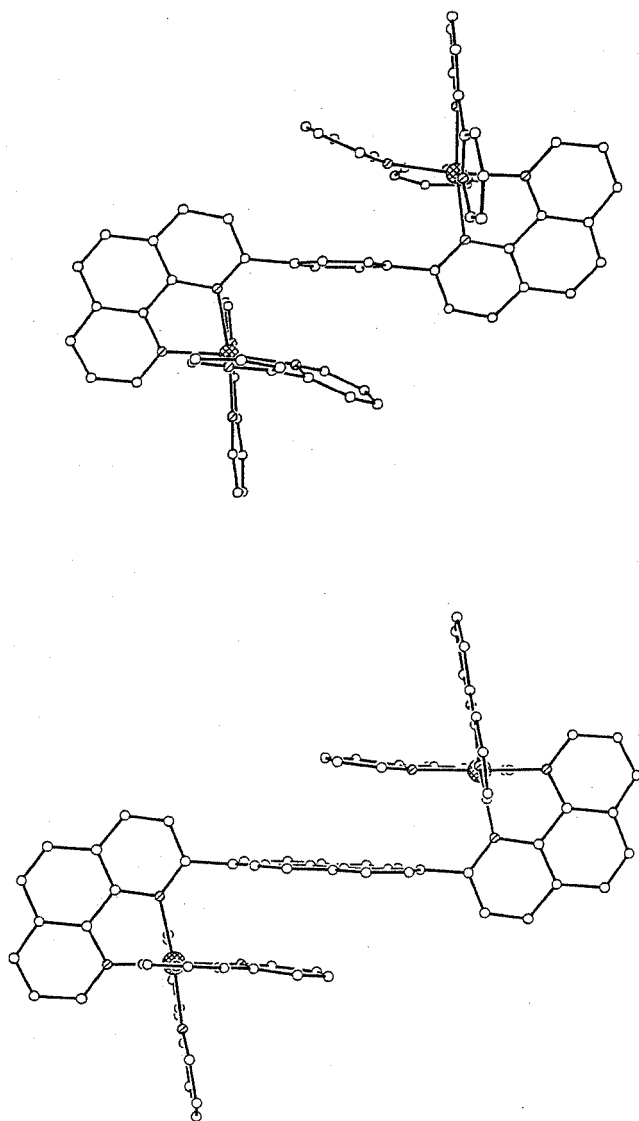


Figure 3. Analogous side views of the cation of  $[(bpy)_2Ru(6)Ru(bpy)_2](PF_6)_4$  (top) and  $[(D_8)bpy)_2Ru(3)Ru([D_8]bpy)_2](PF_6)_4$  (bottom)

These molecules show absorption and emission characteristics consistent with what we observe, but at higher energy, apparently due, in part, to conformational mobility about the 2,2' bond of bpy, which thus provides less delocalization than phen. The fact that the electronegative nitrogen atom in the 4-bpy-substituted systems is two bonds further remote from pyrene than for the 2-phen of **3** and **8** may also have some influence.

The Stokes shift is the difference between the absorption and emission maxima and, to some extent, provides a measure of geometric changes that occur upon electronic excitation. For **3–5** we observe values of 65–71 nm which are consistent with the model compound **8** (73 nm) and slightly larger than the 58 and 67 nm Fages observed for his two bpy-based systems in acetonitrile at room temperature. A similar 5-bpy-substituted pyrene reported by Rettig and co-workers shows a Stokes shift of 92 nm.<sup>[21]</sup> The 2,7-disubstituted pyrene **2** shows a large Stokes shift of 101 nm, consistent with the more longitudinal organization of this molecule.

The longest wavelength absorption for  $Ru^{II}$  complexes of this type typically involves a metal-to-ligand charge transfer (MLCT) in which the photoexcited electron is promoted from a metal d-orbital to a low-lying ligand  $\pi^*$ -orbital. One expectation for the pyrene-bridged complexes was that  $\pi$ – $\pi$  interaction through the central bpy-pyrene-bpy stack would affect an MLCT state associated with the bpy ligand. Increased delocalization should produce a bathochromic shift in the MLCT absorption. For the four dinuclear pyrene complexes involving **2–5** as well as the mononuclear model **8** and the tetrahydropyrene **1**, the lowest energy absorption band appears at 447–450 nm. The dinuclear pyrene-containing systems also show a pyrene  $\pi$ – $\pi^*$  absorption at 367–382 nm, which is lower in energy than the mononuclear analogue **8** (357 nm). Interestingly, the complex  $[Ru(phen)([D_8]bpy)_2]^{2+}$  absorbs at 448 nm, within 1–2 nm of all four pyrene-bridged complexes.

At room temperature the dinuclear complexes of **2–5** show weak emissions at 612–615 nm that are similar to the

Table 1. Photophysical data for phen-pyrene ligands and their  $Ru^{II}$  complexes

Compound	Absorption <sup>[a]</sup> $\lambda_{max}$ [nm] (log $\epsilon$ ) <sup>[a]</sup>	Emission <sup>[a]</sup> $\lambda_{em}$ [nm]	
		298K	77K
<b>1</b>	369 (4.40), 338 (4.28), 264 (4.20)	403, 423 <sup>[c]</sup>	
<b>2</b> <sup>[b]</sup>	359 (4.60), 341 (4.97), 342 (5.01), 311 (4.93), 260(4.68)	460, 488 <sup>[c]</sup>	
<b>3</b>	373 (3.97), 281 (4.08), 266 (4.10), 230 (4.35)	444 <sup>[c]</sup>	
<b>4</b>	373 (4.36), 283 (4.47), 267 (4.49), 230 (4.74)	444 <sup>[c]</sup>	
<b>5</b>	370 (4.32), 286 (4.50), 264 (4.51), 231 (4.82)	435 <sup>[c]</sup>	
<b>8</b>	359 (4.37), 342 (4.40), 276 (4.63), 238 (4.86)	432	
$[(D_8)bpy)_2Ru(1)Ru([D_8]bpy)_2]^{4+}$	450 (4.34), 443 (4.28), 422 (4.40), 287 (5.05)	613 (w)	584 <sup>[d]</sup>
$[(D_8)bpy)_2Ru(2)Ru([D_8]bpy)_2]^{4+}$	448 (4.42), 424 (4.36), 367 (4.49), 284 (5.12), 232 (4.95)	615 (w)	605 <sup>d</sup>
$[(D_8)bpy)_2Ru(3)Ru([D_8]bpy)_2]^{4+}$	447 (4.47), 380 (4.50), 284 (5.11), 267 (5.09), 228 (4.98)	614 (w)	615 <sup>d</sup>
$[(D_8)bpy)_2Ru(4)Ru([D_8]bpy)_2]^{4+}$	449 (4.47), 382 (4.49), 284 (5.21), 267 (5.19), 230 (5.00)	615 (w)	615 <sup>d</sup>
$[(D_8)bpy)_2Ru(5)Ru([D_8]bpy)_2]^{4+}$	449 (4.37), 382 (4.32), 282 (5.12), 230 (4.93)	612 (w)	611 <sup>d</sup>
$[Ru(8)(bpy)_2]^{2+}$	448 (4.12), 337 (4.40), 268 (4.90), 233 (4.90)	610	
$[Ru(phen)([D_8]bpy)_2]^{2+}$	448 (4.31), 285 (4.91), 263 (4.87)	615	580 <sup>[d]</sup> <sup>[e]</sup>

<sup>[a]</sup>  $10^{-5}$  M in  $CH_3CN$  at 25 °C. <sup>[b]</sup>  $10^{-5}$  M in  $CH_2Cl_2$  at 25 °C. <sup>[c]</sup>  $10^{-6}$  M in  $CH_3CN$  at 25 °C. <sup>[d]</sup>  $10^{-5}$  M in EtOH/MeOH (4:1). <sup>[e]</sup> Measured for the protio-bpy analogue, ref.<sup>[19]</sup>



Table 2. Electrochemical data for pyrene-bridged ligands and their Ru<sup>II</sup> complexes

Compound	OX	$E_{1/2}$ [a]	RED
[Ru(phen)(bpy) <sub>2</sub> ] <sup>2+</sup>	+1.32 (82)		−1.30 (91), −1.49 (112)
[Ru(8)([D <sub>8</sub> ]bpy) <sub>2</sub> ] <sup>2+</sup>	+1.30		
[(D <sub>8</sub> ]bpy) <sub>2</sub> Ru(1)Ru([D <sub>8</sub> ]bpy) <sub>2</sub> <sup>4+</sup>	+1.29 (120)		−1.31 (140), −1.49 (190)
[(D <sub>8</sub> ]bpy) <sub>2</sub> Ru(2)Ru([D <sub>8</sub> ]bpy) <sub>2</sub> <sup>4+</sup>	+1.32 (100)		−1.28 (180), −1.44 (150)
[(D <sub>8</sub> ]bpy) <sub>2</sub> Ru(3)Ru([D <sub>8</sub> ]bpy) <sub>2</sub> <sup>4+</sup>	+1.31 (240)		−1.27 (71), −1.41 (irr.)
[(D <sub>8</sub> ]bpy) <sub>2</sub> Ru(4)Ru([D <sub>8</sub> ]bpy) <sub>2</sub> <sup>4+</sup>	+1.31 (180)		−1.28 (240), −1.41 (irr.)
[(D <sub>8</sub> ]bpy) <sub>2</sub> Ru(5)Ru([D <sub>8</sub> ]bpy) <sub>2</sub> <sup>4+</sup>	+1.31 (180)		−1.28 (240), −1.41 (irr.)

[a] Solutions were 0.1 M TBAP in CH<sub>3</sub>CN; sweep rate 200 mV s<sup>−1</sup>; the number in parentheses is the difference [mV] between the anodic and cathodic waves; irr. = irreversible.

model compounds. At 77 K, the emission properties do not change appreciably for the complexes of **3–5** while those of the complex of **2** is shifted to 605 nm. By comparison, the dinuclear complex of the bridged biphenyl system **1**, which does not possess the pyrene chromophore, shows a stronger 77 K emission shifted to 584 nm. This 29-nm thermally induced Stokes shift compares well with that of 35 nm observed for [Ru(phen)(bpy)<sub>2</sub>]<sup>2+</sup> and is characteristic for emission of a triplet MLCT state. The implication is that, due to the lack of a thermally induced Stokes shift, the emissions from the complexes involving the pyrenyl ligands **2–5** may not be MLCT-based but rather associated with an intraligand (IL) state, possibly a triplet IL state involving pyrene.

Schmehl and co-workers<sup>[22]</sup> have recently examined a similar dinuclear Ru<sup>II</sup> complex involving the 1,6-bis(2,2'-bipyrid-4-yl)pyrene bridging ligand reported earlier by Fages.<sup>[20]</sup> A detailed photophysical study indicated that emission was not consistent with a <sup>3</sup>MLCT state, rather a triplet IL state was suggested instead. An easy test for this possibility is to measure the 77 K luminescence of the ligands **2–5** in the presence of an external heavy atom donor, which should promote intersystem crossing and emission of the triplet state (phosphorescence). Low-temperature spectra of the ligands were, therefore, recorded in the presence of ethyl iodide. For ligand **3** we observe a band at 615 nm, which is virtually identical to the spectrum of [(D<sub>8</sub>]bpy)<sub>2</sub>Ru(3)-Ru([D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>. The data for the other systems was less clear. Future time-resolved measurements and transient spectroscopy should help in elucidating the origin of the emissive state. It is noteworthy that other Ru<sup>II</sup> complexes of bpy and phen have been reported in which each ligand contains one or two pyrene appendages attached at the 5-position.<sup>[23–24]</sup> These systems emit rather strongly and the excited state lifetime can be related to the number of pyrene appendages.

The electrochemical data summarized in Table 2 further verify the lack of metal–metal interaction. The oxidations are all in the range +1.29 to +1.32 V, as expected for the metal-based Ru<sup>II</sup>-to-Ru<sup>III</sup> conversion. The reductions are typically ligand-based and fall in the expected range of −1.27 to −1.31 V. It is difficult to assign this reduction to a phen or a bpy ligand in the complex. If the reduction involved a phen-type ligand, then the second reduction

would involve a bpy and variation in the second reduction potential might be expected. These second reductions, however, fall in the narrow range of −1.41 to −1.44 V, excluding this possibility.

## Conclusions

We have described the preparation of four new pyrene-bridged bis(phen) ligands **2–5** and the tetrahydro precursor **1**. Dinuclear Ru<sup>II</sup> complexes prepared from all five systems, with [D<sub>8</sub>]bpy as the auxiliary ligand, have been characterized by <sup>1</sup>H NMR and electronic spectroscopy and by electrochemical analysis. A crystal structure of the dinuclear complex of **3** evidences a much less congested environment than its benzene-bridged analogue. Nevertheless, the expected electronic effects of  $\pi$ – $\pi$  interactions through the central bpy-pyrene-bpy sandwich appear to be lacking. Future studies will involve systems with pyrene more intimately involved in the 1,4-diimine chelating unit.

## Experimental Section

**General:** Nuclear magnetic resonance spectra were recorded at 300 or 600 MHz for <sup>1</sup>H and at 75 MHz for <sup>13</sup>C{<sup>1</sup>H} referenced to TMS in CDCl<sub>3</sub> and to the solvent peak in all other solvents (CD<sub>3</sub>CN). Electronic spectra were obtained with a Perkin-Elmer Lambda 3B spectrophotometer. Fluorescence spectra were obtained with a Perkin-Elmer LS-50 luminescence spectrometer. Cyclic voltammetry (CV) was carried out in a conventional three-electrode cell with a BAS-27 voltammeter and a Houston Instruments model 100 X-Y recorder according to a previously described procedure.<sup>[25]</sup> Mass spectra were obtained with a Hewlett–Packard 5989B mass spectrometer (59987A electrospray) using atmospheric pressure ionization at 160 °C. Elemental analyses were performed by National Chemical Consulting, P. O. Box 99, Tenaflly, NJ 07670, U.S.A. Melting points were measured with a Hoover capillary melting point apparatus and are not corrected. The microwave reactions were carried out in a household microwave oven modified according to a previously published description.<sup>[16]</sup> The 2,7-diacetyl-4,5,9,10-tetrahydropyrene,<sup>[15]</sup> 2,7-diacetylpyrene,<sup>[15]</sup> 1,6-, 1,8-, and 1,3-diacetylpyrene,<sup>[10]</sup> [Ru([D<sub>8</sub>]bpy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O,<sup>[17]</sup> and 8-amino-7-quinolinecarbaldehyde (**8**)<sup>[11]</sup> were prepared according to known procedures. CH<sub>3</sub>CN used for cyclic voltammetry was dried by reflux with calcium hydride followed by distillation. All other solvents were used without further purification.

**2,7-Bis(2'-[1',10']phenanthrolyl)-4,5,9,10-tetrahydropyrene (1):** A mixture of 2,7-diacetyl-4,5,9,10-tetrahydropyrene (**14**, 300 mg, 0.69 mmol), 8-amino-7-quinolinecarbaldehyde (**12**, 240 mg, 138 mmol) and KOH (120 mg) in absolute EtOH (25 mL) was refluxed for 8 h. The solid which formed was collected, washed with H<sub>2</sub>O (2 × 20 mL), EtOH (3 × 10 mL), and dried to provide **1** as an orange solid (370 mg, 96% yield), m.p. > 270 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.27 (d', *J* = 4.7, 2.5 Hz, 2 H, H-9), 8.31 (m, 4 H), 8.18 (d, 2 H), 8.14 (s, 4 H, H-1, H-3, H-6, H-8), 7.80 (AB q, 4 H, H-5', H-6'), 7.66 (dd, *J* = 7.9, 3.4 Hz, 2 H, H-8'), 3.13 (s, 8 H, CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 157.8, 149.9, 138.0, 136.5, 136.2, 136.0, 131.5, 128.9, 127.3, 126.3, 125.7, 125.4, 122.6, 120.5, 28.3 ppm. MS: *m/z* (%) = 562 (100) [M]. C<sub>40</sub>H<sub>22</sub>N<sub>4</sub>·3H<sub>2</sub>O (647): calcd. C 77.92, H 5.19, N 9.09; found C 77.08, H 4.53, N 8.74.

**2,7-Bis(2'-[1',10']phenanthrolyl)pyrene (2):** According to the procedure described for **1**, 2,7-diacetylpyrene (**15**, 80 mg, 0.28 mmol) was condensed with **12** (100 mg, 0.58 mmol) in absolute EtOH (15 mL) for 8 h. The resultant yellow-orange residue was crystallized from chloroform to give **2** as a pale yellow solid (110 mg, 71% yield), m.p. > 270 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.33 (d, *J* = 4.3 Hz, 2 H, H-9'), 9.21 (s, 4 H, H-4, H-5, H-9, H-10), 8.47 (AB q, 4 H, H-3', 4'), 8.35 (d, 2 H, H-7'), 8.32 (s, 2 H, H-1, H-3, H-6, H-8), 7.86 (AB q, 4 H, H-5', H-6'), 7.69 (dd, *J* = 7.6, 3.1 Hz, 2 H, H-8') ppm. A <sup>13</sup>C{<sup>1</sup>H} NMR spectrum could not be obtained due to poor solubility. MS: *m/z* (%) = 558 (100) [M]. C<sub>40</sub>H<sub>22</sub>N<sub>4</sub>·H<sub>2</sub>O (576): calcd. C 83.33, H 4.16, N 9.72; found C 83.36, H 4.08, N 9.07.

**1,6-Bis(2'-[1',10']phenanthrolyl)pyrene (3):** A mixture of 1,6-diacetylpyrene (**9**, 200 mg, 0.69 mmol), **12** (265 mg, 1.53 mmol), and KOH (120 mg) in absolute EtOH (30 mL) was refluxed overnight. After cooling to 25 °C, the residue was filtered off, washed with H<sub>2</sub>O (2 × 20 mL) then CHCl<sub>3</sub> (2 × 20 mL). The resulting solid was then recrystallized from CHCl<sub>3</sub> to provide **3** as a pale yellow solid (290 mg, 75% yield), m.p. > 280 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.24 (dd, *J* = 4.4, 1.4 Hz, 2 H, H-9'), 8.53 (d, *J* = 9.5 Hz, 2 H), 8.47 (dd, *J* = 8.3, 2.9 Hz, 4 H), 8.31 (d, *J* = 8.9 Hz, 4 H), 8.12 (dd, *J* = 8.9, 4.5 Hz, 4 H), 7.95 (AB q, 4 H, H-5', H-6'), 7.65 (dd, *J* = 8.6, 4.4 Hz, 2 H, H-8') ppm. A <sup>13</sup>C{<sup>1</sup>H} NMR spectrum could not be obtained due to poor solubility. MS: *m/z* (%) = 559 (100) [M + 1]. C<sub>40</sub>H<sub>22</sub>N<sub>4</sub>·H<sub>2</sub>O (558): calcd. C 83.33, H 4.16, N 9.72; found C 83.83, H 3.83, N 9.85.

**1,8-Bis(2'-[1',10']phenanthrolyl)pyrene (4):**<sup>[14]</sup> A mixture of 1,8-diacetylpyrene (**10**, 146 mg, 0.51 mmol), **12** (183 mg, 1.06 mmol), and KOH (100 mg) in absolute EtOH (20 mL) was refluxed for 12 h. After cooling to 25 °C, H<sub>2</sub>O (20 mL) was added and the aqueous layer extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The organic layer was then dried (MgSO<sub>4</sub>) and the solvent evaporated to dryness. The resultant residue was washed with Et<sub>2</sub>O (2 × 25 mL) to provide **4** as a yellow solid (265 mg, 93% yield), m.p. > 270 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.14 (d, *J* = 3.3 Hz, 2 H, H-9'), 8.32–8.23 (m, 8 H), 8.16–8.13 (m, 4 H), 7.96 (d, *J* = 8.1 Hz, 2 H), 7.74 (d, *J* = 8.7 Hz, 2 H), 7.65–7.57 (m, 4 H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 159, 149, 145.8, 145.7, 136.3, 136.1, 136, 131, 128.8, 128.5, 128.4, 127.9, 127.1, 126.4, 126.3, 125.7, 125.5, 125.2, 124, 123 ppm. MS: *m/z* (%) = 559 (100) [M + 1]. C<sub>40</sub>H<sub>22</sub>N<sub>4</sub>·0.5H<sub>2</sub>O (567): calcd. C 84.66, H 4.05, N 9.88; found C 84.73, H 3.67, N 9.50.

**1,3-Bis(2'-[1',10']phenanthrolyl)pyrene (5):** A mixture of 1,3-diacetylpyrene (**11**, 109 mg, 0.38 mmol), **12** (131 mg, 0.76 mmol), and KOH (120 mg) in absolute EtOH (35 mL) was refluxed for 24 h.

After cooling to 25 °C, H<sub>2</sub>O (60 mL) was added and a yellow solid precipitated. The solid was purified on Al<sub>2</sub>O<sub>3</sub>, eluting with CH<sub>2</sub>Cl<sub>2</sub>, to provide **5** (152 mg, 72% yield), m.p. > 270 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.14 (d, *J* = 4.1 Hz, 2 H, H-9'), 8.80 (s, 1 H), 8.41 (dd, *J* = 8.0, 2.6 Hz, 4 H), 8.22 (dd, *J* = 10.3, 7.7 Hz, 4 H), 8.0–8.15 (m, 5 H), 7.84 (AB q, 4 H, H-5', H-6'), 7.60 (dd, *J* = 8.1, 4.8 Hz, 2 H, H-8') ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 150.6, 136.6, 136.1, 136 (2 C), 131.6, 130.9, 129.7, 129.3, 129, 128.6, 127.7, 126.8 (2 C), 126.7 (2 C), 126.3, 126.2, 125.6, 125.4, 123, 120.2 ppm. MS: *m/z* (%) = 560 (100) [M + 2]. C<sub>40</sub>H<sub>22</sub>N<sub>4</sub>·1.45CH<sub>2</sub>Cl<sub>2</sub> (698): calcd. C 73.30, H 3.65, N 8.22; found C 73.30, H 3.60, N 7.86.

**[(D<sub>8</sub>]bpy)<sub>2</sub>Ru(1)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>:** A mixture of **1** (60 mg, 0.10 mmol) and [Ru[(D<sub>8</sub>]bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (111 mg, 0.21 mmol) in ethylene glycol (6 mL) was heated in a microwave oven under Ar for 30 min. After cooling, the mixture was poured into H<sub>2</sub>O (20 mL). A solution of NH<sub>4</sub>PF<sub>6</sub> (49 mg, 0.3 mmol) in H<sub>2</sub>O (2 mL) was then added, and the mixture stirred for 15 min. The resultant precipitate was filtered off, dried, and purified by chromatography on alumina, eluting with toluene/CH<sub>3</sub>CN (1:1), to provide an orange solid (75 mg, 36% yield), m.p. > 280 °C. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 25 °C): δ = 8.73 (d, *J* = 9.3 Hz, H-4'), 8.62 (d, *J* = 8.8 Hz, H-7'), 8.33 (AB q, H-5', H-6'), 7.90 (d, *J* = 4.9 Hz, H-9'), 7.69 (d, *J* = 7.3 Hz, H-3'), 7.65 (dd, *J* = 6.8, 4.9 Hz, H-8'), 7.0 (s, H-2/H-5), 5.7 (s, H-4/H-9), 2.15–2.30 (CH<sub>2</sub> under solvent peak). MS: *m/z* (%) = 1857 (100) [M + 1 – PF<sub>6</sub>].

**[(D<sub>8</sub>]bpy)<sub>2</sub>Ru(2)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>:** According to the procedure described for [(D<sub>8</sub>]bpy)<sub>2</sub>Ru(1)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>, a mixture of **2** (40 mg, 0.07 mmol) and [Ru[(D<sub>8</sub>]bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (77 mg, 0.14 mmol) in ethylene glycol (6 mL) was heated in a microwave oven to provide a red solid (26.5 mg, 19% yield), m.p. > 280 °C. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 25 °C, two sets of peak in a 1:1 ratio for the two diastereomers): δ = 8.88 (d, *J* = 7.3 Hz, H-4'), 8.65 (d, *J* = 8.4 Hz, H-7'), 8.4 (AB q, H-5', H-6'), 8.21 (s, H-1/H-8), 8.18 (s, H-1/H-6), 8.06 (d, *J* = 7.0 Hz, H-3'), 7.97 (d, *J* = 5.1 Hz, H-4/H-9), 7.89 (s, H-9/H-10), 7.87 (d, *J* = 5.6 Hz, H-9'), 7.66 (dd, *J* = 7.0, 5.3 Hz, H-8'), 7.63 (s, H-4/H-5), 7.56 (d, *J* = 9.0 Hz, H-5/H-10), 6.85 (s, H-3/H-6), 6.81 (s, H-3/H-8) ppm. MS: *m/z* (%) = 1851 (100) [M – PF<sub>6</sub>].

**[(D<sub>8</sub>]bpy)<sub>2</sub>Ru(3)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>:** According to the procedure described for [(D<sub>8</sub>]bpy)<sub>2</sub>Ru(1)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>, a mixture of **3** (60 mg, 0.10 mmol) and [Ru[(D<sub>8</sub>]bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (115 mg, 0.21 mmol) in ethylene glycol (6 mL) was heated in a microwave oven to provide a red solid (120 mg, 60% yield), m.p. > 280 °C. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 25 °C, two sets of peaks in a 5:1 ratio for the two diastereomers), major isomer: δ = 8.97 (d, *J* = 7.3 Hz, H-4'), 8.71 (d, *J* = 8.4 Hz, H-7'), 8.48 (AB q, H-5', H-6'), 8.13 (d, *J* = 7.0 Hz), 8.10 (d, *J* = 7.0 Hz, H-3'), 7.97 (d, *J* = 7.0 Hz), 7.88 (d, *J* = 5.7 Hz, H-9'), 7.69 (dd, *J* = 7.0, 5.3 Hz, H-8'), 7.21 (d, *J* = 7.8 Hz, 1 H), 6.42 (d, 2 H) ppm. MS: *m/z* (%) = 1853 (100) [M + 2 – PF<sub>6</sub>].

**[(D<sub>8</sub>]bpy)<sub>2</sub>Ru(4)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>:** The same procedure described for [(D<sub>8</sub>]bpy)<sub>2</sub>Ru(1)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> was used. A mixture of **4** (60 mg, 0.10 mmol) and [Ru[(D<sub>8</sub>]bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (115 mg, 0.21 mmol) in ethylene glycol (6 mL) was heated in a microwave oven to provide a red solid (89 mg, 45% yield), m.p. > 280 °C. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 25 °C, two sets of peaks in a 9:1 ratio for the two diastereomers), major isomer: δ = 8.94 (d, *J* = 7.3 Hz, H-4'), 8.67 (d, *J* = 8.4 Hz, H-7'), 8.45 (AB q, H-5', H-6'), 8.10 (d, *J* = 7.0 Hz), 8.08 (d, *J* = 7.0 Hz, H-3'), 7.95 (d, *J* = 7.0 Hz), 7.87 (d, H-9'), 7.68 (dd, *J* = 7.0, 5.3 Hz, H-8'), 7.57 (d, *J* = 7.0 Hz, 1

H), 7.18 (d, 1 H,  $J = 7.8$  Hz), 7.40 (d, 2 H) ppm. MS:  $m/z$  (%) = 1853 (100) [ $M + 2 - PF_6$ ].

**[(D<sub>8</sub>]bpy)<sub>2</sub>Ru(5)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>:** According to the procedure described for [(D<sub>8</sub>]bpy)<sub>2</sub>Ru(1)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>, a mixture of **5** (60 mg, 0.10 mmol) and [Ru(D<sub>8</sub>]bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (115 mg, 0.21 mmol) in ethylene glycol (6 mL) was heated in a microwave oven under Ar for 30 min to provide a red solid (60 mg, 43% yield), m.p. > 280 °C. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  = 8.81 (d,  $J = 7.3$  Hz, H-4'), 8.69 (d,  $J = 8.4$  Hz, H-7'), 8.45 (AB q, H-5', H-6'), 8.38–8.31 (m, H-6, H-7), 7.85 (s, H-2), 7.82 (d,  $J = 7.0$  Hz, H-9'), 7.67 (dd,  $J = 7.0, 5.3$  Hz, H-8'), 7.62 (d,  $J = 7.0$  Hz, H-3'), 7.43 (d,  $J = 7.8$  Hz, H-3), 6.26 (d,  $J = 7.8$  Hz, H-4) ppm. MS:  $m/z$  (%) = 1853 (100) [ $M + 2 - PF_6$ ].

**X-ray Determination of [(D<sub>8</sub>]bpy)<sub>2</sub>Ru(3)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>:** All measurements were made with a Siemens SMART platform diffractometer equipped with a 1 K CCD area detector. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in  $\omega$  and an exposure time of 30 s per frame. The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on  $I$  was < 1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A  $\psi$  scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 7934 reflections having  $I > 10\sigma(I)$ , and these, along with other information pertinent to data collection and refinement, are listed in Table 3. The Laue symmetry was determined to be  $-1$ , and the space group was shown to be either  $P1$  or  $P\bar{1}$ ; the latter was chosen based on successful refinement. The asymmetric unit consists of one-half cation situated about an inversion center, two PF<sub>6</sub> anions, two acetonitrile molecules, one toluene and one dichloromethane molecule. One of the anions, and all of the various solvent molecules, are disordered and were modeled as ideal rigid bodies or by using distance constraints. Three separate orientations were found for the dichloromethane, with a total population of about 75%. It is presumed that some solvent was lost during sample handling, and all calculations are based on 100% occupancy of the solvent. CCDC-199738 contains the supplementary crystallographic data which can be obtained free of charge at

www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 3. Crystallographic data for [(D<sub>8</sub>]bpy)<sub>2</sub>Ru(3)Ru[(D<sub>8</sub>]bpy)<sub>2</sub>] <sup>4+</sup>

Empirical formula	C <sub>104</sub> H <sub>54</sub> D <sub>32</sub> Cl <sub>4</sub> F <sub>24</sub> N <sub>16</sub> P <sub>4</sub> Ru <sub>2</sub>
Formula mass	2515.90
<i>a</i> [Å]	12.3445(5)
<i>b</i> [Å]	13.9165(6)
<i>c</i> [Å]	18.0631(8)
$\alpha$ [°]	104.225(1)
$\beta$ [°]	94.019(1)
$\gamma$ [°]	114.575(1)
<i>V</i> [Å <sup>3</sup> ]	2682.7(2)
<i>Z</i>	1
Space group	$P\bar{1}$
<i>T</i> [°C]	–50
$\lambda$ [Å]	0.71073
$\rho_{\text{calcd}}$ [g cm <sup>–3</sup> ]	1.557
$\mu$ [cm <sup>–1</sup> ]	5.38
$R_1 = \Sigma F_o  -  F_c /\Sigma F_o $	0.0563
$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	0.1527
$w = [\sigma^2(F_o^2) + (0.0769 P)^2 + (9.3529 P)]^{-1}$ , $P = (F_o^2 + 2F_c^2)/3$	



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