Synthesis of a linear bis-porphyrin with a $Ru(phen)_2^{2+}$-complexed 2,2′-bipyridine spacer

James I. Bruce, Jean-Claude Chambron,*† Philipp Kölle and Jean-Pierre Sauvage*

Laboratoire de Chimie Organo-Minérale, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, 67000 Strasbourg, France

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A linear bis-porphyrin bridged by a 5,5′-diphenyl-2,2′-bipyridine rod-like spacer complexing a $[Ru(phen)_2]^{2+}$ fragment has been synthesized in 7.4% yield by one-pot condensation of 3,5-di-*tert*-butylbenzaldehyde, 4,4′-dimethyl-3,3′-dihexyl-2,2′-methylenedipyrrole and the $[Ru(phen)_2]^{2+}$ complex of 5,5′-bis(*p*-formylphenyl)-2,2′-bipyridine, followed by chloranil oxidation. The protected dialdehyde (5,5′-bis[(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]-2,2′-bipyridine) was obtained in 80% yield by Suzuki coupling of 2-[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]-4,4,5,5-tetramethyl-1,3-dioxaborolane and 5,5′-dibromo-2,2′-bipyridine, using $[Pd(PPh_3)_4]$ as catalyst. A new procedure is reported for the preparation of 5,5′-dibromo-2,2′-bipyridine, which is obtained in 80% yield by Stille homocoupling of 2,5-dibromopyridine in the presence of hexamethylditin.

Introduction

Bis-porphyrin conjugates are attracting considerable attention as many electron transfer proteins involve pairs of porphyrin analogues as redox partners. Among those, examples involving cytochromes as well as bacteriochlorophylls can be borrowed from the photosynthetic machinery of purple bacteria such as *Rhodopseudomonas viridis*.[1] We have been interested for several years in mimicking the *oblique* arrangements in pairs of chromophores taken from the special pair/bacteriochlorophyll/bacteriopheophytin triad of the bacterial Reaction Centers. For that purpose we designed and synthesized bis-porphyrins with covalent bridges such as the 2,9-diphenyl-1,10-phenanthroline (dpp) ligand, which enforces a 60° angle between the porphyrin planes.[2] Precursors to phototriggered donor–acceptor conjugates were obtained by metallation with Zn(II) and Au(III).[3a–c] We observed that the rate of electron transfer from the photoexcited Zn porphyrin donor to the Au porphyrin acceptor could be substantially increased by coordination of a transition metal to the bridging chelate by means of rotaxane formation (Fig. 1, structure (a)).[3d,e]

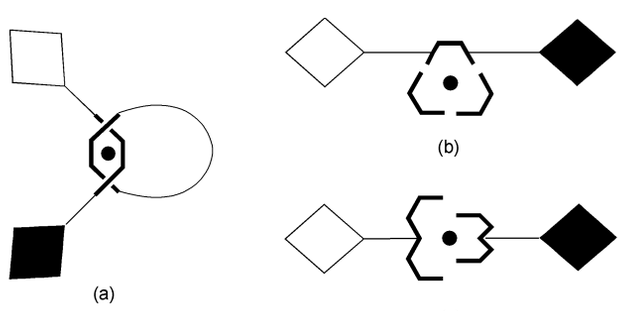

Fig. 1 Schematic representation of selected mixed-metal bis-porphyrin arrays containing a transition metal complex fragment as spacer. The thick lines represent bidentate (a and b) or terdentate (c) chelates. The black disk is a transition metal. Metalloporphyrins are represented by diamonds (empty = Zn(II); full = Au(III)).

† *Present address*: LIMSAG (UMR 5633), Université de Bourgogne, Faculté des Sciences Gabriel, 6, boulevard Gabriel, 21000 Dijon, France

In this paper we describe our synthetic efforts to covalently and rigidly link two porphyrins in a strict linear arrangement using the 5,5′-diphenylene-2,2′-bipyridine chelate as spacer (Fig. 1, structure (b)). A few examples of bis-porphyrins incorporating the 2,2′-bipyridine subunit are known,[4] and several linear bis-porphyrins involving bridging metal complex fragments such as $[M(terpy)_2]^{n+}$ (where M = Ru(II)[5a–c] or Ir(III)[5d–f]) or $[M(phen)_2]^{n+}$ (where M = Cu(I) or Zn(II))[6] have been synthesized in our laboratory and elsewhere. However, the latter correspond to structure (c) of Fig. 1, in which the metal has been shown to play both the role of an assembling species, linking together the porphyrin modules, and a redox relay mediating photoinduced electron transfer between the Zn and the Au porphyrin termini in the case of $M(terpy)_2^{n+}$-bridged systems.[5] An exception is a multiporphyrin-containing [2]-rotaxane, in which the bridging phenanthroline chelate is connected to the porphyrin stoppers by amide linkages.[7] For practical reasons (see below), the $[Ru(phen)_2]^{2+}$ moiety had to be attached to the bipyridine spacer prior to porphyrin construction, thus providing a new $[Ru(diimine)_3]^{2+}$–porphyrin conjugate.[8]

Results and discussion

5,5′-Diphenyl-2,2′-bipyridine itself is not a very common ligand, compared to the 4,4′-diphenyl analogue, and only a few of its complexes with Ru(II) have been described.[9a] The free ligand has been prepared by Raney nickel coupling of 3-phenylpyridine,[9b] a method that does not tolerate heat sensitive functional groups and that suffers from very moderate yields. In recent preparations of materials incorporating the 5,5′-diaryl-2,2′-bipyridine motif, aromatic cross-coupling reactions involving 5,5′-dibromo-2,2′-bipyridine as electrophile have been used with much success. Tilley and coworkers have prepared 5,5′-bis(4-trimethylsilylphenyl)-2,2′-bipyridine in 90% yield by Stille coupling with $Me_3SiC_6H_4SnMe_3$.[10] Suzuki coupling was used by Klemm and coworkers to prepare polymers incorporating the 5,5′-bis(2,5-dihexylphenyl)-2,2′-bipyridine motif, using 2,5-dihexylbenzene-1,4-diboronic acid as nucleophile.[11a] The same reaction has been applied to (5,5′-dibromo-2,2′-bipyridine)-bis(2,2′-bipyridine)ruthenium-(II) bis(hexafluorophosphate), affording a conjugated polymer

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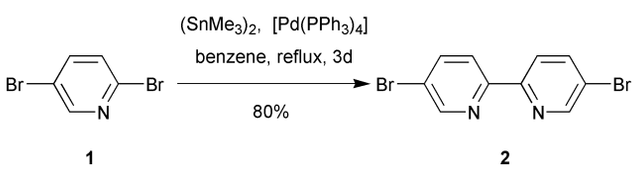
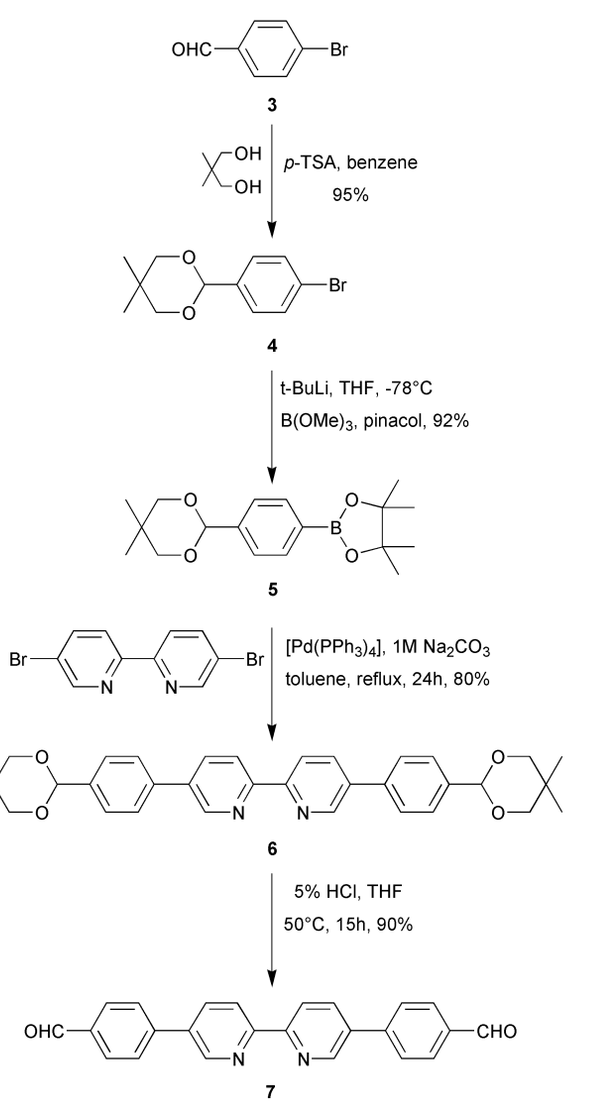
containing an appended ruthenium(II) bipyridine complex.[11b] In the present case, we also found it very convenient to use a Suzuki coupling[12] between 5,5′-dibromo-2,2′-bipyridine and the appropriate aromatic boronic ester to prepare the functionalized precursor of the 5,5′-diphenylene-2,2′-bipyridine bridge.

Accordingly, the linear bis-porphyrins $\mathbf{8}^{2+}$ (free-base) and $\mathbf{11}^{2+}$ (Zn complex) were synthesized in several steps from the key compounds 5,5′-dibromo-2,2′-bipyridine **2** and 2-[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]-4,4,5,5-tetramethyl-1,3-dioxaborolane **5**, as shown in Schemes 1–4. Earlier reports describing the preparation of 5,5′-dibromo-2,2′-bipyridine (**2**) involve Ullman-type coupling of 2-chloro-5-bromopyridine,[13] multistep transformations from 5,5′-disubstituted-2,2′-bipyridines,[14] or direct bromination of the 2,2′-bipyridine hydrobromide salt.[15] The latter method also produces 5-bromo-2,2′-bipyridine, which has to be separated from its disubstituted homologue. The yield of isolated 5,5′-dibromo-2,2′-bipyridine



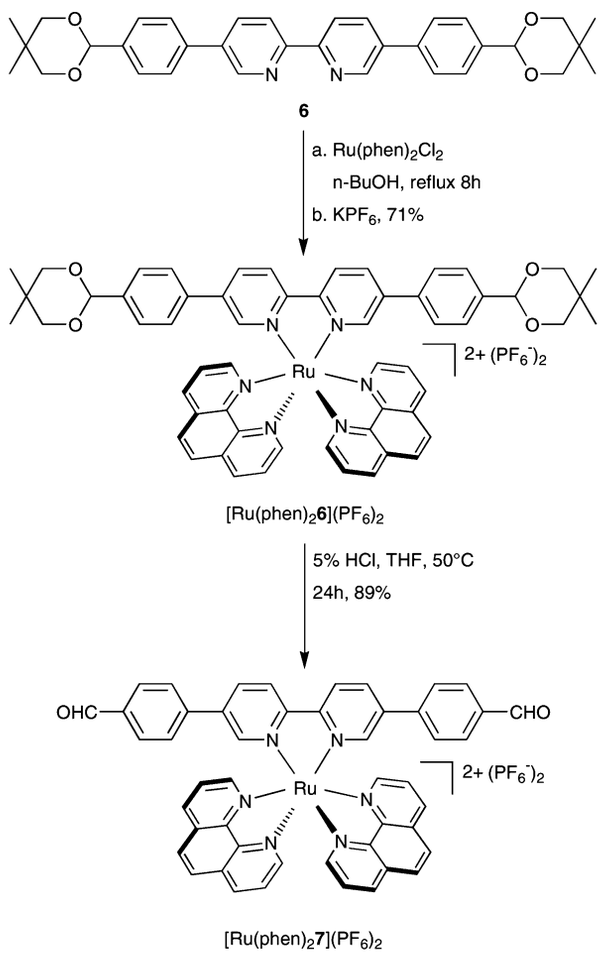
Scheme 1



Scheme 2

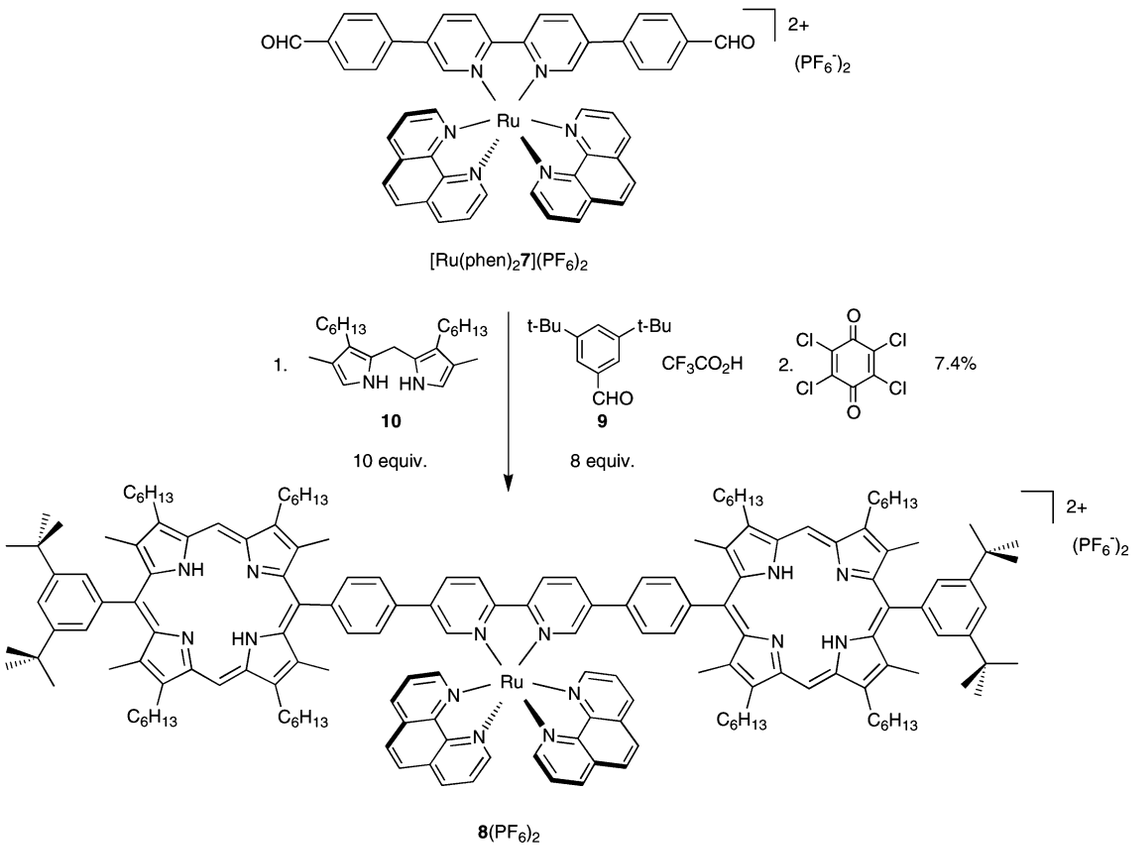
is <50%. Adapting a procedure developed by Torrado and Imperiali[16] for making non-symmetrical methyl 5′-nitro-2,2′-bipyridine-5-carboxylate by Stille coupling of methyl 2-[(trifluoromethyl)sulfonyl]pyridine-5-carboxylate and 2-(trimethylstannyl)-5-nitropyridine, we found that simple heating of commercially available 2,5-dibromopyridine (**1**) and hexamethylditin in the presence of $[Pd(PPh_3)_4]$ afforded, after 3 days reaction in refluxing benzene, the desired 5,5′-dibromo-2,2′-bipyridine (**2**) in 80% yield after chromatography. This one-pot reaction allowed the preparation of **2** in 4–5 g scale amounts.

Separately, as shown in Scheme 2, boronic ester **5** was obtained in 80% yield by treating *p*-(5,5-dimethyl-1,3-dioxan-2-yl)bromobenzene **4** with *t*-BuLi (2 equiv.) followed by sequential addition of trimethyl borate and pinacol.[17] Subsequent coupling with 5,5′-dibromo-2,2′-bipyridine **2** (0.5 equiv.) using Suzuki conditions ($[Pd(PPh_3)_4]$, 1 mol dm^{-3} aqueous Na_2CO_3, toluene, reflux) afforded the protected dialdehyde **6** in 80% yield after flash chromatography. The corresponding dialdehyde **7**, which was obtained in 90% yield by hydrolysis with 5% aqueous HCl in THF at 50 °C, turned out to be poorly soluble in common organic solvents, and in our hands, did not react with the appropriate reagents (see below) to form the bis-porphyrin. Therefore, in the next step, the functionalized 5,5′-diphenyl-2,2′-bipyridine derivative **6** was directly complexed to Ru(II), by reaction with $Ru(phen)_2Cl_2$ in refluxing *n*-butanol (Scheme 3). The deep-orange complex $[Ru(phen)_2\mathbf{6}]^{2+}$ was precipitated in 71% yield as its PF_6^- salt. Deprotection was done as above and afforded the dialdehyde $[Ru(phen)_2\mathbf{7}](PF_6)_2$ in 89% yield.



Scheme 3

Bis-porphyrin $[\mathbf{8}](PF_6)_2$ was formed in the one-pot reaction[18] of dialdehyde $[Ru(phen)_2\mathbf{7}](PF_6)_2$ (1 equiv.), 3,5-di-*tert*-butylbenzaldehyde (**9**)[19] (8 equiv.) and 3,3′-dihexyl-4,4′-dimethyl-2,2′-methylenedipyrrole (**10**)[20] (10 equiv.) in dichloromethane containing a few drops of trifluoroacetic acid, first at room temperature, then at reflux after the addition of tetrachloro-*p*-quinone (chloranil) to achieve oxidation of the porphyrinogen intermediates (Scheme 4). The desired compound was purified



Scheme 4

by repeated column chromatography on silica gel and alumina, and isolated in 7.4% yield. Subsequent reaction with two equivalents of $Zn(OAc)_2{\cdot}2H_2O$ afforded bis-porphyrin [**11**]$(PF_6)_2$. It can be noted that, in the course of the chromatographic purification of bis-porphyrin [**8**]$(PF_6)_2$, the porphyrin–Ru conjugate [**12**]$(PF_6)_2$, which bears a free aldehyde function, could be isolated in 2% yield from the reaction mixture.

The bis-porphyrins were characterized by ^{1}H-NMR, FAB–MS and UV–Vis. The data compiled in the Experimental section are in agreement with the expected structures (Scheme 5), with signatures of the porphyrins and the Ru complex fragment. For example, the following correlations were found in the ROESY maps of bis-porphyrin [**11**]$(PF_6)_2$: op-CH_{3d}, CH_{3d}-α_d, α_d-*meso*, *meso*-α_p, α_p-CH_{3p}, CH_{3p}-m, o-γ, o-α, 4–5, and 6–7, which, taken together with the COSY correlations could allow full assignment of the spectrum.

Conclusion

We have described the multistep synthesis of a linear bis-porphyrin rigidly bridged by a 5,5′-diphenylene-2,2′-bipyridine spacer complexing a $[Ru(phen)_2]^{2+}$ metal complex fragment. It is noteworthy that the key starting material, 5,5′-dibromo-2,2′-bipyridine, was prepared in good yield using a new route, *i.e.* Stille homocoupling of 2,5-dibromopyridine. Formally, the two porphyrins rings are separated by four *p*-phenylene-like groups, which makes our system a higher homologue of the existing bis-porphyrin compounds connected by up to three *p*-phenylene linkers.[21]

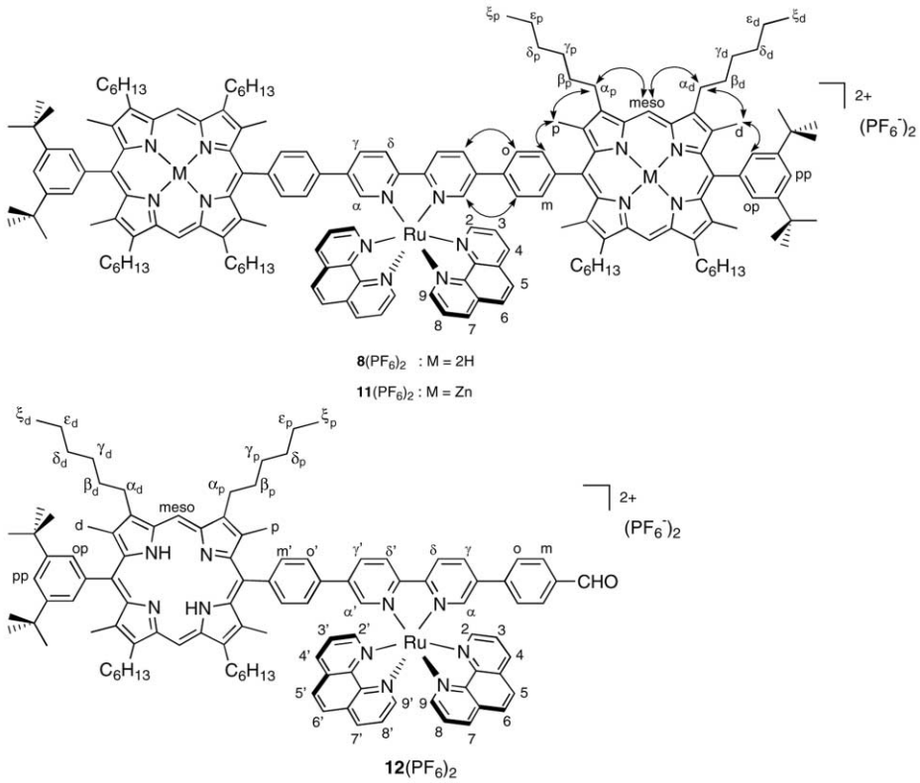
Experimental

General methods

Oxygen or water-sensitive reactions were conducted under a positive pressure of argon in oven-dried glassware, using Schlenk techniques. Benzene and toluene were distilled from Na, THF was distilled from Na–benzophenone, and CH_2Cl_2 was distilled from P_2O_5 prior to use. Common reagents and materials were purchased from commercial sources. The following materials were prepared according to literature procedures: *p*-(5,5-dimethyl-1,3-dioxan-2-yl)bromobenzene (**1**),[22] $[Ru(phen)_2Cl_2]$,[23] 3,3′-dihexyl-4,4′-dimethyl-2,2′-methylenedipyrrole (**10**),[20] and 3,5-di-*tert*-butylbenzaldehyde (**9**).[19] Thin-layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F_{254} (E. Merck). Column chromatography was carried out on silica gel 60 (E. Merck, 70–230 mesh). ^{1}H NMR spectra were obtained on either Bruker WP 200 SY (200 MHz) or AM 400 (400 MHz) spectrometer. NMR chemical shifts δ are expressed in ppm relative to TMS. The coupling constants *J* are measured in Hz. Labels of the protons of the bis-porphyrins are provided in Scheme 5. Fast atom bombardment mass spectrometry (FAB MS) data were recorded in the positive ion mode with a xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a ZAB–HF mass spectrometer. Melting points were determined in open capillary tubes on a Büchi 530 apparatus, and are uncorrected. Elemental analyses were performed by the Service de Microanalyse de l'Institut de Chimie de Strasbourg.

5,5′-Dibromo-2,2′-bipyridine 2

2,5-Dibromopyridine (8.00 g, 0.0338 mol), hexamethylditin (5.53 g, 0.0169 mol) and $[Pd(PPh_3)_4]$ (0.80 g) were refluxed in benzene (250 cm^3) for 65 h under argon. The reaction mixture was cooled and ether (200 cm^3) added. An off-white precipitate was filtered off and chromatographed on silica gel. Eluting with $CHCl_3$–CH_3OH (99.9 : 0.1) gave **2** as a white solid (4.21 g, 80%), mp 225.5–226.5 °C (lit.[13] 224–225 °C); δ_H (200 MHz; $CDCl_3$; Me_4Si) 8.71 (2H, d, $J_{1,4}$ 2, α-H), 8.30 (2H, dd, $J_{1,5}$ 0.6, $J_{1,3}$ 8.5, δ-H), 7.94 (2H, dd, $J_{1,4}$ 2.3, $J_{1,3}$ 8.5, γ-H).



Scheme 5 Structural formulae of compounds [**8**]$(PF_6)_2$, [**11**]$(PF_6)_2$, and [**12**]$(PF_6)_2$, with atom labelling used in the ^{1}H-NMR assignments. Double ended arrows show main ROESY correlations.

2-[4-(5,5-Dimethyl-1,3-dioxan-2-yl)phenyl]-4,4,5,5-tetramethyl-1,3-dioxaborolane 5

To a cold solution of *p*-(5,5-dimethyl-1,3-dioxan-2-yl)bromobenzene **4** (1.00 g, 3.68 mmol) in THF (40 cm^3) at −75 °C under argon, a solution of *t*-BuLi (1.4 mol dm^{-3} in pentane, 5.52 cm^3, 7.74 mmol) was slowly added, keeping the temperature below −70 °C. This was followed 20 min later by trimethyl borate (0.451 cm^3, 4.05 mmol). The temperature was allowed to rise slowly up to room temperature over 2.5 h. Pinacol (0.982 g, 8.31 mmol) was added and 10 min later the reaction was quenched with acetic acid (0.215 cm^3, 3.77 mmol). The reaction mixture was filtered through Celite, the filter washed with diethyl ether and the solvents removed from the filtrate under reduced pressure. The yellow residue was dissolved in $CHCl_3$–H_2O (50 : 50, 40 cm^3). The organic phase was separated and washed with water (3 × 10 cm^3). It was dried over Na_2SO_4, filtered and the chloroform removed under reduced pressure to leave a residue which was recrystallized from cyclohexane. Compound **5** was obtained as a white crystalline solid (0.98 g, 80%), mp 170.5–172 °C (Found: C, 67.75; H, 8.64. $C_{18}H_{27}BO_4$ requires C, 67.94; H, 8.55%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.82 (2H, d, $J_{1,3}$ 8.2, Ar–H), 7.51 (2H, d, $J_{1,3}$ 7.9, Ar–H), 5.41 (1H, s, CH), 3.72 (4H, q, J_{AB} 11.0, CH_2), 1.35 (12H, s, CH_3), 1.30 (3H, s, CH_3), 0.81 (3H, s, CH_3).

5,5′-Bis[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]-2,2′-bipyridine 6

A mixture of **2** (1.00 g, 3.18 mmol), **5** (2.23 g, 7 mmol) and $[Pd(PPh_3)_4]$ (0.868 g) was set under vacuum for 4 h, and stored under argon. Argon was bubbled through separate aliquots of toluene (260 cm^3) and 1 mol dm^{-3} aqueous Na_2CO_3 (260 cm^3), and the degassed solvents were added to the mixture *via* cannula. The reaction was vigorously stirred and refluxed under argon for 24 h. It was cooled to room temperature and a grey precipitate filtered off. The solid was dissolved in $CHCl_3$, filtered and passed through a short column of silica gel, eluting with $CHCl_3$. The resulting pale-yellow solid was washed with ethanol and dried to give **6** as a white solid (1.25 g, 80%), mp >250 °C (Found: C, 71.26; H, 6.64; N, 4.81. $C_{34}H_{36}N_2O_4{\cdot}2H_2O$ requires C, 71.31; H, 7.04; N, 4.89%); δ_H (200 MHz; $CDCl_3$; Me_4Si): 8.93 (2H, d, $J_{1,4}$ 2.3, α-H), 8.51 (2H, d, $J_{1,3}$ 8.2, δ-H), 8.04 (2H, dd, $J_{1,3}$ 8.3, $J_{1,4}$ 2.3, γ-H), 7.67 (8H, s, Ar–H), 5.48 (2H, s, CH), 3.76 (8H, dd, J_{AB} 11.0, CH_2), 1.33 (6H, s, CH_3), 0.84 (6H, s, CH_3).

5,5′-Bis[*p*-formylphenyl]-2,2′-bipyridine 7

Diacetal **6** (0.200 g, 0.37 mmol) was suspended in THF (70 cm^3) and 5% aq. HCl was added. The suspension was heated to 50 °C and the resulting clear solution stirred for 15 h. The reaction mixture was neutralized with 10% aq. Na_2CO_3 (24 cm^3). The precipitate was filtered off and dried under vacuum (0.132 g, 95%); δ_H (200 MHz; CF_3CO_2D; Me_4Si) δ_H 9.47 (2H, d, $J_{1,4}$ 2.7, α-H), 8.75 (2H, s, CHO), 8.35 (2H, d, $J_{1,3}$ 8.4, δ-H), 8.15 (2H, dd, $J_{1,3}$ 8.1, $J_{1,4}$ 2.5, γ-H), 7.67 (4H, br d, $J_{1,3}$ 5.7, *o*-H or *m*-H), 7.33 (4H, br d, $J_{1,3}$ 5.7, *m*-H or *o*-H).

{5,5′-Bis[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]-2,2′-bipyridine}bis(1,10-phenanthroline)ruthenium(II) hexafluorophosphate $[Ru(phen)_2\mathbf{6}](PF_6)_2$

A mixture of *cis*-dichloro bis(1,10-phenanthroline)ruthenium (0.408 g, 0.766 mmol) and **6** (0.450 g, 0.84 mmol) was refluxed in *n*-butanol (200 cm^3) for 8 h under argon. The reaction mixture was filtered to remove unreacted material and a saturated aqueous solution of KPF_6 (40 cm^3) added to the orange filtrate. The mixture was stirred overnight and the orange precipitate filtered off, washed with water, diethyl ether and dried to give $[Ru(phen)_2\mathbf{6}](PF_6)_2$ as an orange solid (0.63 g, 71%) (Found: C, 53.46; H, 3.94; N, 5.89. $C_{58}H_{52}F_{12}N_6O_4P_2Ru{\cdot}H_2O$ requires: C, 53.33; H, 4.17; N, 6.43%); δ_H (200 MHz; CD_3CN; Me_4Si): 8.67 (2H, dd, $J_{1,4}$ 1.2, $J_{1,3}$ 8.3, 4-H or 7-H), 8.63 (2H, d, $J_{1,3}$ 9.4, δ-H), 8.58 (2H, dd, $J_{1,4}$ 1, $J_{1,3}$ 8.3, 7-H or 4-H), 8.37 (2H, dd, $J_{1,4}$ 1.2, $J_{1,3}$ 5.3, 2-H or 9-H), 8.30 (2H, dd, $J_{1,4}$ 2.1, $J_{1,3}$ 8.4, γ-H), 8.25 (4H, dd, J_{AB} 9.0, 5-H and 6-H), 7.98 (2H, dd, $J_{1,4}$ 1.2, $J_{1,3}$ 5.3, 9-H or 2-H), 7.83 (2H, dd, $J_{1,3}$ 5.4, $J_{1,3}$ 8.4, 3-H or 8-H),

7.79 (2H, d, $J_{1,4}$ 2.3, α-H), 7.61 (2H, dd, $J_{1,3}$ 5.2, $J_{1,3}$ 8.2, 8-H or 3-H), 7.46 (4H, d, $J_{1,3}$ 8.3, *m*-H), 7.27 (4H, d, $J_{1,3}$ 8.4, *o*-H), 5.40 (2H, s, CH), 3.67 (8H, dd, J_{AB} 11, CH_2), 1.21 (6H, s, CH_3), 0.78 (6H, s, CH_3).

[5,5′-Bis(4-formylphenyl)-2,2′-bipyridine]bis(1,10-phenanthroline)ruthenium(II) hexafluorophosphate [Ru(phen)$_2$7](PF$_6$)$_2$

[Ru(phen)$_2$**6**](PF$_6$)$_2$ was dissolved in THF (230 cm^3) and 5% aqueous HCl (58 cm^3), and the reaction mixture stirred at 50 °C for 24 h. A saturated aqueous solution of KPF_6 (16 cm^3) was added, followed by water (77 cm^3). The THF was removed under reduced pressure. The orange precipitate was filtered off, washed with water, ethanol and diethyl ether, and dried to give [Ru(phen)$_2$**7**](PF$_6$)$_2$ as a dark orange solid (0.411 g, 89%), mp >260 °C (dec.) (Found: C, 51.98; H, 2.83; N, 7.16. $C_{48}H_{32}F_{12}N_6O_2P_2Ru$ requires C, 51.67; H, 2.89; N, 7.53%); δ_H (200 MHz; CD_3CN; Me_4Si): 10.0 (2H, s, CHO), 8.69 (2H, d, $J_{1,3}$ 8.6, δ-H), 8.68 (2H, dd, $J_{1,4}$ 1.2, $J_{1,3}$ 8.1, 4-H or 7-H), 8.57 (2H, dd, $J_{1,4}$ 1.2, $J_{1,3}$ 8.4, 7-H or 4-H), 8.38 (2H, dd, $J_{1,4}$ 1.2, $J_{1,3}$ 5.2, 2-H or 9-H), 8.37 (2H, dd, $J_{1,4}$ 2, $J_{1,3}$ 8.5, γ-H), 8.25 (4H, dd, J_{AB} 8.7, 5-H and 6-H), 7.95 (2H, dd, $J_{1,4}$ 1.2, $J_{1,3}$ 4.8, 9-H or 2-H), 7.88 (2H, d, $J_{1,4}$ 4.4, α-H), 7.88 (4H, d, $J_{1,3}$ 8.4, *m*-H), 7.84 (2H, dd, $J_{1,3}$ 5.3, $J_{1,3}$ 8.2, 3-H or 8-H), 7.60 (2H, dd, $J_{1,3}$ 5.3, $J_{1,3}$ 8.2, 8-H or 3-H), 7.48 (4H, d, $J_{1,3}$ 8.1, *o*-H); *m*/*z* (FAB) 971.2 ([M − PF$_6^-$]$^+$).

[8](PF$_6$)$_2$. [Ru(phen)$_2$**7**](PF$_6$)$_2$ (94.5 mg, 0.0846 mmol), 3,5-di-*tert*-butylbenzaldehyde **9** (174.7 mg, 0.689 mmol) and 3,3′-dihexyl-4,4′-dimethyl-2,2′-methylenedipyrrole **10** (343 mg, 1 mmol) were dissolved in dichloromethane under argon. Trifluoroacetic acid (3 drops) was added and the reaction mixture stirred at room temperature overnight. Tetrachloro-*p*-benzoquinone (0.656 g, 2.67 mmol) was added and the reaction mixture refluxed for 2 h. After cooling to room temperature, it was neutralized with 10% aqueous Na_2CO_3. The organic phase was separated, washed with water (2 × 200 cm^3), and stirred with a 5% aqueous solution of KPF_6 (100 cm^3) overnight. After separation, it was washed with water (2 × 200 cm^3) and the solvent removed under reduced pressure. The crude product was chromatographed on alumina. Elution with CH_2Cl_2–CH_3OH (1.3–1.5%) afforded 0.0322 g of impure [**8**](PF$_6$)$_2$; elution with CH_2Cl_2– CH_3OH (2.5–5%) afforded 0.0402 g of impure [**12**](PF$_6$)$_2$. These fractions were further purified by repeated column chromatography on alumina, eluting with CH_2Cl_2–CH_3OH. Porphyrin [**12**](PF$_6$)$_2$ (see below) was isolated as an orange material after preparative TLC (alumina, CH_2Cl_2–CH_3OH (0.5–1.5%)) (3.20 mg, 2%). Bis-porphyrin [**8**](PF$_6$)$_2$ was obtained as a dark orange solid (17.74 mg, 7.4%); $\lambda_{max}(CH_2Cl_2)$/nm 265 (ε/dm^3 mol^{-1}cm^{-1} 59000), 412 (419000), 508 (25600), 540 (14600), 574 (13000) and 627 (1900); δ_H (400 MHz; CD_2Cl_2; Me_4Si): 10.273 (4H, s, *meso*-H), 8.762 (2H, dd, $J_{1,3}$ 8.34, $J_{1,4}$ 1.20, 7-H), 8.693 (2H, d, $J_{1,3}$ 8.43, δ-H), 8.649 (2H, dd, $J_{1,3}$ 5.23, $J_{1,4}$ 1.20, 9-H), 8.602 (2H, dd, $J_{1,3}$ 8.35, $J_{1,4}$ 1.93, γ-H), 8.522 (2H, dd, $J_{1,3}$ 8.34, $J_{1,4}$ 1.01, 4-H), 8.288 (2H, d, $J_{1,3}$ 8.80, 6-H), 8.199 (2H, dd, $J_{1,3}$ 5.31, $J_{1,4}$ 1.28, 2-H), 8.179 (2H, d, $J_{1,3}$ 9.72, 5-H), 8.152 (br s, 2H, α-H), 8.135 (2H, dd, $J_{1,3}$ 8.25, $J_{1,3}$ 5.32, 8-H), 8.116 (4H, d, $J_{1,3}$ 8.25, *m*-H), 7.932 (4H, d, $J_{1,4}$ 1.83, *op*-H), 7.870 (2H, t, $J_{1,4}$ 1.83, *pp*-H), 7.785 (2H, dd, $J_{1,3}$ 8.25, $J_{1,3}$ 5.32, 3-H), 7.634 (4H, d, $J_{1,3}$ 8.25, *o*-H), 4.010 (16H, br m, α_p-H and α_d-H), 2.503 (12H, s, CH_{3d}), 2.427 (12H, s, CH_{3p}), 2.221 (16H, sext, β_p-H and β_d-H), 1.782 (16H, quintet, γ_p-H and γ_d-H), 1.522 (36H, s, C*H*$_3$), 1.522 (16H, m, δ_p-H and δ_d-H), 1.405 (16H, quartet, ε_p-H and ε_d-H), 0.937 (12H, t, $J_{1,3}$ 7.33, ξ_p-H or ξ_d-H), 0.929 (12H, t, $J_{1,3}$ 7.33, ξ_d-H or ξ_p-H), −2.445 (4H, br s, NH); *m*/*z* (FAB) 2839.6 ([M^{2+} + 2PF$_6^-$ + H$^+$]$^+$, 0.8%), 2693.6 ([M^{2+} + PF$_6^-$]$^+$, 5), 2547.7 ([M^{2+} + e$^-$]$^+$, 4.6), 1346.3 ([M^{2+} + PF$_6^-$ + H$^+$]$^{2+}$/2, 2.3), 1273.8 ([M^{2+}]/2, 4), 462 ([Ru(phen)$_2^{2+}$ + e$^-$]$^+$, 100).

[11](PF$_6$)$_2$. [**8**](PF$_6$)$_2$ (7.37 mg, 0.0026 mmol) was dissolved in chloroform (4 cm^3) under argon. A solution of $Zn(OAc)_2{\cdot}2H_2O$ (1 cm^3, 7.94 × 10^{-6} mol) in methanol was added. The reaction mixture was refluxed for 1.5 h. The resulting solution was diluted with water (10 cm^3) and shaken with a saturated aqueous solution of $NaHCO_3$ (10 cm^3). The organic layer was washed twice with water, concentrated to 10 cm^3 and treated with a 5% aqueous solution of KPF_6 (10 cm^3) for 4 h. The organic layer was separated, washed 3 times with water, and the solvent removed under reduced pressure leaving [**11**](PF$_6$)$_2$ as a red solid (6.10 mg, 79%); $\lambda_{max}(CH_2Cl_2)$/nm 265 (ε/dm^3 mol^{-1} cm^{-1} 58000), 414 (521000), 540 (28400), 574 (14200); δ_H (400 MHz; CD_2Cl_2; Me_4Si): 10.202 (4H, s, *meso*-H), 8.80 (2H, br d, $J_{1,3}$ 8, δ-H), 8.793 (2H, dd, $J_{1,3}$ 8.28, $J_{1,4}$ 1.12, 7-H), 8.680 (2H, dd, $J_{1,3}$ 5.26, $J_{1,4}$ 1.19, 9-H), 8.67 (2H, br dd, $J_{1,3}$ 8, γ-H), 8.553 (2H, dd, $J_{1,3}$ 8.35, $J_{1,4}$ 1.06, 4-H), 8.343 (2H, d, $J_{1,3}$ 8.97, 6-H), 8.234 (2H, d, $J_{1,3}$ 8.98, 5-H), 8.225 (2H, dd, $J_{1,3}$ 5.25, $J_{1,4}$ 1.19, 2-H), 8.162 (2H, s, α-H), 8.150 (2H, d, $J_{1,3}$ 8.27, $J_{1,3}$ 5.33, 8-H), 8.111 (4H, d, $J_{1,3}$ 7.99, *m*-H), 7.929 (4H, d, $J_{1,4}$ 1.83, *op*-H), 7.869 (2H, t, $J_{1,4}$ 1.83, *pp*-H), 7.801 (2H, dd, $J_{1,3}$ 8.28, $J_{1,3}$ 5.33, 3-H), 7.634 (4H, d, $J_{1,3}$ 8.13, *o*-H), 3.981 (16H, quint, α_p-H and α_d-H), 2.468 (12H, s, CH_{3d}), 2.375 (12H, s, CH_{3p}), 2.195 (16H, sept, β_p-H and β_d-H), 1.777 (16H, quint, γ_p-H and γ_d-H), 1.526 (36H, s, CH_3), 1.526 (16H, m, δ_p-H and δ_d-H), 1.402 (16H, m, ε_p-H and ε_d-H), 0.943 (12H, t, $J_{1,3}$ 7.29, ξ_p-H or ξ_d-H), 0.931 (12H, t, $J_{1,3}$ 7.29, ξ_d-H or ξ_p-H); *m*/*z* (FAB) 2818.7 ([M^{2+} + PF$_6^-$]$^+$, 6.0%), 2675.0 ([M^{2+} + e$^-$]$^+$, 5.4), 1409.8 ([M^{2+} + PF$_6^-$ + H$^+$]$^{2+}$/2, 1.9), 1337.8 ([M^{2+}]/2, 4.5), 462.1 ([Ru(phen)$_2^{2+}$ + e$^-$]$^+$, 100).

[12](PF$_6$)$_2$. For isolation, see preparation of bis-porphyrin [**8**](PF$_6$)$_2$; δ_H (400 MHz; CD_2Cl_2; Me_4Si): 10.250 (2H, s, *meso*-H), 10.013 (1H, s, CHO), 8.710 (1H, d, hidden, $J_{1,3}$ 8.25, δ′-H), 8.708 (1H, dd, $J_{1,3}$ 8.43, $J_{1,4}$ 1.29, 7-H or 7′-H), 8.684 (1H, dd, $J_{1,3}$ 8.43, $J_{1,4}$ 1.28, 7′-H or 7-H), 8.653 (1H, d, $J_{1,3}$ 8.62, δ-H), 8.608 (1H, dd, $J_{1,3}$ 8.44, $J_{1,4}$ 2.02, γ′-H), 8.546 (1H, dd, $J_{1,3}$ 5.04, $J_{1,4}$ 1.19, 9-H), 8.533 (1H, dd, $J_{1,3}$ 5.04, $J_{1,4}$ 1.19, 9′-H), 8.517 (1H, dd, $J_{1,3}$ 8.07, $J_{1,4}$ 1.47, 4-H or 4′-H), 8.513 (1H, dd, $J_{1,3}$ 8.35, $J_{1,4}$ 1.38, 4′-H or 4-H), 8.315 (1H, dd, $J_{1,3}$ 8.07, $J_{1,4}$ 1.84, γ-H), 8.289 (2H, d, $J_{1,3}$ 8.81, 6-H or 6′-H), 8.237 (1H, d, $J_{1,3}$ 8.99, 6′-H or 6-H), 8.192 (1H, d, $J_{1,3}$ 8.99, 5-H or 5′-H), 8.173 (1H, d, $J_{1,3}$ 8.98, 5′-H or 5-H), 8.134 (1H, dd, $J_{1,3}$ 5.32, $J_{1,4}$ 1.29, 2-H), 8.100 (1H, dd, $J_{1,3}$ 6.61, $J_{1,4}$ 1.29, 2′-H), 8.084 (1H, br s, α′-H), 8.087 (2H, d, $J_{1,3}$ 7.70, m′-H), 8.059 (1H, dd, $J_{1,3}$ 8.72, $J_{1,3}$ 5.60, 8-H or 8′-H), 8.051 (1H, dd, $J_{1,3}$ 5.32, $J_{1,3}$ 8.44, 8′-H or 8-H), 7.913 (2H, d, $J_{1,4}$ 1.84, *op*-H), 7.900 (1H, s, α-H), 7.895 (2H, m, $J_{1,3}$ 8.44, *m*-H), 7.859 (1H, t, $J_{1,4}$ 1.83, *pp*-H), 7.752 (1H, dd, $J_{1,3}$ 8.53, $J_{1,3}$ 5.23, 3-H or 3′-H), 7.744 (1H, dd, $J_{1,3}$ 8.35, $J_{1,3}$ 5.04, 3′-H or 3-H), 7.593 (2H, d, $J_{1,3}$ 8.44, *o*′-H), 7.491 (2H, d, $J_{1,3}$ 8.07, *o*-H), 3.989 (8H, quartet, α_p-H and α_d-H), 2.486 (6H, s, CH_{3d}), 2.389 (6H, s, CH_{3p}), 2.190 (8H, sext, β_p-H and β_d-H), 1.762 (8H, sext, γ_p-H and γ_d-H), 1.518 (18H, s, CH_3), 1.518 (8H, m, δ_p-H and δ_d-H), 1.386 (8H, quartet, ε_p-H and ε_d-H), 0.916 (6H, t, $J_{1,3}$ 7.25, ξ_p-H or ξ_d-H), 0.913 (6H, t, $J_{1,3}$ 7.25, ξ_d-H or ξ_p-H), −2.477 (2H, br s, NH); *m*/*z* (FAB) 1832.5 ([M^{2+} + PF$_6^-$]$^+$, 12%), 1687.2 ([M^{2+} + e$^-$]$^+$, 17), 843.8 ([M^{2+}]/2, 11), 462.1 ([Ru(phen)$_2^{2+}$ + e$^-$]$^+$, 100).

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