Synthesis of a Linear Assembly Consisting of a Central Ru(Phen)$_3^{2+}$ Derivative and Two Peripheral Porphyrins

Xavier J. Salom-Roig,[a] Jean-Claude Chambron,[a,b] Christine Goze,[a] Valérie Heitz,[a] and Jean-Pierre Sauvage*[a]

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A ruthenium(II) precursor complex containing a bis-phenanthroline ligand, leading to a controlled helical structure around the metal centre, and a third phenanthroline-type ligand has been prepared. The spatial arrangement of the system is such that two chemical groups are disposed *trans* to one another on an axis running through the Ru centre. By appropriate functional group transformation, these two groups can be attached to monosubstituted zinc(II) porphyrins (PZn) to afford a linear array consisting of a central ruthenium(II) complex and two peripheral PZn motifs.

Introduction

Mimicking the charge separation process, which is one of the key early events of photosynthesis,[1] has focussed the attention of many groups using artificial multicomponent systems incorporating one or several porphyrins as chromophores.[2] Spectacular examples have been reported which lead, in a few cases, to long-lived, charge-separated states.[3,4] These synthetic systems have in common a good geometrical control over the disposition of the various components [photoactive centre(s), donor and acceptor groups]. In order to avoid fast charge recombination, linear and rigid arrays seem to be particularly well adapted since they prevent unfavourable folding of the ensemble.

Our team has used transition metal complexes extensively as photo- and electroactive groups to construct multicomponent species able to undergo charge separation. In each case, the central metal also has an important gathering and orienting function. In particular, we have used Ru^{II},[5,6] Os^{II} [5] or Ir^{III},[7] often in conjunction with porphyrins.[6,7] In each case, the central unit was a bis-terpy complex (terpy = 2,2′,6′,2"-terpyridine), the spatial arrangement of the two ligands providing the system with a well-defined axis (Figure 1, type I).

The present report is concerned with the synthesis of a linear molecular array. This consists of a central ruthenium(II) complex belonging to a newly described family of compounds which possess a well-defined axis[10] and two peripheral porphyrins (Figure 1, type III).

Results and Discussion

The multicomponent system described here, **PZn-Ru-PZn**, is shown in Figure 2. The central complex is such that the two porphyrinic groups are located on different sides of the ruthenium compound, with an estimated edge-to-edge distance of about 32 Å and an average centre-to-centre separation of about 41 Å.

For the synthesis of **PZn-Ru-PZn** we prepared first the bis-chelating ligand **1** (Figure 3), made up of two 7-(*p*-anisyl)-1,10-phenanthroline (phen) subunits connected by a *p*-$(CH_2)C_6H_4(CH_2)_2$- spacer through their 4-positions, as reported earlier.[10] The Ru(phen)$_3^{2+}$ derivative **4** was obtained as follows: treatment of freshly prepared $[RuCl_2(CH_3CN)_4]$[11] with stoichiometric amounts of **1** in refluxing 1,2-dichloroethane afforded **2**. The reaction was carried out in a dilute medium so as to favour intramolecular reactions. The two chloride ligands were then thermally exchanged for 4,7-diphenyl-1,10-phenanthroline (4,7-dpp) in a 7:1 mixture of ethanol and water, without previous isolation of **2**. The complex obtained was precipitated by addition of KPF_6, which afforded **[3]**$(PF_6)_2$ as an orange solid in 45% overall yield after purification by column chromatography. Finally we took advantage of the stability and solubility of ruthenium(II) complexes of **1**, by deprotection of the anisoyl substituents under mild conditions using boron tribromide in dichloromethane solution to furnish **4** in 83% yield .[12]

The preparation of the zinc porphyrin was performed as shown in Figure 4.[13] Pyrrole and a 3:1 mixture of 3,5-di-

[a] Laboratoire de Chimie Organo-Minérale, UMR 7513 du CNRS, Université Louis Pasteur, Faculté de Chimie, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France
[b] Present address: Université de Bourgogne, Faculté des Sciences Gabriel, LIMSAG, UMR 5633 du CNRS, 6, Boulevard Gabriel, 21100 Dijon, France

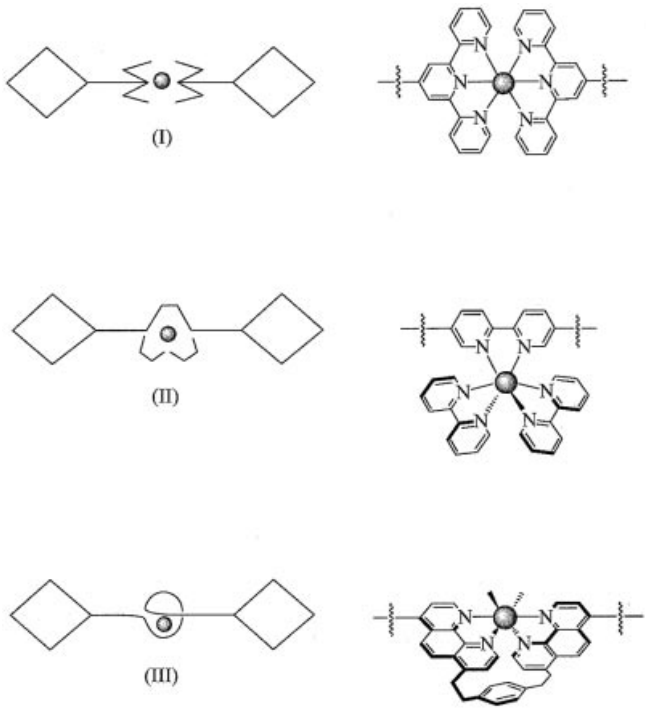

Figure 1. Three possible ligand sets around an octahedral metal centre, affording a well-identified axis on which additional photo- and/or electroactive groups such as porphyrins (represented as diamonds) can be attached; (I) a bis-terpy complex: the axis runs through the two 4′ carbon atoms of the terpy ligands and the metal centre; (II) One of the three bidentate ligands has been functionalised so as to provide an axis to the complex. One possibility is to use the 5- and 5′-positions of a 2,2′-bipyridine[8] or the 3- and 8-positions of a 1,10-phenanthroline.[9] In this case, the axis will, of course, not run through the central metal; (III) the presently described system contains a three-bidentate ligand complex. It clearly shows a helical arrangement built on two ligands and their linker. The axis runs through the central metal.

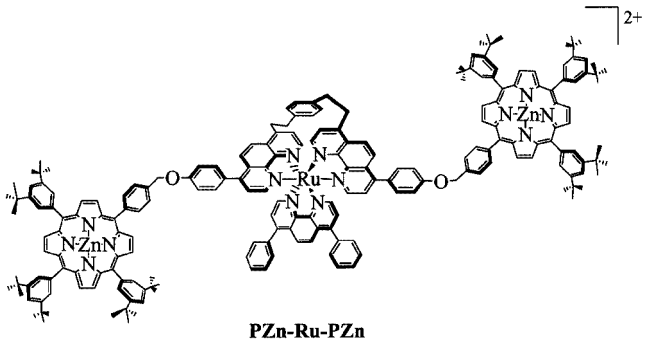

Figure 2. Chemical structure and approximate geometrical arrangement of **PZn-Ru-PZn**

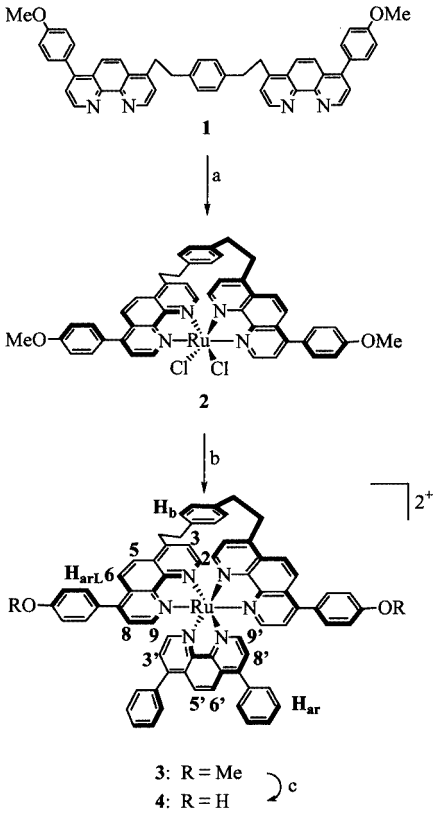

Figure 3. Reagents and conditions: (a) $[RuCl_2(CH_3CN)_4]$, $ClCH_2CH_2Cl$, reflux; (b) 4,7-dpp, EtOH/H_2O (7:1), reflux, 5 h, 45% two steps; (c) BBr_3, CH_2Cl_2, −78 °C, 83%

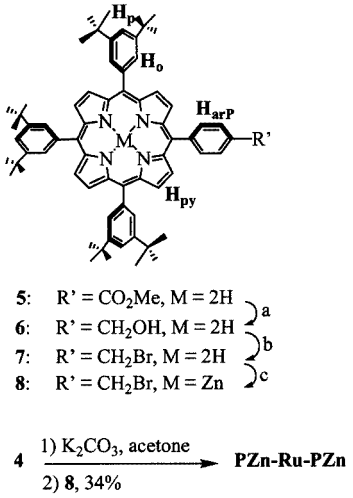

Figure 4. Reagents and conditions: (a) $LiAlH_4$, THF, 0 °C, 89%; (b) CBr_4, PPh_3, CH_2Cl_2, 78%; (c) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH (7:1), 97%

tert-butylbenzaldehyde[14,15] and methyl 4-formylbenzoate were refluxed in propionic acid, yielding the ester porphyrin derivative **5** in 5% yield after column chromatography. The ester function was then reduced by treatment of **5** with $LiAlH_4$ in THF giving **6** in 89% yield. Intermediate **6** was brominated with CBr_4 in the presence of PPh_3 to give the bromoporphyrin derivative **7** in 78% yield. Metallation with $Zn(OAc)_2$ in a mixture of $CHCl_3$ and MeOH at reflux resulted in the desired zinc porphyrin **8** in nearly quantitative yield (97%).

Finally, two zinc porphyrins were linked to the ruthenium complex **4** via ether bond formation. Thus, a solution of porphyrin **8** in acetone was added to an excess of the dianion of **4**, generated by addition of K_2CO_3, and the resulting mixture was heated in refluxing acetone for 24 h. The **PZn-**

Ru-PZn assembly was obtained in 34% yield after purification by column chromatography (Figure 4).

The ES-MS mass spectrum of **PZn-Ru-PZn** shows a major peak at 1581.1 a.m.u. corresponding to the doubly charged species. The ^{1}H NMR spectrum was fully assigned by 2D ROESY experiments. The visible part of the electronic absorption spectra shows three $\pi \rightarrow \pi^*$ transitions for the zinc(II) porphyrin part of **PZn-Ru-PZn** (Soret band at 417 nm and Q transitions at 551 and 590 nm) and a MLCT transition at 459 nm for the ruthenium(II) complex (Figure 5a). Upon excitation at 551 nm at room temperature, two intense emission bands at 600 and 646 nm were observed, attributed to the zinc porphyrin component of **PZn-Ru-PZn** showing that quenching of the luminescence of the porphyrin units is only limited (Figure 5b).

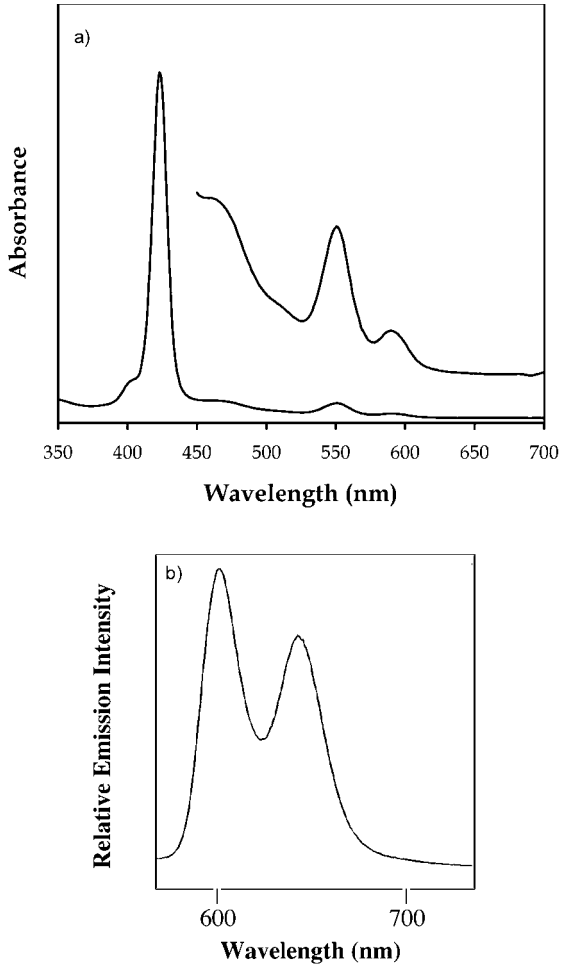

Figure 5. (a) Absorption and (b) emission spectra of **PZn-Ru-PZn** in dichloromethane at room temperature

Conclusion

We have demonstrated that the ruthenium(II) complex **3**, containing an axis running through the Ru centre, is a convenient precursor for the preparation of assemblies in which a maximal spatial separation between the electroactive components can be controlled. Research which builds on these precursors continues and future studies will be reported in due course.

Experimental Section

General Remarks. Dry solvents were obtained by distillation from suitable dessicants (THF from Na/benzophenone and CH_2Cl_2 from P_2O_5). The other anhydrous solvents were of commercial analytical grade: acetonitrile, dimethylformamide, methanol, absolute ethanol, 1,2-dichloroethane, propionic acid, chloroform. Reactions were performed under an atmosphere of argon using standard Schlenk techniques. Thin-layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F_{254} (Merck). After elution, the plates were either scrutinized under a UV lamp or exposed to I_2. Column chromatography was carried out on silica gel 60 (Merck, 70−230 mesh). UV/Vis spectra were recorded on a Bio-Tek Instruments UVIKON XL spectrophotometer. Mass spectroscopic data were recorded on ZAB-HF (FAB) spectrometer. Electrospray mass spectrometry (ES-MS) were recorded in the positive-ion mode with VG-BIOQ triple quadripole. The ^{1}H NMR spectra were recorded on Bruker WP200SY (200 MHz) spectrometer. Chemical shifts in ppm are referenced downfield from tetramethylsilane. Labels of the protons of the complexes **3** and **4**, porphyrins and the final product **PZn-Ru-PZn** are provided in Figure 3 and 4. All porphyrins reported below were isolated as purple solids (m.p. > 300 °C). Other reagents and solvents were commercially available and used without purification.

[$RuCl_2(CH_3CN)_4$]: [$RuCl_2(DMSO)_4$] (80 mg, 0.165 mmol, 1equiv.) was refluxed for 2 h in degassed acetonitrile (11 mL) under argon. The reaction mixture was allowed to cool to room temperature and then poured into diethyl ether (100 mL). The resulting precipitate was decanted and washed with diethyl ether (3 × 50 mL). After filtration under argon a yellow solid was obtained. This product was used in the next step without further purification.

[3](PF_6)$_2$: The freshly prepared [$RuCl_2(CH_3CN)_4$] and **1** (116 mg , 0.165 mmol, 1 equiv.) were each dissolved in 50 mL of 1,2-dichloroethane.[10] The two solutions were simultaneously added dropwise to refluxing 1,2-dichloroethane (1.5 L) at a rate of 4 mL/h using a special high dilution glassware and vigorous mechanical stirring. The resulting dark violet mixture was then refluxed for a further 4.5 hours. After removal of the solvent a violet solid **2**, was obtained.

The resulting complex **2**, used without further purification, was suspended in a mixture of ethanol (15 mL) and water (2 mL) and then 4,7-dpp (55 mg ,0.165 mol, 1equiv.) was added. The resulting mixture was refluxed for 5 h. The violet reaction mixture rapidly turned orange upon heating. After cooling, the solvents were evaporated and the resulting orange solid was dissolved in acetone (40 mL) and stirred with a saturated aqueous solution of KPF_6 (20 mL) for 5 h. Acetone was evaporated and the resulting precipitate filtered, washed with water and chromatographed on silica using CH_2Cl_2/MeOH (40:1) as eluent to give 107 mg (45%) of [**3**](PF_6)$_2$, as an orange solid. TLC: one spot, R_f = 0.78 (SiO_2; CH_2Cl_2/MeOH, 9:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.90−3.56 (m, 8 H, CH_2), 3.91 (s, 6 H, CH_3), 6.27 (d, J = 8.9 Hz, 2 H, H_b), 6.60 (d, J = 8.9 Hz, 2 H, H_b), 7.11 (d, J = 8.6 Hz, 4 H, H_{arL}), 7.15 (d, J = 5.2 Hz, 2 H, H_3), 7.47 (d, J = 5.2 Hz, 2 H, H_2), 7.54−7.64 (m, 16 H, H_{arL},H_8, H_{ar}), 7.73 (d, J = 5.4 Hz, 2 H, $H_{3',8'}$), 7.96 (d, J = 5.4 Hz, 2 H, H_9), 8.17 (d, J = 9.3 Hz, 2 H, H_5), 8.25 (s, 2 H, $H_{5',6'}$), 8.30 (d, J = 9.3 Hz, 2 H, H_6), 8.68 (d, J = 5.4 Hz, 2 H, $H_{2',9'}$)

ppm. UV/Vis (CH_2Cl_2): λ (ε) = 229 nm (72800 mol·L^{-1}·cm^{-1}), 278 (79200), 462 (13900). ES (+) MS: *m*/*z* [M − 2PF_6]$^{2+}$/2 = 568.2 (calcd. 568.2).

Preparation of [4](PF$_6$)$_2$: BBr_3 (1.0 M in CH_2Cl_2; 0.26 mL, 0.264 mol, 4 equiv.) was added to a stirred solution of [**3**](PF_6)$_2$ (74.9 mg, 0.066 mmol, 1equiv.) in freshly distilled CH_2Cl_2 (10 mL) at −78 °C under argon. After 2 h stirring at −78 °C, the solution was allowed to warm to room temperature, quenched with water and filtered. The resulting orange solid was washed with water and stirred in a mixture of CH_2Cl_2 (5 mL) and a saturated aqueous solution of KPF_6. The phases were separated and the aqueous one extracted with CH_2Cl_2. The solvent was evaporated to give 60.8 mg (83%) of [**4**](PF_6)$_2$ as an orange solid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 3.05−3.25 (m, 4 H, CH_2), 3.40−3.50 (m, 2 H, CH_2), 3.93−4.0 (m, 2 H, CH_2), 6.28 (d, *J* = 9.0 Hz, 2 H, H_b), 6.73 (d, *J* = 9.0 Hz, 2 H, H_b), 7.05 (d, *J* = 8.6 Hz, 4 H, H_{arL}), 7.31 (d, *J* = 5.7 Hz, 2 H, H_3), 7.35 (d, *J* = 5.5 Hz, 2 H, H_2), 7.54 (d, *J* = 8.4 Hz, 4 H, H_{arL}), 7.60−7.70 (m, 12 H, H_{ar}, H_8), 7.77 (d, *J* = 5.4 Hz, 2 H, $H_{3',8'}$), 7.99 (d, *J* = 5.55 Hz, 2 H, H_9), 8.28 (d, *J* = 9.5 Hz, 2 H, H_5), 8.30 (s, 2 H, $H_{5',6'}$), 8.53 (d, *J* = 9.5 Hz, 2 H, H_6), 8.63 (d, *J* = 5.5 Hz, 2 H, $H_{2',9'}$) ppm. UV/Vis (CH_2Cl_2) λ (ε) = 230 nm (72500 mol·L^{-1}·cm^{-1}), 274 (79600), 462 (22100). FAB (+) MS: *m*/*z* [M − PF_6]$^+$ = 1108.3 (calcd. 1107.5); [M − 2PF_6]$^{2+}$/2 = 554.1 (calcd. 553.7).

5-(4-Methoxycarbonylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)-porphyrin (5): Pyrrole (10.2 mL, 0.147 mol, 3.9 equiv.) was added dropwise at 130 °C to a solution of methyl 4-formylbenzoate (6.23 g, 0.038 mol, 1equiv.) and 3,5-di-*tert*-butylbenzaldehyde[14] (24.11 g, 0.110 mol, 3.1 equiv.) in propionic acid (640 mL). The reaction mixture was refluxed for 1.5 h. The propionic acid was then evaporated off and the resulting precipitate was purified by chromatography on silica gel (hexane/EtOAc 375:1) affording the methoxyporphyrin **5** (1.57 g, 5%) as a purple solid. TLC: one spot, R_f = 0.42 (SiO_2; hexane/EtOAc, 9:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = −2.63 (s, 2 H, NH), 1.58 (s, 54 H, CH_3), 4.15 (s, 3 H, OCH_3), 7.86 (m, 3 H, H_p), 8.15 (d, *J* = 1.5 Hz, 6 H, H_o), 8.38 (d, *J* = 7.9 Hz, 2 H, H_{arP}), 8.49 (d, *J* = 7.9 Hz, 2 H, H_{arP}), 8.85 (d, *J* = 4.7 Hz, 2 H, H_{py}), 8.87 (m, 6 H, H_{py}) ppm.

5-(4-Hydroxymethylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)-porphyrin (6): $LiAlH_4$ (122 mg, 3.21 mmol, 3 equiv.) was slowly added to a dry THF solution (200 mL) of **5** (1.06 g, 1.05 mmol, 1 equiv.) at 0 °C. The solution was stirred at room temperature under argon overnight in the dark. The reaction mixture was quenched by addition of EtOAc (10 mL) followed by addition of a 10% HCl solution (200 mL). The organic layer was separated and washed with a saturated Na_2CO_3 solution, dried over $MgSO_4$, and concentrated in vacuo. Purification by column chromatography on silica gel with hexane/EtOAc (190:1) as eluent gave **6** (870 mg, 89%) as a purple solid. M.p. > 300 °C . TLC: one spot, R_f = 0.41 (hexane/EtOAc, 4:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = −2.64 (s, 2 H, NH), 1.53 (s, 54 H, CH_3), 5.02 (s, 2 H, CH_2), 7.75 (d, *J* = 8.1 Hz, 2 H, H_{arP}), 7.78−7.80 (m, 3 H, H_p), 8.07−8.09 (m, 6 H, H_o), 8.23 (d, *J* = 8.1 Hz, 2 H, H_{arP}), 8.84 (d, *J* = 5.0 Hz, 2 H, H_{py}), 8.89 (d, *J* = 5.0 Hz, 2 H, H_{py}), 8.90 (s, 4 H, H_{py}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.8, 31.9, 65.4, 119.4, 121.1, 121.5, 121.6, 125.3, 129.8, 130.0, 131.5, 140.2, 141.4, 141.9, 148.8 ppm. UV/Vis (CH_2Cl_2): λ (ε) = 420 nm (426000 mol·L^{-1}·cm^{-1}), 517 (15100), 553 (9900), 593 (5000), 649 (5600). FAB (+) MS: *m*/*z* = 981.4 [MH^+]; $C_{69}H_{81}ON_4$ requires 981.6.

5-(4-Bromomethylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (7): PPh_3 (210 mg, 0.8 mmol, 3.2 equiv.) and CBr_4 (266 mg, 0.8 mmol, 3.2 equiv.) were added at room temperature under argon to a stirred solution of porphyrin **6** (257 mg, 0.246 mmol, 1 equiv.) in dry CH_2Cl_2 (65 mL). After stirring in the dark overnight the reaction mixture was washed with a saturated aqueous solution of $NaHCO_3$ (10 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification by column chromatography on silica gel with hexane/EtOAc (100:1) as eluent afforded **7** (214 mg, 78%) as a purple solid. TLC: one spot, R_f = 0.9 (hexane/EtOAc, 4:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = −2.56 (s, 2 H, NH), 1.65 (s, 54 H, CH_3), 4.86 (s, 2 H, CH_2), 7.79 (d, *J* = 8.1 Hz, 2 H, H_{arP}), 7.92 (m, 3 H, H_p), 8.22 (m, 6 H, H_o), 8.28 (d, *J* = 8.1 Hz, 2 H, H_{arP}), 8.94 (d, *J* = 5.0 Hz, 2 H, H_{py}), 9.02 (d, *J* = 5.0 Hz, 2 H, H_{py}), 9.05 (s, 4 H, H_{py}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.8, 31.8, 35.1, 121.1, 121.5, 127.4, 129.7, 129.9, 131.5, 134.9, 141.3, 142.8, 141.4, 142.8, 148.8 ppm. UV/Vis (CH_2Cl_2): λ (ε) = 421 nm (399900 mol·L^{-1}·cm^{-1}), 517 (15000), 553 (8400), 592 (4500), 649 (4900). FAB (+) MS: *m*/*z* = 1044.3 [MH^+]; $C_{69}H_{80}BrN_4$ requires 1044.9.

5-(4-Bromomethylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)-porphyrinatozinc(II) (8): $Zn(OAc)_2$·$2H_2O$ (42 mg, 0.191 mmol, 1.4 equiv.) in MeOH (2 mL) was added to a solution of porphyrin **7** (144 mg, 0.138 mmol, 1 equiv.) in $CHCl_3$ (14 mL). The mixture was heated at 80 °C for 3 h. The solvent was evaporated in vacuo and the resulting solid residue was subjected to column chromatography on silica gel with hexane/EtOAc (50:3) as eluent to afford the pure zinc(II) porphyrin **8** (148 mg, 97%) as an intense purple solid. TLC: one spot, R_f = 0.7 (SiO_2; hexane/EtOAc, 4:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.57 (s, 54 H, CH_3), 4.88 (s, 2 H, CH_2), 7.83 (d, *J* = 7.9 Hz, 2 H, H_{arP}), 7.92 (m, 3 H, H_p), 8.23 (m, 6 H, H_o), 8.32 (d, *J* = 7.9 Hz, 2 H, H_{arP}), 9.06 (d, *J* = 4.7 Hz, 2 H, H_{py}), 9.14 (d, *J* = 4.7 Hz, 2 H, H_{py}), 9.16 (s, 4 H, H_{py}). UV/Vis (CH_2Cl_2): λ (ε) 423 nm (544000 mol·L^{-1}·cm^{-1}), 551 (20700), 590 (6100). FAB (+) MS: *m*/*z* = 1107.7 [MH^+]; $C_{67}H_{78}BrN_4Zn$ requires 1106.6.

[PZn-Ru-PZn](PF$_6$)$_2$: K_2CO_3 (7 mg, 6.4 mmol, 2.5 equiv.) was added to a solution of [**4**](PF_6)$_2$ (26 mg, 0.023 mmol, 1 equiv.) in acetone (5 mL). The resulting suspension was refluxed during 2 h and then the porphyrin **8** (34.6 mg, 0.031 mmol, 1.4 equiv.) in acetone (5 mL) was added with a cannula. The solution was refluxed for 24 h. After cooling to room temperature, the mixture was stirred overnight with a saturated aqueous solution of KPF_6 (5 mL). The phases were separated and the aqueous phase extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), filtered and evaporated in vacuo. After purification by chromatography on silica gel with a CH_2Cl_2/MeOH (75:1) mixture as eluent and by preparative TLC, to give 18.5 mg (34%) of [**PZn-Ru-PZn**](PF_6)$_2$. TLC: one spot, R_f = 0.52 (SiO_2; CH_2Cl_2/ MeOH, 6:1). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.12−3.18 (m, 2 H, CH_2), 3.27−3.30 (m, 2 H, CH_2), 3.38−3.52 (m, 2 H, CH_2), 3.92−4.03 (m, 2 H, CH_2), 5.58 (s, 4 H, OCH_2), 6.35 (d, *J* = 9.6 Hz, 2 H, H_b), 6.70 (d, *J* = 8.5 Hz, 2 H, H_b), 7.20 (d, *J* = 5.55 Hz, 2 H, H_3), 7.43 (d, *J* = 5.55 Hz, 2 H, H_2), 7.48 (d, *J* = 8.9 Hz, 4 H, H_{arL}), 7.60−7.70 (m, 12 H, H_{ar}, H_8), 7.73 (d, *J* = 5.55 Hz, 2 H, $H_{3',8'}$), 7.77 (d, *J* = 8.9 Hz, 4 H, H_{arL}), 7.85 (t, *J* = 1.85 Hz, 6 H, H_p), 7.92 (d, *J* = 8.2 Hz, 4 H, H_{arP}), 8.01 (d, *J* = 5.25 Hz, 2 H, H_9), 8.10−8.11 (m, 12 H, H_o), 8.31 (d, *J* = 8.0 Hz, 4 H, H_{arP}), 8.33 (s, 2 H, $H_{5',6'}$) 8.34 (d, *J* = 8.8 Hz, 2 H, H_5), 8.47 (d, *J* = 9.25 Hz, 2 H, H_6), 8.63 (d, *J* = 5.55 Hz, 2 H, $H_{2',9'}$), 8.98−9.03 (m, 16 H, H_{py}). UV/Vis (CH_2Cl_2): λ (ε) 417 nm (294500 mol·L^{-1}·cm^{-1}), 551 (39800), 590 (13900). ES (+) MS: *m*/*z* = 1580.9 [M − 2PF_6]$^{2+}$/2; requires 1581.1.

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