Letter

A combined covalent and coordination approach to dendritic multiporphyrin arrays based on ruthenium(II) porphyrins

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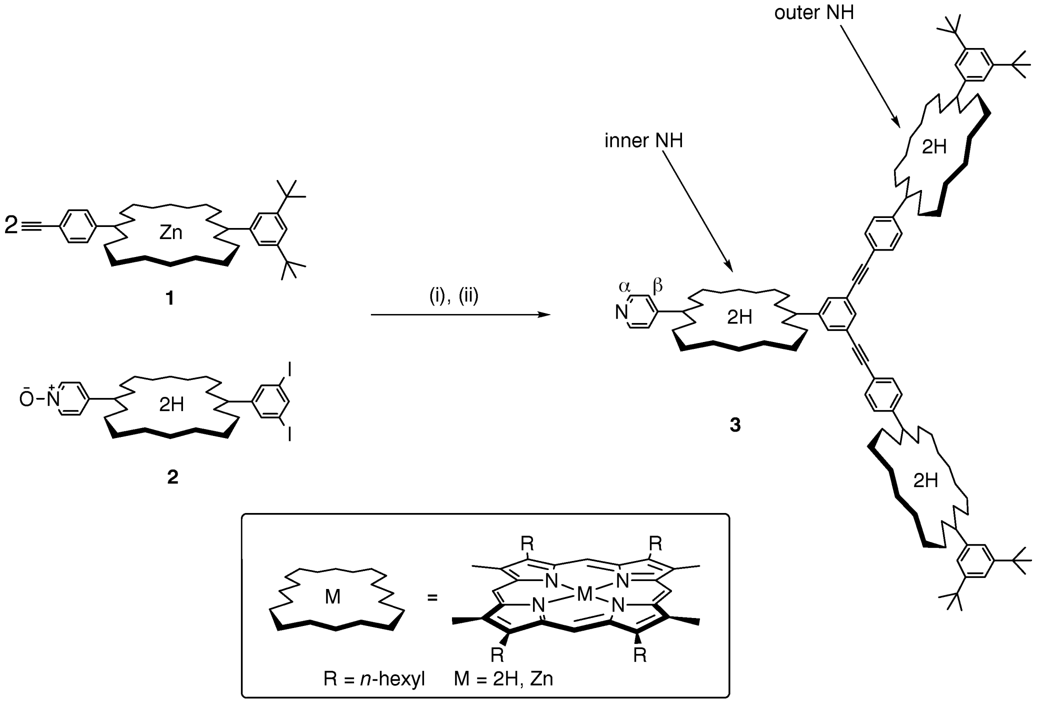
Two strategies have been employed in the construction of multiporphyrin arrays; the principles are illustrated by a seven-porphyrin array consisting of two three-porphyrin dendrons coordinated to a single ruthenium(II) porphyrin, and by a six-porphyrin array containing three ruthenium(II) porphyrin monomers coordinated to a tripyridyl porphyrin trimer. These systems possess both redox and photophysical functionality built-in to the overall structure.

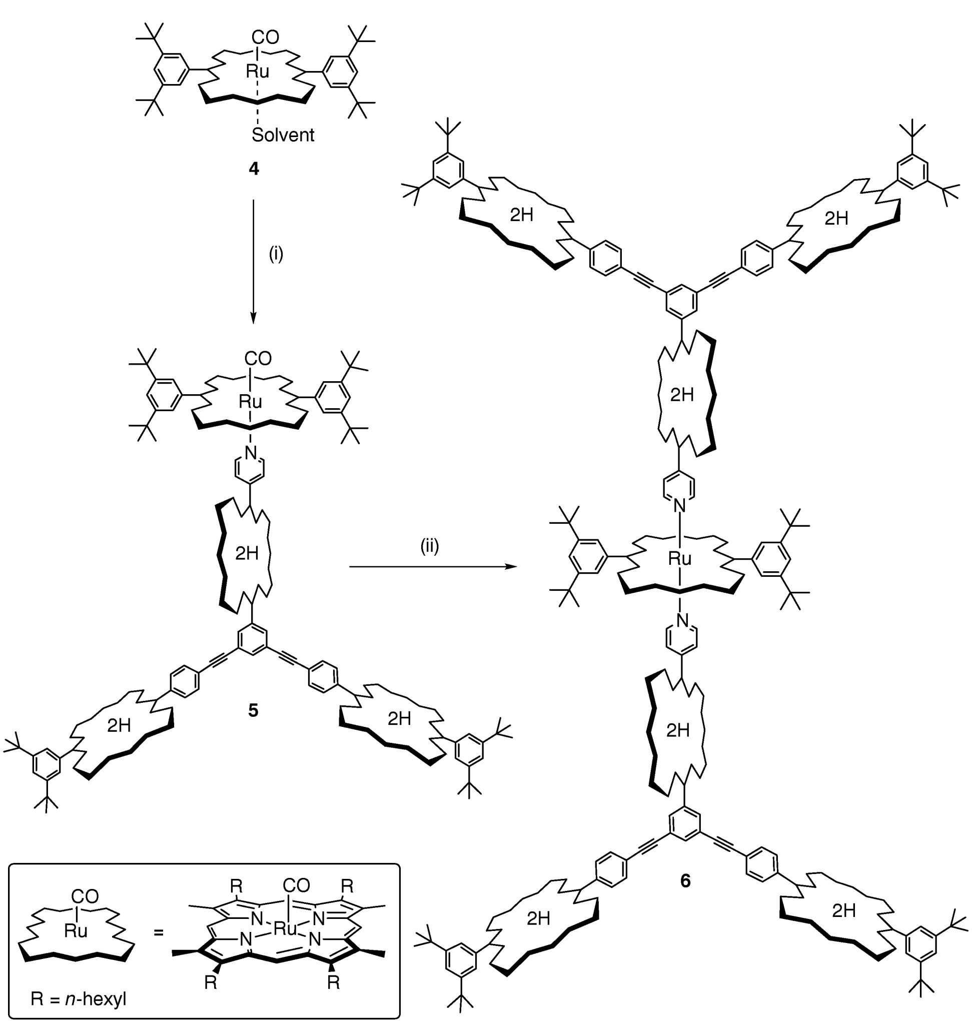
We present here two approaches leading to large arrays of porphyrins. In essence, our approaches employ oligomeric porphyrins as donor ligands that coordinate to ruthenium(II) porphyrin monomers.[1,2] The principles are illustrated here by a seven-porphyrin array containing two three-porphyrin dendrons coordinated to a single ruthenium(II) porphyrin and by a six-porphyrin array containing three ruthenium(II) porphyrin monomers coordinated to a tripyridyl porphyrin trimer. This strategy can be extended to dendritic arrays, and is complementary to a related approach we have described elsewhere.[3]

Our first approach is based on porphyrin oligomers (dendrons) that contain pyridine units for coordination to ruthenium(II) porphyrin monomer building blocks (Scheme 1). Porphyrin monomers **1** and **2** were synthesised according to previously reported procedures.[4] A palladium-mediated coupling reaction of **1** and **2**, followed by removal of the pyridine *N*-oxide protecting group by PCl_3, affords the pyridyl porphyrin dendron **3** in 55% yield. The *N*-oxide-protected pyridyl porphyrin **2** gave higher yields than the unprotected analogue and allowed easier chromatographic separation of the *N*-oxide-protected dendron **3** following the palladium coupling.

The ruthenium(II) porphyrin **4**, used as the core of the large arrays, was synthesised essentially as described previously.[5] Complexation of **4** with a stoichiometric amount of dendron **3** at room temperature (Scheme 2), produced the mono-coordinated complex **5** by displacement of the labile solvent ligand, leaving the axially bound CO ligand intact. Characterisation of these solution-state arrays by ^{1}H NMR spectroscopy allowed assignment of the resonances of the array, in particular the NH resonances associated with the coordinated dendron **3**, which appear as four sharp singlets in a 2 : 2 : 1 : 1 ratio for the outer and inner NHs (Fig. 1), whilst three sharp resonances (1 : 1 : 2) were evident for the *meso* protons. Characteristic upfield shifts for the doublets (δ 5.86 for the β-pyridyl protons) of the ruthenium-bound pyridyl protons were also identified. Addition of a further equivalent of **3** to **5** under photolysis conditions[6] for 24 h leads to displacement of the



Scheme 1 (*i*) $Pd_2(dba)_3$, $AsPh_3$, NEt_3, CH_2Cl_2, 25 °C, 14 h. (*ii*) PCl_3, CH_2Cl_2, 25 °C, 16 h.



Scheme 2 (*i*) 1 equiv. of **3**, C_6D_6, 25 °C. (*ii*) 1 equiv. of **3**, C_6D_6, *hν*, 24 h.

axial CO ligand of **4** (Scheme 2) affording mixtures of both mono- **5** and bis-coordinated **6** species as judged by ^{1}H NMR. The bis-coordinated complex **6** can be characterised by two new singlets corresponding to the inner NH protons, in addition to upfield-shifted resonances for the *meso* signals and the β-pyridyl doublet (δ 5.42) of the metal-bound dendron **3**.

Our second approach was to construct porphyrin oligomers containing tethered pyridine units to act as multidentate ligands for the coordination of ruthenium(II) monomer building blocks (Scheme 3). Porphyrin monomer **7** was synthesised according to standard procedures,[4] while palladium coupling of **7** and **2**, with subsequent deprotection of the *N*-oxide as before, affords the tridentate trimer ligand **8** in 61% yield. Titration of three equivalents of **4** in $CDCl_3$ solution (mM) to a solution of **8** provides the hexamer array **9** (Scheme 4), the integrity of which was confirmed by ^{1}H NMR spectroscopy (Fig. 2). The two *meso* resonances of **8** are observed in a 1 : 2 ratio corresponding to the two types of pyridine-appended porphyrins of the ligand (P1 and P2). In the hexamer array **9** four *meso* resonances are observed, two for the P1 and P2 components of the central trimer and two for the ruthenium porphyrins bound to P1 and P2 of the ligand (Ru-P1 and Ru-P2). In addition, two new doublets in a 1 : 2 ratio are observed at δ 5.84 and 5.81 assigned to P1 and P2 ruthenium-bound β-pyridine protons of **8**. The neighbouring α^1 and α^2 protons are hidden in the congested aliphatic region, but could be identified at δ 1.66 and 1.64 with the aid of a COSY spectrum. In the NOESY spectrum two crosspeaks are detected between the α- and β-pyridine protons of **8** and the Ru-P1 and Ru-P2 *meso* resonances, allowing assignment of the P1, P2, Ru-P1 and Ru-P2 *meso* protons and consequently the aromatic and aliphatic resonances.

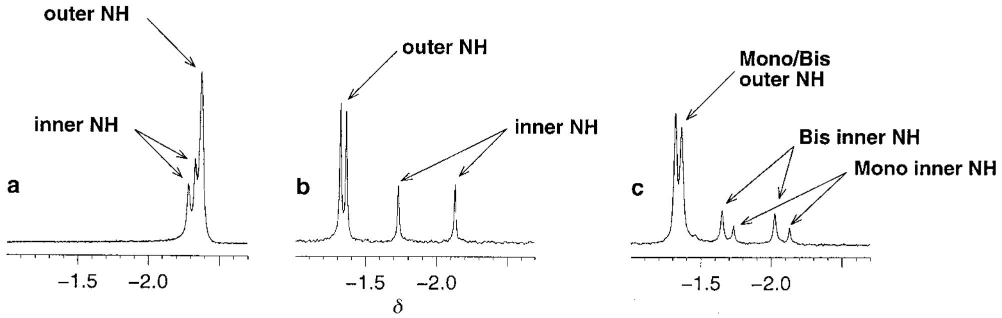
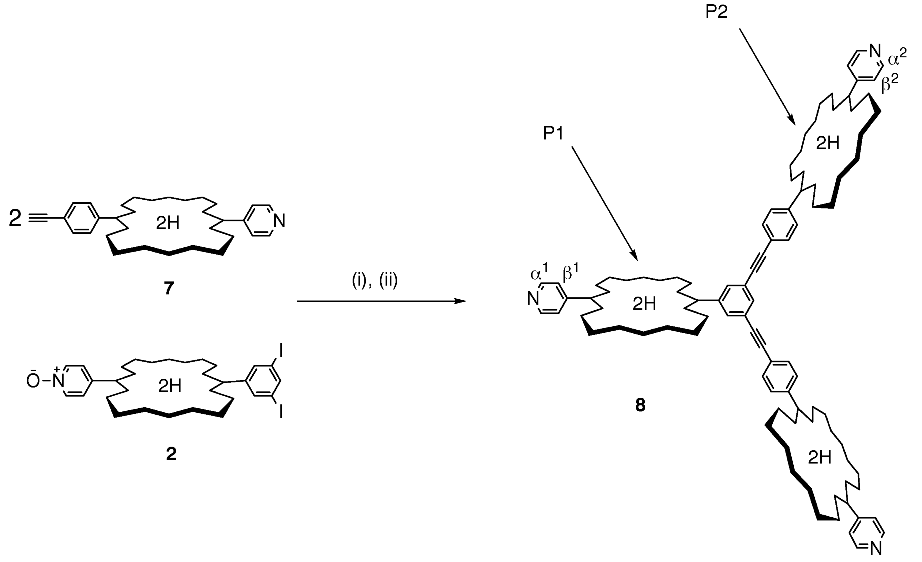


Fig. 1 High-field region of the ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 300 K) after photolysis of ruthenium(II) porphyrin **4** in the presence of the pyridine porphyrin dendron. The NH resonances of the dendron **3** in the ^{1}H NMR showing (*a*) free dendron **3**, (*b*) mono-coordinated complex **5** and (*c*) mixture of both mono- **5** and bis- **6** coordinated species.



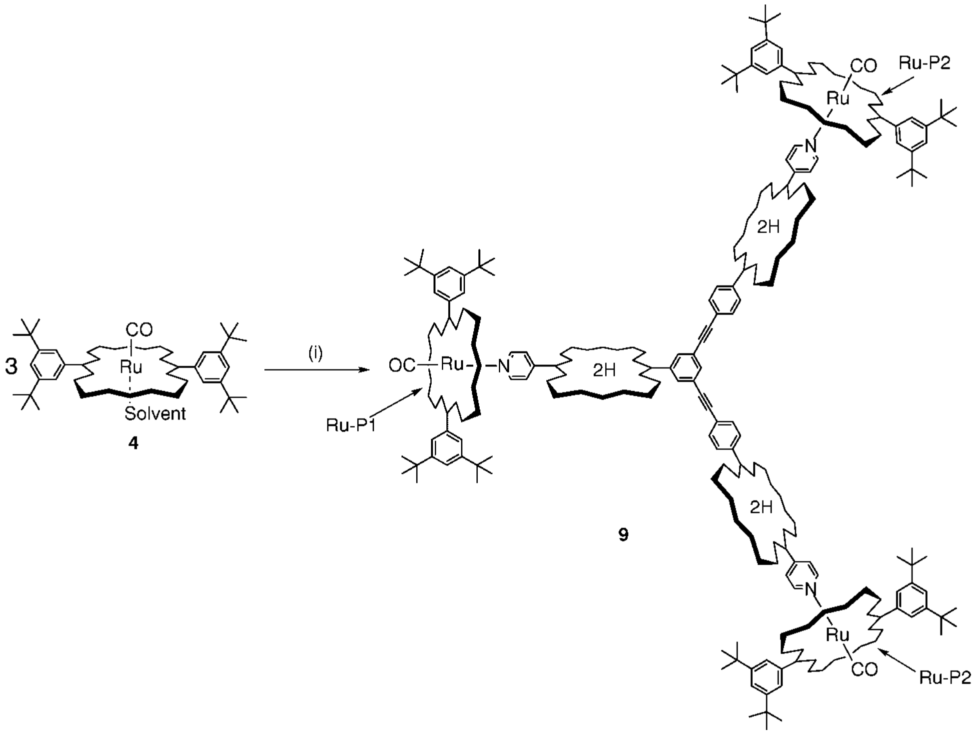
Scheme 3 (*i*) $Pd_2(dba)_3$, $AsPh_3$, NEt_3, CH_2Cl_2, 25 °C, 14 h. (*ii*) PCl_3, CH_2Cl_2, 25 °C, 16 h.

As yet, crystals of **9** suitable for X-ray diffraction analysis have not been obtained. However, we have prepared smaller coordination arrays; suitable crystals of **10**[7] were prepared by treatment of one equivalent of the tridentate ligand tripyridyltriazine (Py_3T) with three equivalents of **4** in CH_2Cl_2 (Scheme 5). After many attempts only very small single crystals of **10** could be grown. The best crystals were obtained by slow solvent diffusion of methanol into a toluene solution. These crystals proved to be too small to determine the structure by normal laboratory X-ray methods, so it was necessary to exploit the high intensity of a synchrotron radiation source to obtain the structure. The structure (Fig. 3) consists of three ruthenium porphyrins each axially bound to the pyridine nitrogens of the Py_3T ligand, with the aromatic rings of Py_3T coplanar. All the porphyrin aryl substituents lie perpendicular to the central Py_3T ligand, presumably due to steric constraints. The angles of the Py_3T nitrogens with respect to the porphyrin plane are in the range of 85–90°, and the $Ru–N_{(Py3T)}$ distances [2.19(3), 2.22(8) and 2.15(6) Å] are similar to those reported previously.[8] No mass spectral characterisation was possible for any of these coordination arrays: even when neutral matrices were used we observed only ions due to the ligand and ruthenium porphyrin core.

The two strategies employed demonstrate the ease with which functionality can be incorporated into large multiporphyrin arrays. Variation in the structural framework of the porphyrin building blocks and investigations into the photophysical properties are currently being undertaken.

Experimental

^1H NMR spectra (400, 500 or 800 MHz) were recorded on Bruker DRX-400, DRX-500 or DRX-800 spectrometers, respectively. ^{13}C NMR spectra were obtained on a DRX-400 operating at 100.6 MHz. All NMR measurements were carried out at room temperature in deuterochloroform unless otherwise specified. Routine UV/visible spectra were obtained on a Uvikon 810 spectrometer in 10 mm oven-dried cuvettes. Distilled solvents were used throughout and when used dry, were freshly obtained from the solvent stills. Triethylamine and



Scheme 4 (*i*) 1 equiv. of **8**, $CDCl_3$, 25 °C.

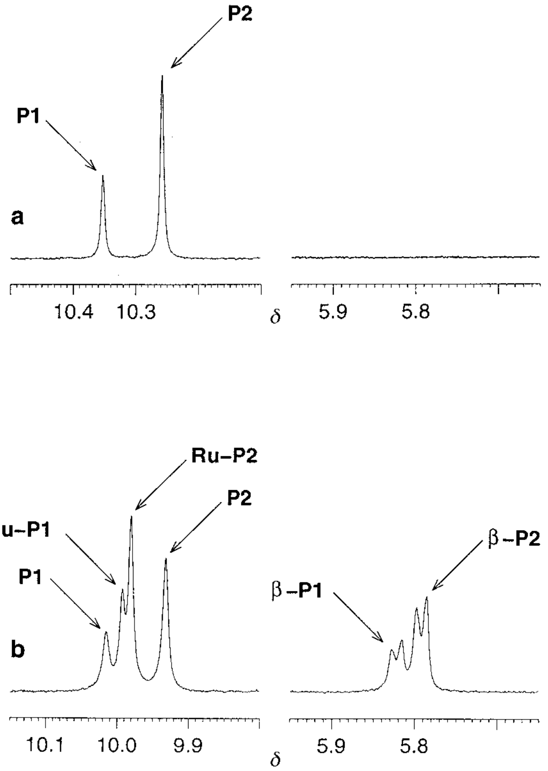


Fig. 2 Selected downfield regions of the ^1H NMR spectrum (400 MHz, $CDCl_3$, 300 K) demonstrating assembly of ruthenium building blocks around tridentate trimer ligand **8**; (*a*) free tridentate trimer ligand **8** and (*b*) hexamer complex **9**.

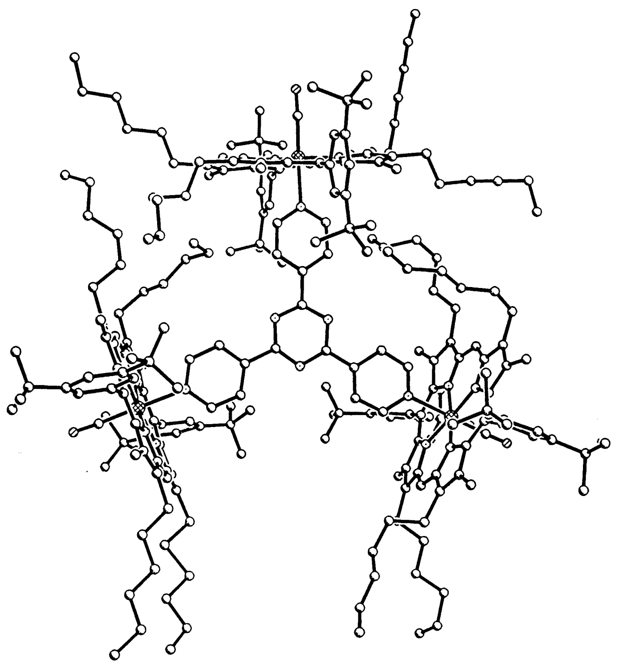
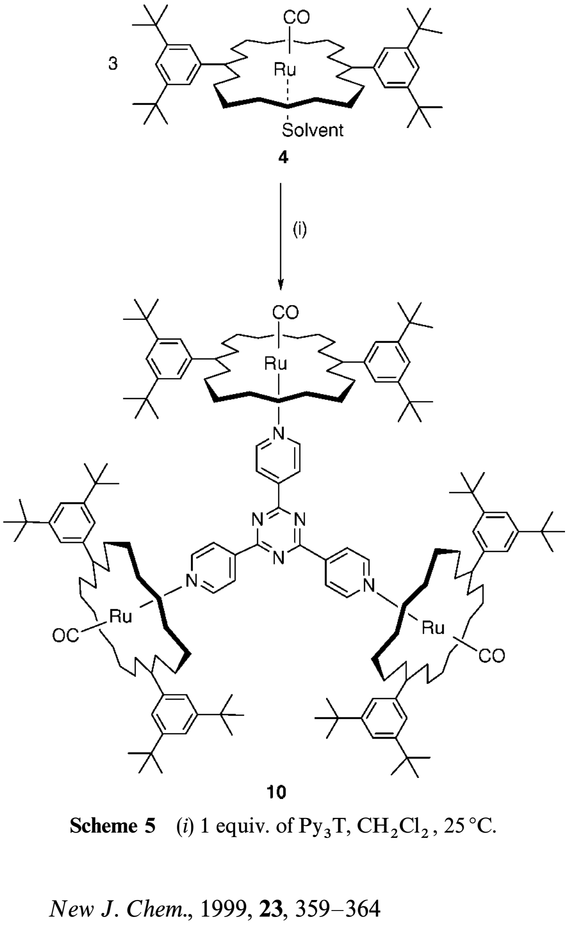


Fig. 3 A ball-and-stick representation of the X-ray structure of **10**.

dichloromethane (CH_2Cl_2) were distilled from CaH_2 under argon while toluene and tetrahydrofuran (THF) were distilled from CaH_2 or sodium, also under argon. MALDI-TOF mass spectra were recorded on a Kratos Analytical Ltd Kompact MALDI IV mass spectrometer. A nitrogen laser (337 nm, 85 kW peak laser power, 3 ns pulse width) was used to desorb the sample ions, and the instrument was operated in linear time-of-flight mode with an accelerating potential of 20 kV. Results from 50 laser shots were signal-averaged to give one spectrum. An aliquot (1 μl) of a saturated solution of the matrix (sinapinic acid) was deposited on the sample plate surface. Before the matrix completely dried, a small volume (1 μl) of analytes (dissolved in dichloromethane–chloroform at 1 mg ml^{-1}) was layered on the top of the matrix and allowed to air-dry.



Scheme 5 (*i*) 1 equiv. of Py_3T, CH_2Cl_2, 25 °C.

Syntheses

Synthesis of dendron 3: Complex **1** (137.7 mg, 130.8 μmol), **2** (70.0 mg, 62.3 μmol), $Pd_2(dba)_3$ (8.5 mg, 9.3 μmol), and $AsPh_3$ (33.2 mg, 74.7 μmol) were dissolved in freshly distilled CH_2Cl_2 (8 ml) and NEt_3 (8 ml). The solution was saturated with argon (three freeze–thaw cycles) and stirred at room temperature for 14 h, after which the solvent was removed *in vacuo* and the residue chromatographed through SiO_2, eluting first with $C_6H_{14} : CHCl_3 : EtOAc$ (5 : 1 : 1) until a first band clearly separated. The elution was continued with $C_6H_{14} : CHCl_3 : EtOAc$ (4 : 1 : 1) giving the *N*-oxide analogue of **3** (135 mg, 73%) as a fine dark red powder. The *N*-oxide analogue of **3** (35.0 mg, 11.8 μmol) was dissolved in freshly distilled CH_2Cl_2 (20 ml) and cooled to 0 °C. PCl_3 (5.1 μl, 58.8 μmol) was added dropwise and the solution was stirred under dry air for 16 h, after which the solution was washed with $NaHCO_3$ (2 × 100 ml) and H_2O (3 × 100 ml), and the solvent was removed *in vacuo*. The compound was recrystallized by layered addition of methanol to a chloroform solution of **3**, filtered, and dried *in vacuo* to afford a red powder of **3** (19.2 mg, 55%). ^1H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 2H, inner *meso)*, 10.24 (s, 4H, outer *meso)*, 9.05 (d, *J* = 4.8 Hz, 2H, α-py), 8.54 (t, *J* = 1.5 Hz, 1H, inner Ar*H*), 8.53 (t, *J* = 1.5 Hz, 2H, inner Ar*H*), 8.14 (d, *J* = 8.1 Hz, 4H, outer Ar*H*), 8.12 (d, *J* = 4.8 Hz, 2H, β-py), 8.05 (d, *J* = 8.1 Hz, 4H, outer Ar*H*), 7.92 (d, *J* = 1.8 Hz, 4H, outer Ar*H*), 7.81 (t, *J* = 1.8 Hz, 2H, outer Ar*H*), 4.12 (m, 8H, inner Por-C*H*$_2$), 4.00 (m, 16H, outer Por-C*H*$_2$), 2.88 (s, 6H, inner pyrrolic C*H*$_3$), 2.58 (s, 12H, outer pyrrolic C*H*$_3$), 2.56 (s, 6H, inner pyrrolic C*H*$_3$), 2.47 (s, 12H, outer pyrrolic CH_3), 2.33 (m, 8H, inner Por-CH$_2$-CH_2), 2.20 (m, 16H, outer Por-CH$_2$-CH_2), 1.86 [m, 8H, inner Por-(CH$_2$)$_2$-CH_2], 1.74 [m, 16H, outer Por-(CH$_2$)$_2$-CH_2], 1.58 [m, 8H, inner Por-(CH$_2$)$_3$-CH_2], 1.51 (s, 36H, Bu^t), 1.48 [m, 16H, outer Por-(CH$_2$)$_3$-CH_2], 1.38 [m, 24H, inner/outer Por-(CH$_2$)$_4$-CH_2], 0.99 [m, 12H, inner Por-(CH$_2$)$_5$-CH_3], 0.90 [m, 24H, Por-(CH$_2$)$_5$-CH_3], −2.28 (s, 1H, inner N*H*), −2.33 (s, 1H, inner N*H*), −2.37 (s, 4H, outer N*H*); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 152.3, 150.8, 149.9, 149.0, 145.3, 144.7, 144.0, 2 × 143.5, 143.1, 141.9, 141.6, 141.5, 141.4, 140.9, 136.7, 136.2, 135.7, 135.4, 133.2, 131.0, 129.7, 127.6, 123.4, 122.8, 121.1, 119.6, 116.6, 116.2, 114.6, 97.5, 97.0, 90.9, 89.6, 35.1, 33.5, 33.3, 32.1, 32.0, 31.7, 30.1, 30.0, 26.8, 22.8, 15.6, 2 × 15.0, 14.3, 14.2, 14.1; UV/vis λ_{max} (CH$_2$Cl$_2$)/nm: 411, 507, 541, 547, (log[ε/M^{-1} cm^{-1}]) 5.8, 4.8, 4.2, 4.3; MALDI-MS: $C_{199}H_{261}N_{13}$ requires 2835.37, found 2834.91 (MH$^+$).

General procedure for photolysis reaction: Complex **3** (13.6 mg, 4.8 μmol) and **4** (2.9 mg, 2.3 μmol) contained in a quartz NMR tube (Aldrich) were dissolved in C_6D_6 (1 ml). The tube was degassed by evacuating the area above the sample solution at room temperature and exposed to a 60 W broad-band mercury lamp for 24 h.

Preparation of 5: Complex **5** was prepared from the stoichiometric addition of **3** to **4**. ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.23 (s, 4H, outer *meso*), 10.07 (s, 2H, Ru *meso*), 10.02 (s, 2H, inner *meso*), 8.47 (t, *J* = 1.7 Hz, 1H, inner Ar*H*), 8.38 (d, *J* = 1.7 Hz, 2H, inner Ar*H*), 8.11 (d, *J* = 8.0 Hz, 4H, outer Ar*H*), 8.05 (t, *J* = 1.7 Hz, 2H, Ru Ar*H*), 7.99 (d, *J* = 8.0 Hz, 4H, outer Ar*H*), 7.91 (d, *J* = 1.7 Hz, 6H, Ru/outer Ar*H*), 7.82 (t, *J* = 1.7 Hz, 2H, outer Ar*H*), 7.81 (t, *J* = 1.7 Hz, 2H, outer Ar*H*), 5.86 (d, *J* = 6.5 Hz, 2H, β-py), 3.98 (t, *J* = 7.2 Hz, 16H, outer Por-CH_2), 3.89 (br t, 8H, Ru Por-CH_2), 3.70 (br t, 8H, inner Por-CH_2), 2.75 (s, 6H, inner pyrrolic CH_3), 2.55 (s, 12 H, Ru pyrrolic CH_3), 2.46 (s, 12H, outer pyrrolic CH_3), 2.45 (s, 12H, outer pyrrolic CH_3), 2.27–2.14 (m, 32H, Ru/inner/outer Por-CH$_2$-CH_2), 2.17 (s, 6H, inner pyrrolic CH_3), 1.94 [m, 8H, Ru Por-(CH$_2$)$_2$-CH_2], 1.84–1.63 [m, 24H, inner/outer Por-(CH$_2$)$_2$-CH_2], 1.57 (s, 18H, Ru Bu^t), 1.53 (s, 18H, Ru Bu^t), 1.51 (s, 36H, outer Bu^t), 1.48–1.27 [m, 66H, Ru/inner/outer Por-(CH$_2$)$_3$-CH_2, Por-(CH$_2$)$_4$-CH_2, α-py], 0.95–0.87 [m, 48H, Ru/inner/outer Por-(CH$_2$)$_5$-CH_3], −2.39 (s, 2H, outer N*H*), −2.40 (s, 2H, outer N*H*), −2.66 (s, 1H, inner N*H*), −2.97 (s, 1H, inner N*H*); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 149.9, 149.7, 149.1, 148.3, 145.3, 145.0, 144.7, 143.8, 143.5, 2 × 143.4, 143.2, 143.1, 142.9, 142.7, 142.5, 141.6, 141.5, 141.4, 141.3, 141.1, 141.0, 140.9, 137.6, 136.6, 136.0, 2 × 135.7, 134.3, 133.2, 130.9, 128.3, 127.8, 127.5, 125.1, 123.3, 122.7, 121.1, 2 × 120.7, 119.6, 116.5, 116.1, 112.7, 98.7, 97.2, 97.0, 90.8, 89.5, 58.4, 35.2, 35.1, 35.0, 33.3, 33.1, 32.0, 2 × 31.9, 2 × 31.7, 31.6, 2 × 30.0, 2 × 29.9, 26.9, 26.8, 22.8, 3 × 22.7, 18.4, 15.5, 15.0, 14.9, 14.2, 14.1, 13.4; UV/vis λ_{max} (CH$_2$Cl$_2$)/nm: 407, 509, 574, (log[ε/M^{-1}cm^{-1}]) 5.8, 4.8, 4.3.

Synthesis of tridentate trimer 8: Complex **8** was synthesised by a similar procedure to that reported above for **3**, except that **7** was used instead of **1** (yield: 61%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.33 (s, 2H, P1 *meso*), 10.26 (s, 4H, P2 *meso*), 9.03 (d, *J* = 4.7 Hz, 2H, P1 α-py), 8.98 (d, *J* = 4.7 Hz, 4H, P2 α-py), 8.55 (s, 1H, P1 Ar*H*), 8.54 (s, 2H, P1 Ar*H*), 8.10 (d, *J* = 8.0 Hz, 4H, P2 Ar*H*), 8.06 (d, *J* = 5.1 Hz, 2H, P1 β-py), 8.03 (d, *J* = 8.0 Hz, 4H, P2 Ar*H*), 8.01 (d, *J* = 5.1 Hz, 4H, P2 β-py), 4.10 (m, 8H, P1 Por-CH_2), 3.99 (m, 16H, P2 Por-CH_2), 2.89 (s, 6H, P1 pyrrolic CH_3), 2.57 (s, 12H, P2 pyrrolic CH_3), 2.53 (s, 6H, P1 pyrrolic CH_3), 2.48 (s, 12H, P2 pyrrolic CH_3), 2.31 (m, 8H, P1 Por-CH$_2$-CH_2), 2.20 (m, 16H, P2 Por-CH$_2$-CH_2), 1.85 [m, 8H, P1 Por-(CH$_2$)$_2$-CH_2], 1.74 [m, 16H, P2 Por-(CH$_2$)$_2$-CH_2], 1.58–1.38 [m, 48H, P1/P2 Por-(CH$_2$)$_3$-CH_2, Por-(CH$_2$)$_4$-CH_2], 0.99 [m, 12H, P1 Por-(CH$_2$)$_5$-CH_3], 0.91 [m, 24H, P2 Por-(CH$_2$)$_5$-CH_3], −2.38 (br s, 6H, P1/P2 N*H*); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 150.7, 149.0, 145.0, 144.0, 143.9, 143.7, 142.8, 141.8, 2 × 141.7, 141.4, 2 × 136.1, 135.8, 135.4, 135.2, 133.1, 131.0, 128.4, 123.3, 122.9, 117.4, 114.3, 2 × 97.3, 90.8, 89.7, 33.4, 33.3, 32.0, 31.9, 30.1, 29.9, 29.7, 26.7, 2 × 22.7, 15.6, 14.9, 2 × 14.1; UV/vis λ_{max} (CH$_2$Cl$_2$)/nm: 412, 508, 540, 574, (log[ε/M^{-1} cm^{-1}]), 5.6, 4.5, 3.9, 4.0; MALDI-MS: $C_{181}H_{227}N_{15}$ requires 2612.92, found 2612.54 (MH$^+$).

Preparation of 9: Complex **9** was prepared in solution by stiochiometric addition of **4** to **8**. ^{1}H NMR (800 MHz, CDCl$_3$): δ 10.03 (s, 2H, P1 *meso*), 10.01 (s, 2H, Ru-P1 *meso*), 10.00 (s, 4H, Ru-P2 *meso*), 9.95 (s, 4H, P2 *meso*), 8.39 (s, 1H, P1 Ar*H*), 8.32 (s, 2H, P1 Ar*H*), 8.04 (br t, 6H, Ru-P1 Ar*H*), 7.94 (d, *J* = 8.6 Hz, 4H, P2 Ar*H*), 7.90 (br d, 4H, P2 Ar*H*), 7.89 (s, 6H, Ru-P2 Ar*H*), 7.81 (s, 6H, Ru-P2 Ar*H*), 5.84 (d, *J* = 6.3 Hz, 2H, P1 β-py), 5.81 (d, *J* = 6.3 Hz, 4H, P2 β-py), 3.96 (m, 28H, Por-CH_2), 3.82 (m, 8H, Por-CH_2), 3.68 (m, 4H, Por-CH_2), 3.63 (m, 8H, Por-CH_2), 2.69 (s, 12H, pyrrolic CH_3), 2.44 (s, 24H, pyrrolic CH_3), 2.53 (s, 24H, pyrrolic CH_3), 2.41 (s, 12H, pyrrolic CH_3), 2.26 (m, 24H, Por-CH$_2$-CH_2), 2.13 (m, 4H, Por-CH$_2$-CH_2), 2.02 (m, 8H, Por-CH$_2$-CH_2), 1.91 (m, 4H, Por-CH$_2$-CH_2), 1.87 (m, 8H, Por-CH$_2$-CH_2), 1.79 [m, 36H, Por-(CH$_2$)$_2$-CH_2], 1.70 [m, 4H, Por-(CH$_2$)$_2$-CH_2], 1.66–1.25 [m, 218H, P1/P2 α-py, Por-(CH$_2$)$_2$-CH_2, Por-(CH$_2$)$_3$-CH_2, Por-(CH$_2$)$_4$-CH_2, Bu^t], 0.92–87 [m, 60H, Por-(CH$_2$)$_5$-CH_3], 0.82 [t, *J* = 7.5 Hz, 12H, Por-(CH$_2$)$_5$-CH_3], −2.72 (s, 1H, P1 N*H*), −2.80 (s, 2H, P2 N*H*), −3.02 (s, 1H, P1, N*H*), −3.06 (s, 2H, P2 N*H*); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 199.0, 151.0, 149.7, 144.9, 144.7, 2 × 143.9, 143.8, 143.5, 143.3, 142.9, 142.6, 142.4, 141.4, 140.9, 137.5, 136.0, 134.3, 134.1, 2 × 132.9, 130.9, 128.3, 127.8, 125.0, 120.7, 98.7, 97.0, 35.2, 35.0, 33.2, 33.1, 32.0, 31.9, 31.8, 31.7, 30.0, 29.8, 29.7, 29.3, 26.9, 26.7, 26.5, 22.8, 22.7, 15.0, 14.0; UV/vis λ_{max} (CH$_2$Cl$_2$)/nm: 406, 514, (log[ε/M^{-1} cm^{-1}]) 5.7, 4.6.

Acknowledgements

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Notes and references

1 For multiporphyrin arrays with donor ligands tethered to the porphyrin periphery see: (*a*) W. T. S. Huck, A. Rohrer, A. T. Anilkumar, R. H. Fokkens, N. M. M. Nibbering, F. C. J. M. van Veggel and D. N. Reinhoudt, *New J. Chem.*, 1998, **22**, 165; (*b*) C. M. Drain, F. Nifiatis, A. Vasenko and J. D. Batteas, *Angew. Chem., Int. Ed.*, 1998, **37**, 2344.

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