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A face-to-face porphyrin-sapphyrin pseudo dimer

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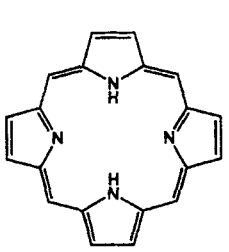
The synthesis and characterization of a new, β-to-*meso*-linked cofacial porphyrin-sapphyrin pseudo dimer ([por]-[sap], 3) is described. This system is the first example in which an expanded porphyrin has been conjugated covalently to a porphyrin and one of the few examples wherein an expanded porphyrin has been incorporated into any type of larger supramolecular array. The first excited singlet state of the free-base porphyrin in 3 was found to lie *ca.* 0.19 eV higher in energy than that of the metal-free sapphyrin subunit. Excitation of 3 at 408 nm, where only porphyrin subunit absorbs, gives rise to virtually no porphyrin-like fluorescence, but instead, gives fluorescence characteristic of the sapphyrin. This is attributed to very efficient intramolecular singlet energy transfer from the porphyrin subunit to the sapphyrin subunit. From time-resolved fluorescence studies the rate of energy transfer must exceed 2×10^{10} sec^{-1}. Studies with the isolated compounds indicated that the rate of Förster energy transfer in 3 should be *ca.* 3×10^{13} sec^{-1}. As such, 3 can be considered to be a good model for the final steps in natural light harvesting complexes.

INTRODUCTION

The porphyrins (e.g., porphine, **1**), as versatile synthetic units, have been among the more widely studied of all macrocyclic systems in recent years. They have, for instance, been used as "building blocks" in the construction of a wide range of multicomponent receptor systems[2] and as the critical precursors for a number of stacked ("face-to-face")[3] and non-stacked[4] dimers. As such, the porphyrins have played an important role in helping to define, among other things, some of the basic fundamentals of multisite supramolecular recognition chemistry and several of the guiding principles associated with model photosynthetic energy and/or electron transfer processes. Surprisingly, however, few examples are known wherein expanded porphyrins such as sapphyrin **2**,[5] large polypyrrolic macrocyclic analogs of porphyrin,[6] have been used to construct multicomponent supramolecular conjugates[7] and none are known where expanded porphyrins are combined with simple porphyrins. In this paper, therefore, we report the synthesis and characterization of a new, β-to-*meso*-linked cofacial porphyrin-sapphyrin pseudo dimer [(Por)-(Sap)], **3**. System **3** contains within one molecular framework two pyrrole-based macrocyclic chromophores that differ both in their chemical properties and excited singlet energetics (by *ca.* 0.19 eV). It acts thus as an efficient photosynthetic model system for the final steps in natural light harvesting complexes and holds promise as being a potentially new anion-*and* cation-binding ditopic receptor.



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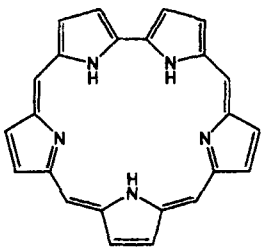

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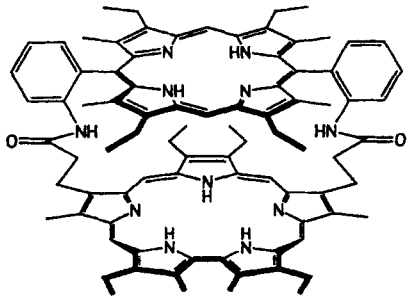

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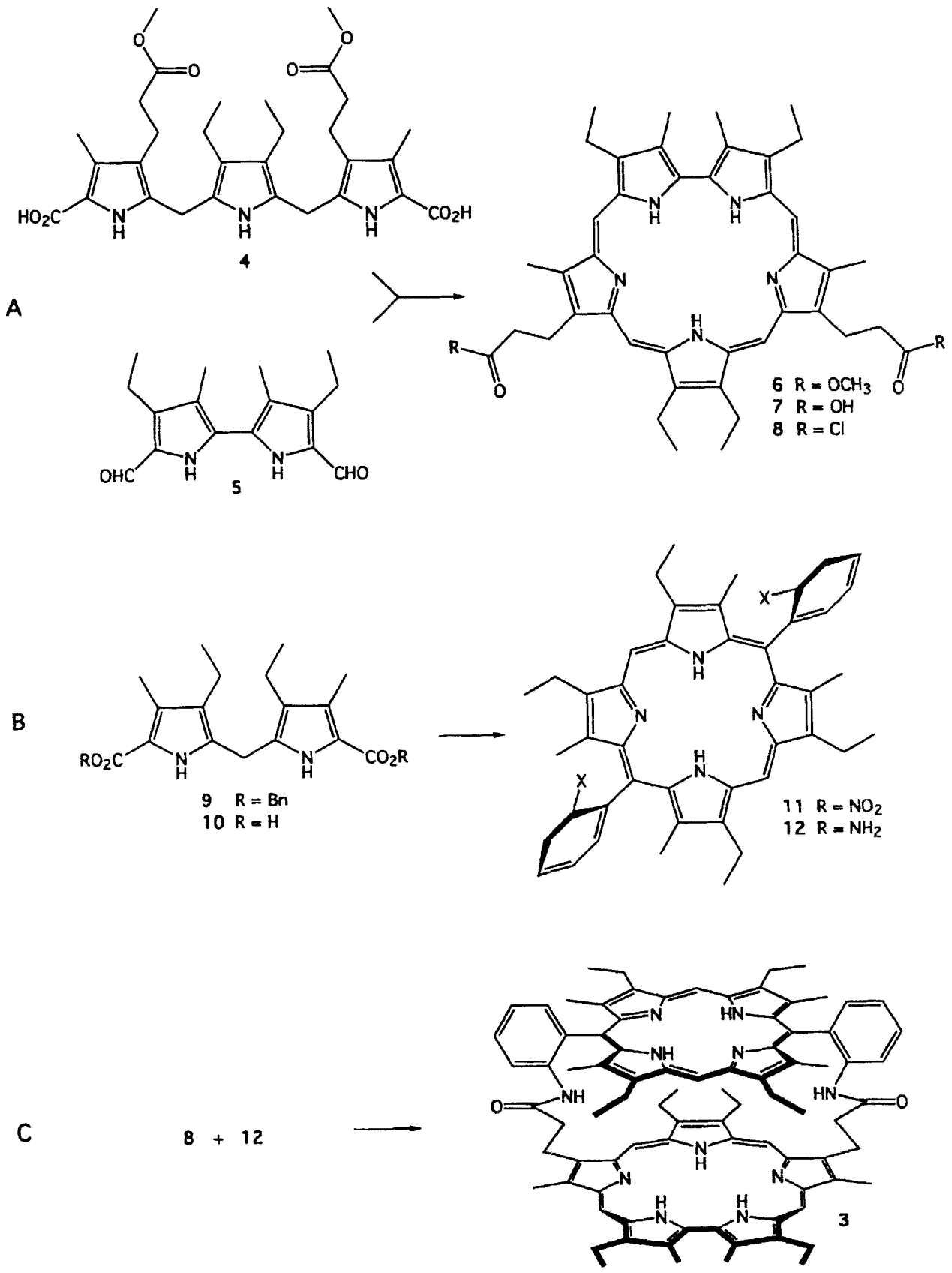
[1]Author to whom correspondence should be sent.



Scheme 1 The synthetic scheme to the porphyrin-sapphyrin pseudo dimer, **3**.

RESULTS AND DISCUSSION

The construction of **3** (Scheme 1) requires the synthesis of two different difunctionalized macrocycles. The first of these, the bis acid chloride of 8,17-bis(carboxyethyl)-3,12,13,22-tetraethyl-2,7,18,23-tetramethylsapphyrin **8** is reported here for the first time with complete experimental,[8] whereas the second, the α,α isomer of 5,15-bis(aminophenyl)porphyrin **12** has already appeared in the literature elsewhere.[2c] An improved synthesis of this latter material has, however, been developed in the context of the present work and is included here.

Part A of Scheme 1 illustrates the synthesis of the sapphyrin-derived bis acid chloride **8**. Briefly, it involves the acid- *or* base-mediated hydrolysis of the bis hydrochloric acid salt of diester **6**, prepared from the oxidative condensation of tripyrrane **4** and bipyrrole **5** in accord with a previously reported procedure,[5c] followed by activation with oxalyl chloride. Good yields are obtained for all these steps, with that for the critical initial sapphyrin-forming reaction being considerably higher than that previously reported, presumably due to isolation and purification of the diacid tripyrrane **4**. Thus, the key precursor **8** could be obtained in large quantity.

As illustrated in Part B of Scheme 1, the necessary α,α bis(aminophenyl) porphyrin, **12**, was prepared by the condensation of the bis acid dipyrromethane **10** (obtained from the diester **9**)[4r,9] with *o*-nitrobenzaldehyde in accord with the recently reported procedure of Anderson and Sanders.[3p] Following reduction and chromatographic purification, the desired α,α isomer **12** was obtained in overall 10% yield.

With precursors **8** and **12** in hand, the title pseudo dimer **3** was obtained in 11% yield following a high dilution condensation procedure effected in dichloromethane. The UV-visible spectrum (Figure 1) of this new compound revealed the presence of both porphyrin and sapphyrin-like Soret bands at 409 and 457 nm, respectively, as would be expected for a system containing both chromophores in the same molecule. Interestingly, however, the molar extinction coefficients are much lower than those seen for the control monomers **6** and **12** alone. Presumably, this is the result of intramolecular self-quenching, a consideration that is discussed in greater detail below.

The presence of two chromophores in **3**, as well as further confirmation of the proposed structure, was obtained from high resolution mass spectrometry (HRMS) and proton NMR spectroscopy. The latter measurements revealed, for instance, the presence of two different sets of internal pyrrolic NH signals (at -4.5–5.2 and -2.4 ppm) that are ascribed to the sapphyrin and porphyrin subunits, respectively. The ^{1}H NMR spectrum also provided evidence for two-different types of meso signals, at ca. 11.7 and 10.2 ppm, respectively, that again could be assigned to the sapphyrin and porphyrin portions of the molecule. Unfortunately, efforts to obtain a satisfactory ^{13}C NMR spectrum proved unsuccessful; even at 125 MHz, there proved to be too many quartenary carbons to permit an appropriate level of resolution.

As can be gleaned from an inspection of Figure 1, the absorption spectra of the free-base porphyrin (Por) and the corresponding sapphyrin (Sap) are sufficiently distinct to permit selective excitation of either chromophore, even in the presence of the other, with monochromatic light. Excited singlet state energy levels were determined for the isolated monomers, **6** and **12**, from the intersection of absorption and fluorescence spectra recorded for the isolated compounds in dilute dichloromethane solutions. The derived values indicate that the first excited singlet state of **6** lies above that of **12** by about 0.19 eV. Furthermore, there is very good overlap between fluorescence emitted by **6** and the ground state absorption spectrum of **12** as shown by Figure 2; analysis of Figure 2 in terms of the Förster theory[10] for dipole-dipole energy transfer gave a value for

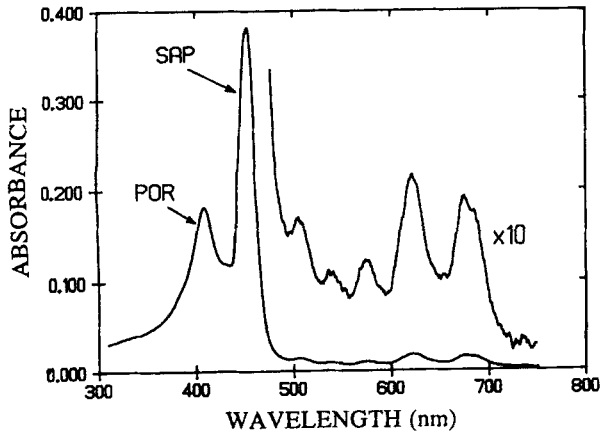


Figure 1 Absorption spectrum of **3** in dichloromethane.

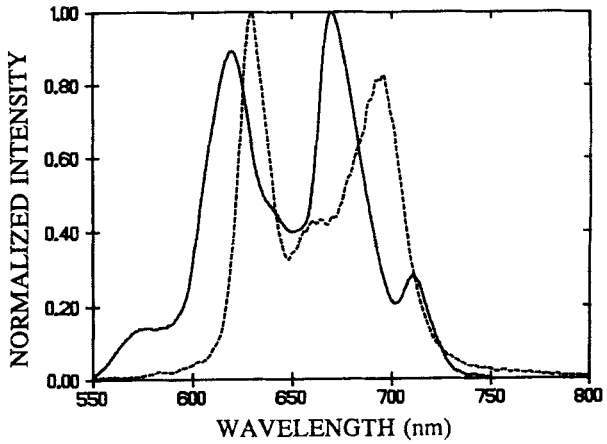


Figure 2 Overlap of the fluorescence emission spectrum of **12** (dotted) with the aborption spectrum of **6** (bold), both in dichloromethane.

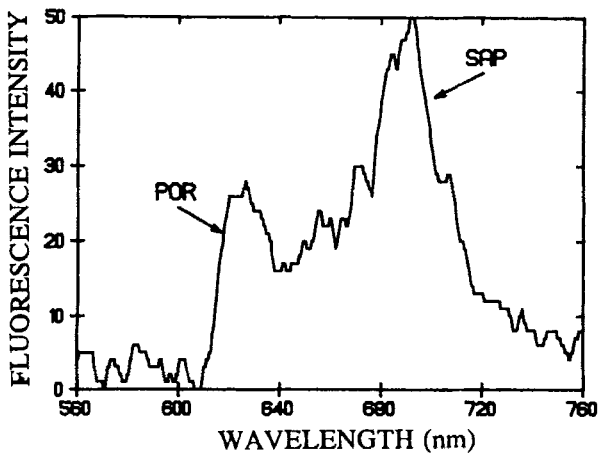


Figure 3 Fluorescence emission spectrum, excited at 408 nm, of pseudo dimer **3** in dichloromethane.

the overlap integral of 1.43×10^{-13} cm^6 mmol. Using this latter value together with photophysical data measured for **6** ($\phi_f = 0.10$; $\tau_f = 10.3$ ns) and estimating the orientation factor as 2 and the center-to-center separation distance as 6 Å, as determined from space-filling molecular models, the rate of singlet (Förster) energy transfer from porphyrin to sapphyrin subunits in **3** was calculated to 3×10^{13} s^{-1}. This value is extremely high and arises because of the very close proximity of the reactants, the excellent overlap of emission and absorption spectra, and the ideal geometry for energy transfer. Because the inherent singlet state lifetime of the porphyrin subunit is relatively long (i.e., $\tau_f = 10.3$ ns), energy transfer from porphyrin to sapphyrin subunits in **3** is expected to be quantitative. Furthermore, an energy gap of 0.19 eV should be sufficient to ensure unidirectional energy transfer.

The absorption spectrum recorded for **3** in dilute dichloromethane solution shows the presence of both porphyrin and sapphyrin chromophores without obvious perturbation (Figure 1). Excitation at 408 nm, where the porphyrin subunit is the sole chromophore, gives rise to fluorescence characteristic of the sapphyrin subunit together with a small amount of porphyrin-like fluorescence (Figure 3). The integrated intensity of this porphyrin-like fluorescence is less than 1% of that observed from an optically-matched, equimolar mixture of **6** and **12** but its fluorescence lifetime was found to be 6.2 ns. The porphyrin-like emission is attributed, therefore, to the presence of a trace impurity in the sample of **3**. The appearance of sapphyrin fluorescence following excitation into the porphyrin Soret band is consistent with rapid intramolecular energy transfer and, by comparison of the various quantum yields, it is concluded that this process is essentially quantitative. Time-resolved fluorescence studies could not resolve emission from the porphyrin subunit in **3** such that the rate of energy transfer must exceed *ca.* 2×10^{10} s^{-1}.

Excitation of **3** at 455 nm, where only the sapphyrin subunit absorbs, gives rise to characteristic sapphyrin fluorescence. The fluorescence quantum yield and lifetime remained similar to those observed following excitation of an optically-matched, equimolar mixture of **6** and **12**. In particular, the fluorescence lifetime of the sapphyrin subunit in 3 is *ca.* 1.2 ns.

The pseudo dimer **3** appears to act as a good model for the natural photosynthetic light harvesting complex where rapid energy transfer among structurally-related pigments takes place. The final energy transfer steps that populate the reaction center complex are known to be extremely fast, probably occurring over some tens of fs. This is similar to the calculated energy transfer rate for **3** and greatly exceeds the rate of any other known model system. Further studies, to be carried out with suitably modified derivatives of **3**, will be aimed at resolving the energy transfer step. This is essential if the mechanism of the natural process is to be elucidated.

FUTURE DIRECTIONS

The pseudo dimer system **3** is also of potential interest as a ditopic receptor. It contains both a metal-complexing porphyrin receptor site as well as a pentapyrrolic sapphyrin, a subunit that is known to bind halide and phosphate type anions at or below neutral pH. Thus the possibility exists that compound **3** could be used to coordinate metal cations and biologically relevant anions at the same time by using to advantage both the porphyrin and sapphyrin binding subunits, respectively. Current work is focused on exploring this possibility.

MATERIALS AND METHODS (EXPERIMENTAL)

Absorption Spectra were recorded with a Hitachi U3210 spectrophotometer and fluorescence spectra were recorded with a fully-corrected Perkin-Elmer spectrofluorimeter. Solutions for fluorescence studies were adjusted to possess an absorbence of *ca.* 0.05 at the excitation wavelength and fluorescence quantum yields were determined using *meso*-tetraphenylporphyrin as a standard. Fluorescence lifetimes were measured by time-correlated, single-photon counting using a frequency-doubled, mode-locked Nd:YAG pumped cavity-dumped dye laser as excitation source. A rhodamine 6G dye laser (excitation wavelength 590 nm) was used to selectively excite the porphyrin chromophore whilst a pyridine-1 dye laser (excitation wavelength 680 nm) was used to excite the sapphyrin chromophore. Fluorescence was isolated from scattered laser light using glass cutoff filters in conjunction with a high radiance monochromater. A Hamamatsu

R2809U microchannel plate phototube was used as detector and, after deconvolution of the instrument response function, the temporal resolution of this setup was *ca.* 50 ps.

8,17-Bis(methoxycarbonylethyl)-3,12,13,22-tetraethyl-2,7,18,23-tetramethylsapphyrin: 2,5-Bis((5-carboxy-3-methoxycarbonylethyl-4-methylpyrrol-2-yl)methyl)-3,4-diethylpyrrole[11] **4** (0.575 g, 1.01 mmol) and 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-bipyrrole[5c] **5** (0.274 g, 1.01 mmol) were dissolved into absolute ethanol (1000 mL) with the aid of a heat gun. When cool, the flask was kept from light, and *p*-toluene sulfonic acid (0.689 g, 4.00 mmol) was added. The reaction was stirred with dioxygen (presaturated with ethanol) bubbling through it for 20 hours. The solvent was then removed *in vacuo* and the residue chromatagraphed on a short silica gel column using 5% methanol in chloroform as the eluent. All dark green fractions were combined, and chromatagraphed again as before. The dark green fraction off the second column was taken up in chloroform and washed with dilute hydrochloric acid. The organic layer was dried over sodium sulfate, filtered, and the solvent removed *in vacuo* to give the crude product. Recrystallization from chloroform/hexanes yielded the dihydrochloride salt of **6** in essentially pure form as an intense blue solid (0.679 – 0.754 g, 85 – 95%). ^{1}H NMR (250 MHz $CDCl_3$) δ -4.91 (s, 2H, NH), -4.61 (s, 1H, NH), -4.30 (s, 2H, NH), 1.32 (t, 6H, -OCH$_2$C$\underline{H}_3$), 2.21 (t, 6H, -CH$_2$C$\underline{H}_3$), 2.32 (t, 6H, -CH$_2$C$\underline{H}_3$), 3.68 (t, 4H, -CH$_2$C$\underline{H}_2$-), 4.13 (s, 6H, -CH$_3$), 4.28 (s, 6H, -CH$_3$), 4.34 (q, 4H, -OC$\underline{H}_2$CH$_3$), 4.56 (q, 4H, -C$\underline{H}_2$CH$_3$), 4.76 (q, 4H, -C$\underline{H}_2$CH$_3$), 5.05 (t, 4H, -C$\underline{H}_2$CH$_2$-), 11.69 (s, 2H, meso), 11.72 (s, 2H, meso); ^{13}C NMR (63 MHz, $CDCl_3$) δ 12.9, 14.2, 15.8, 17.8, 18.5, 20.9, 22.9, 30.9, 37.4, 61.0 (aliphatic), 91.7, 98.5 (meso), 127.1, 129.7, 130.1, 132.4, 135.3, 137.5, 137.6, 137.8, 141.9, 143.1 (aromatic), 172.9 (carbonyl); IR (neat) 3405.6, 2932.1, 1725.0, 1644.0, 1372.3, 1098.0, 621.6 cm^{-1}; UV-vis ($CHCl_3$) λ_{max} 432.5 (39330), 457.5 (427410), 623.5 (11420), 673.5 (13010), 688.5 (11950) nm; HRMS (FAB) *m/e* calc'd for $C_{46}H_{58}N_5O_4$: 744.4488, found 744.4503 (free base).

8,17-Bis(carboxyethyl)-3,12,13,22-tetraethyl-2,7,18,23-tetramethylsapphyrin: Method A: 8,17-Bis(methoxycarbonylethyl)-3,12,13,22-tetraethyl-2,7,18,23-tetramethylsapphyrin **6** (0.100 g, 0.127 mmol) was dissolved in 5 mL of trifluoroacetic acid. Five mL of concentrated hydrochloric acid was added, and the green solution was stirred at 70° C under an N_2 atmosphere for three days. The reaction was then poured into 100 mL distilled water and extracted with dichloromethane. The organic layer was washed with dilute hydrochloric acid, dried over magnesium sulfate, and the solvent removed *in vacuo*. The resulting blue residue can be either used as is or purified further as needed by subjecting to chromatography on silica gel using a gradient eluent consisting of between 1:20 and 3:10 methanol:chloroform. When subject to chromatography, last green fraction to elute is collected, washed again with dilute hydrochloric acid, dried over magnesium sulfate, and solvent removed *in vacuo*. The blue solid, corresponding to the bishydrochloride salt of **7** is then recrystallized from chloroform/hexanes to give 0.092 g of product (yield: Nearly quantitative).

Method B: 8,17-Bis(methoxycarbonylethyl)-3,12,13,22-tetraethyl-2,7,18,23-tetramethylsapphyrin **6** (0.500 g, 0.127 mmol) was dissolved in 50 mL of ethanol. The green solution was brought to reflux under a nitrogen atmosphere, and then 3 mL of aqueous saturated sodium hydroxide solution was added. After 12 hours, the ethanol was removed *in vacuo*, and 100 mL distilled water was added to the residue. The water layer was acidified with hydrochloric acid, and this was extracted with dichloromethane. The organic layer was washed with dilute hydrochloric acid, dried over magnesium sulfate, and the solvent removed *in vacuo*. The blue residue was placed down a silica column using a gradient eluent from 1:20 to 3:10 methanol:chloroform. The last green fraction to elute was collected, washed again with dilute hydrochloric acid, dried over magnesium sulfate, and solvent removed *in vacuo*. The blue solid **7** was recrystallized from chloroform/hexanes (0.260 g, 54%). ^{1}H NMR (250 MHz, $CDCl_3$/CD_3OD) δ 1.92 (s (broad), 16H, -CH$_2$C$\underline{H}_3$ and -CH$_2$C$\underline{H}_2$-), 3.97 (s (broad), 12H, -C$\underline{H}_2$CH$_3$ and -C$\underline{H}_2$CH$_2$-), 11.19 (s, 2H, -OH); ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD) δ 10.94, 14.7, 16.5, 17.0, 19.3, 20.0, 21.8, 28.8, 89.6 (meso), 96.4 (meso), 127.5, 128.1, 130.4, 132.5, 132.7, 137.0, 137.3, 137.4, 141.9, 142.6, 173.8 (-$\underline{C}$OOH); IR (neat) 3426, 2096, 1640, 565 cm^{-1}; UV-Vis (MeOH) λ_{max} 422.0 (42240), 443.0 (266810), 616.5 (9430), 667.0 (10140) nm; HRMS (FAB) *m/e* calc'd for $C_{42}H_{50}N_5O_4$: 688.3863, found 688.3855 (free base).

5,15-Bis(*o*-nitrophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-porphyrin.[12] Palladium (10% on carbon, 0.044g) was added to a solution of 5,5′-bis(benzyloxycarbonyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane[4r,9] **9** (0.523 g, 1.05 mmol) in THF (25 mL) containing two pipet drops of triethylamine. The mixture was stirred at room temperature under an hydrogen atmosphere. After one hour, the mixture was filtered through Celite, and the filtrate evaporated to dryness under reduced pressure. The residue **10** was kept free from light while being dissolved into trifluoroacetic acid (6 mL) under nitrogen at 0° C over a period of twenty minutes. Then, a solution of 2-nitrobenzaldehyde (0.161 g, 1.07 mmol) in methanol (25 mL) was added and the mixture stirred under nitrogen in the dark as it was allowed to warm to room temperature. Two hours later, 2.3-dichloro-5,6-dicyano-1,4-benzoquinone (0.362 g,

1.59 mmol) in THF (13 mL) was added, the reaction stirred for a further two hours, and then evaporated. The residue was taken up into chloroform, and washed with 5 N aqueous sodium hydroxide until the water layer was clear. The organic layer was dried over sodium sulfate, filtered, and the solvent removed *in vacuo*. The red solid was placed down a silica column using chloroform as the eluent. All fractions containing a Soret band (as judged by UV-vis spectroscopy) were combined and the eluent removed *in vacuo*. The resulting solid porphyrin was recrystallized from chloroform/hexanes to give **11** in ca. 19% yield (0.072 g).[13]

PorSap pseudo dimer, 3: To a stirred solution of 8,17-bis(carboxyethyl)-3,12,13,22-tetraethyl-2,7,18,23-tetramethylsapphyrin dihydrochloride **7** (0.026 g, 0.035 mmol) in 30 mL dry dichloromethane under nitrogen was added 1 mL oxalyl chloride and one drop dimethylformamide. After three hours, the solvent was removed in vacuo, and the green/blue residue **8** was placed under hi-vac for 20 minutes. Concurrent with this, *cis*-5,15-bis(*o*-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin[2c] **12** (0.022g, 0.034 mmol), with 1 mL of pyridine and 1 mg *p*-dimethylaminopyridine, was dissolved into 1000 mL dry dichloromethane under nitrogen. To this red solution was added, via dropper funnel over the course of several hours, the sapphyrin diacid chloride (from the oxalyl chloride reaction above) redissolved into the minimum amount of dry dichloromethane. The now-greenish solution was stirred under nitrogen overnight. The solvent was then removed in vacuo. The green residue was taken up in chloroform, washed with dilute aqueous hydrochloric acid, water, and then aqueous sodium bicarbonate. The chloroform layer was separated off and dried over sodium sulfate. After, filtration, the chloroform was removed in vacuo and the residue purified by chromatography on silica gel. For this, a solution of 100:10:1 parts chloroform: methanol:triethylamine was used as the eluent. The first greenish fraction off the column was recrystallized, first from dichloromethane/hexanes and then from dichloromethane/ether to yield 0.005 g of the product **3** (11%). ^{1}H NMR (250 MHz, $CDCl_3$) δ -5.20 (s, 2H, NH (sapphyrin, S)), -4.95 (s, 1H, NH (S)), -4.47 (s, 2H, NH (S)), -2.36 (s, 2H, NH (porphyrin, P)), 1.73 (t, 12H, -$CH_2C\underline{H}_3$ (P)), 2.06 (t, 6H, -$CH_2C\underline{H}_3$ (S)), 2.19 (t, 6H, -$CH_2C\underline{H}_3$ (S)), 2.73 (s, 12H, -CH_3 (P)), 3.62 (q, 4H, -$CH_2C\underline{H}_2$-), 3.97 (q, 8H, -$C\underline{H}_2CH_3$ (P)), 4.10 (s, 6H, -CH_3 (S)), 4.28 (s, 6H, -CH_3 (S)), 4.51 (q, 4H, -$C\underline{H}_2CH_3$ (S)), 4.70 (q, 4H, -$CH_2C\underline{H}_3$ (S)), 5.06 (t, 4H, -$C\underline{H}_2CH_2$-), 7.55 (d, 2H, phenyl (P)), 7.70 (t, 2H, phenyl (P)), 7.78 (t, 2H, phenyl (P)), 7.96 (d, 2H, phenyl (P)), 10.20 (s, 2H, meso (P)), 11.67 (s, 2H, meso (S)), 11.71 (s, 2H, meso (S)), CON<u>H</u> not observed; IR (neat) 3391.8, 2922.2, 2851.6, 2604.3, 2497.4, 1681.8, 1529.8, 1462.9, 1397.9, 1378.3, 1261.0, 1215.3, 1172.1, 1079.6, 1037.4, 759.4, 667.5 cm^{-1}; UV-vis ($CHCl_3$) λ_{max} (ε) 409.0 (125,850), 457.5 (266,530), 507.0 (11,390), 541.0 (7,900), 574.5 (9,430), 623.0 (14,100), 673.5 (13,150), 686.5 (11,270, shoulder) nm; HRMS (FAB) *m/e* calc'd for $C_{86}H_{95}N_{11}O_2$: 1313.7670, found 1313.7678.

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