Strapped Porphyrin  | Very Important Paper |

Short-Chained Anthracene Strapped Porphyrins and their Endoperoxides**

Susan Callaghan,[a] Keith J. Flanagan,[a] John E. O’Brien,[a] and Mathias O. Senge*[a,b]

In memoriam Prof. Charles Michael Drain

Abstract: The syntheses of short-chained anthracene-strapped porphyrins and their Zn(II) complexes are reported. The key synthetic step is a [2+2] condensation between a dipyrromethane and an anthracene bisaldehyde, 2,2′-(((anthracene-9,10-diyldibis(methylene))bis(oxy))dibenzaldehyde. Following exposure to white light, self-sensitized singlet oxygen and the anthracene moieties underwent [4+2] cycloaddition reactions to yield the corresponding endoperoxides. 1H NMR studies demonstrate that the endoperoxide readily formed in [D]chloroform and decayed at 85 °C. X-ray crystallography and absorption spectroscopy were used to confirm macrocyclic distortion in the parent strapped porphyrins and endoperoxides. Additionally, X-ray crystallography indicated that endoperoxide formation occurred exclusively on the outside face of the anthracene moiety.

Introduction

Endoperoxide formation, mediated by [4+2] cycloaddition reactions between an aromatic unit and singlet oxygen, is an emerging strategy for modulating the photochemistry of singlet oxygen. Since this reaction was first described by Moureau, Dufraisse, and Dean,[11] it has found application in bioimaging and is the underlying interaction in probes, for example, singlet oxygen sensor green and a fluorescence probe designed by Mokhir and co-workers.[2] Additionally, endoperoxides of moieties including anthracene, pyridone, and naphthalene have been shown to thermally decay to slowly release singlet oxygen. These systems have found application in therapeutics,[3] oxygen storage devices,[4] and even photolithography.[5]

Porphyrin macrocycles can take on non-planar conformations given the correct conditions. A common method to introduce macrocycle distortion is the substitution of the periphery with bulky groups.[6] These distortion properties are also endowed by short strapped systems, i.e. porphyrins with a connection between two meso-meso or [β-β] carbon atoms, and the nature of the induced distortion can affect the shape and size of the cavity.[7] Strapped systems have been extensively studied, especially as possible heme mimics as the porphyrin cores in these active sites are distorted from planarity due to surrounding proteins.[8] In addition, macrocyclic distortion can lead to interesting chemical properties including organocatalytic activity and use in sensing applications.[6,7a,9] Early systems that achieved significant distortion using short alkyl chains were prepared in the 1980s by the groups of Dolphin, Einstein, and Walker.[10] One may also recall the pioneering works of Staab on porphyrin quinone cyclophanes.[11]

Previous reports of anthracene containing strapped systems (Figure 1, porphyrins 1–4) did not describe macrocyclic distortion.[12] In one study, Traylor and co-workers synthesized anthracene strapped porphyrins as part of a wider study related to ligand binding in natural heme proteins. The anthracene unit was introduced in a double amide bond-forming reaction between an anthracene containing acid chloride unit and an amine-containing porphyrin. To further restrict the binding pocket, they performed a cycloaddition reaction with 1-phenyl-1H-pyrrole-2,5-dione to yield compound 3. To the best of our knowledge, this is the only example of a cycloaddition reaction across an anthracene strapped porphyrin.[12b] In 1991, Osuka et al. reported porphyrin 5 and were able to confirm that strap length was related to macrocyclic distortion using NMR and absorption spectroscopy.[13] Moreover, recent interest in the development of general methods for the synthesis of strapped porphyrin systems and their stereochemical properties has revitalized interest in this family of tetrapyrroles.[14]

With these concepts in mind, we designed anthracene strapped systems with a short chain to induce macrocyclic distortion and restrict the size of the cavity, thereby shielding one face of the anthracene moiety. The anthracene moiety acts as

[a] School of Chemistry, Trinity College Dublin, The University of Dublin, Trinity Biomedical Sciences Institute, 152-160 Pearse Street, Dublin 2, Ireland
E-mail: sengem@tcd.ie; twitter: @mathiassenge
www: https://chemistry.tcd.ie/staff/people/mos/Home.html
[b] Institute for Advanced Study (TUM-IAS), Technische Universität München, Lichtenberg-Str. 2a, 85748 Garching, Germany
E-mail: sengem@tcd.ie1192728311927283

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the site for a reversible [4+2] cycloaddition with self-sensitized singlet oxygen via action of the porphyrin photosensitizer component. The reversibility at elevated temperatures is expected to find application in oxygen storage devices.

Results and Discussion

Single strapped porphyrins (Scheme 1, porphyrins 19–21) were prepared using condensation reactions between an anthracene
containing bisaldehyde, 2,2'-(antracene-9,10-diylbis(methylene))bis(oxo))dbenzaldehyde 8, and dipyromethane (DPM) or a DPM derivative. This approach was chosen to ensure that the "trans" (5,15) isomer would be the major product as we aimed to position the anthracene moiety above the porphyrin core to induce maximum macrocycle distortion. This would also differentiate the two faces of the anthracene unit with regard to endoperoxide formation. Firstly, bromine was introduced to unsubstituted anthracene (compound 6) using paraformaldehyde, 33 % HBr in acetic acid and KI. A substitution reaction with salicylaldehyde in the presence of a base and KI in DMF yielded the bisaldehyde 8, using a procedure adapted from literature. Either paraformaldehyde, benzaldehyde or bromobenzaldehyde was condensed with excess pyrrole using trifluoroacetic acid (TFA) as a catalyst. The reactions were monitored using a bromine chamber. Yields between 28 % and 79 % were obtained and these condensation reactions were performed on multigram scales.

We then synthesized DPM 9 using a literature adapted procedure and prepared the DPM derivatives 10 and 11 to allow for the expansion of the porphyrin library (Scheme 1). Either paraformaldehyde, benzaldehyde or bromobenzaldehyde was condensed with excess pyrrole using trifluoroacetic acid (TFA) as a catalyst. The reactions were monitored using a bromine chamber. Yields between 28 % and 79 % were obtained and these condensation reactions were performed on multigram scales.

Each DPM (9-11) was then condensed with the bisaldehyde 8, using dichloromethane (DCM) and TFA as an acid catalyst. After 3.5 h at r.t., triethylamine (TEA) was added to neutralize the TFA (Scheme 1). An oxidation step using p-chloranil followed. This step is key to inducing macrocyclic distortion. As the initially formed porphyrinogen is not conjugated the structure is not rigid. Upon oxidation, the macrocyclic is flattened and a "bowstring effect" induces distortion. The porphyrins were purified using column chromatography and recrystallization and yields between 14 % and 19 % were obtained (Scheme 1). A similar synthetic strategy was employed by Osuka et al. for the synthesis of porphyrin 5 and they obtained a 25 % yield, which is consistent with our moderate yields.

We also synthesized the Zn(II)metallated derivatives of porphyrins 19-21 to yield porphyrins 16-18. This was achieved using Zn(II)acetate, methanol and DCM as solvents and yields between 47 % and 98 % were obtained (Scheme 1). It was found that heating to 80 °C compared to initial attempts at r.t., decreased the reaction time. The products were purified using silica chromatography and recrystallization. We also condensed the Zn(III)metallated derivatives of porphyrins 19-21 to yield porphyrins 16-18. This was achieved using Zn(II)acetate, methanol and DCM as solvents and yields between 47 % and 98 % were obtained (Scheme 1). It was found that heating to 80 °C compared to initial attempts at r.t., decreased the reaction time. The products were purified using silica chromatography and recrystallization.

Endoperoxides of the parent porphyrins (22-24) were then prepared. The parent porphyrins were dissolved in [D]chloroform and irradiated with a white light source in an NMR tube. The reactions were monitored by 1H NMR and yields were quantitative in all cases. We then used endoperoxide 22 to study thermal decay. After endoperoxide formation, the [D]chloroform was removed and replaced with deuterated [D6]DMSO. The sample was heated to 85 °C in accordance with other anthracene derivatives to induce thermal decay of the endoperoxide. At t = 0 h the NH proton signal of endoperoxide 22 is observed at –3.34 ppm. In the aromatic region, we observed the CH protons of the anthracene endoperoxide as two multiplets at 5.91 and 4.81 ppm. It is noteworthy that the CH protons of the anthracene endoperoxide have a lower chemical shift than unsubstituted anthracene, which is attributed to ring current effects. Following heating over 2 h, the signals for the CH protons of the anthracene endoperoxide at 5.91 and 4.81 ppm slowly decay with an appearance of aromatic signals at 5.74 and 4.97 ppm that correspond to the CH protons of anthracene. Only minor changes in the chemical shifts of the CH protons of the anthracene and endoperoxide units are noted as we expect they are under the influence of similar ring current effects. The NH protons also undergo changes. The endoperoxide signal at –3.34 ppm decays and the parent NH signal appears at –3.50 ppm. The endoperoxide NH signal is deshielded in comparison to the parent because of the electronegative oxygen atoms of the endoperoxide. Over the course of the 2 h we also see an emergence of other signals, which are especially evident in the NH region. These signals may indicate the formation of rearranged endoperoxide porphyrin products; thus, it can be concluded that the thermal decay of 19 in [D6]DMSO is not quantitative (Figure 2).

We attempted the synthesis of the analogous "trans" (5,15 and 10,20) double-strapped system of porphyrin 19 to further increase macrocyclic distortion. Firstly, we adopted the direct synthesis approach, which was used by Reddy and Chandrasekar in the synthesis of similar phenyl-strapped porphyrins. We condensed pyrrole with compound 8 under both Adler Longo and Lindsey conditions on multigram scales. In a second approach, we used compound 8 to synthesize the corresponding bisDPM and then condensed this in a 1:1 ratio with compound 8 under Lindsey conditions. The product was identified by mass spectrometry (HRMS (MALDI-TOF) m/z calcd. for C70H51N4O4 [M + H]^+: 1083.3910, 1083.3909 found) but pure isolation was not achieved due to π-stacking of the anthracene moieties.

To further investigate changes in the macrocyclic core upon endoperoxide formation and the introduction of a short strap we studied the absorption spectra of the strapped systems and compared them to 5,15-diphenylporphyrin 25 as a non-strapped analogue. In Figure 3, the normalized absorption spectra of 5,15-diphenylporphyrin 25 (blue), parent porphyrin 19 (black), and endoperoxide, 22 (red) recorded in DCM are pre-
presented to exemplify this phenomenon. We can see that 5,15-diphenylporphyrin (25) has a Soret absorption maximum at 408 nm and upon the introduction of the strap, there is a red-shift of 10 nm to 418 nm (19), an indication of increased macrocycle distortion. The slight bathochromic shift of 2 nm between the parent porphyrin 19 and endoperoxide 22 may indicate minor changes in macrocyclic distortion. Also of note are the bands between 330–400 nm in 19 that represent the anthracene moiety. These are not present in the endoperoxide absorption spectrum as conjugation is disrupted. The red-shift pattern is also repeated for porphyrins 20, 21, 23, and 24, which show a significant bathochromic shift when compared to 5,15-diphenylporphyrin (25) and a minor shift upon endoperoxide formation (Table 1).

Figure 3. Normalized absorption spectra of porphyrins 25, 19, and 22 in DCM as an example to show how the strap induces distortion. *Absorption wavelength range for anthracene moiety.

In order to investigate the macrocycle conformation in more detail, single-crystal X-ray crystallographic studies were undertaken and the X-ray crystal structures of porphyrins 19 and 22 were determined (Figure 4). The crystal structure of 22 showed endoperoxide formation exclusively on the outer face of the anthracene moiety, thus making this a face-selective photoreaction. 1H NMR spectroscopy did not provide any evidence of inner face endoperoxide formation in solution as only one NH signal was observed for the endoperoxide. If the endoperoxide oxygens were on the inner face of the anthracene directly above the porphyrin plane we would expect a different NH chemical shift to that found for structure 22. We postulate that this is a result of steric hindrance as the outer face is more available for binding and repulsion form the electronegative cavity.

To study the relative effects of the strap and endoperoxide formation on macrocyclic distortion the structures of 19 and 22 were compared to that of 5,15-diphenylporphyrin 25. Two structures have been reported in the literature for the latter; a DCM solvated form (25-DCM) and one without solvent molecules (25). Figure 4 shows that there is significant macrocycle distortion in porphyrins 19 and 22, which contain straps, compared to 5,15-diphenylporphyrin, 25. The structural differences are quite drastic and have been graphically outlined in Fig. S1–S8 with different views of both porphyrins 19 and 22.

Table 1. Absorption maxima (λ_{max}) of strapped porphyrins, endoperoxides and 5,15-diphenylporphyrin, 25 recorded in DCM.

| Porphyrin | λ_{max} [nm] |
|-----------|-------------|
| 25        | 408, 504, 538, 577, 632 |
| 19        | 359, 378, 418, 511, 543, 584, 632 |
| 22        | 420, 515, 545, 587, 632 |
| 20        | 360, 384, 431, 526, 564, 600, 658 |
| 23        | 433, 528, 567, 601, 657 |
| 21        | 361, 382, 432, 527, 565, 601, 658 |
| 24        | 434, 529, 566, 604, 660 |

Figure 4. Molecular structure in the crystal of 25 (20), 19, and 22 (left to right) viewed at a tilted angle (top) and the side view (bottom). Thermal displacements are given at 50 % for 19 and 22. The structure of 25 is drawn isotropically.
The skeletal deviation plots show that the strapped systems (porphyrins 19 and 22) display increased out-of-plane ring distortion, with the meso-carbons presenting the largest deviations (Fig. S9). In the normal-coordinate structural decomposition (NSD)\textsuperscript{[23–25]} plots – a means to identify and quantify macrocycle distortion modes – a simple trend becomes evident. Porphyrins 19 and 22 show an inverse relationship between out-of-plane (oop) and in-plane (ip) distortion modes. This is represented by an increase in the oop modes while the ip modes are significantly decreased (Fig. S10). Both 25 and 25-DCM show a preference for the ruffled ($B_{1u}$) mode with 25-DCM having a slightly increased contribution to this mode. For porphyrins 19 and 22 there is an increase in the contribution of the $B_{1u}$ mode with a second smaller contribution to the domed ($A_{2g}$) mode. The structure of 22 shows a slightly larger contribution to the $B_{1u}$ mode compared to 19 which is also reflected in the $\Delta_{\text{oop}}$ with the evident trend being $25 \leq 25-\text{DCM} < 19 \leq 22$. Moving to the $\text{ip}$ distortion modes both 25 and 25-DCM have significant contributions to the meso-stretching ($B_{2g}$) mode with a secondary contribution to the breathing ($A_{1g}$) mode. In the structure of 19, a decrease in the $B_{2g}$ mode is evident compared to 25 with little to no contribution noted in the other $\text{ip}$ distortion modes. For the structure of compound 22, the main contributions have now shifted to the N-stretching ($B_{1u}$) and $A_{1g}$ modes with almost equal contributions to both modes. The specific trend seen in the $\Delta_{\text{ip}}$ is $25 \leq 25-\text{DCM} > 19 \geq 22$.

The geometrical changes in the porphyrin macrocycle are listed in Table 2. The bond lengths around the porphyrin macrocycle do not show any significant changes. A similar situation is noted in the bond angles; however, in four areas there are significant changes to be noted. These are in the N–C(1,9,11,19)–C(10,20)–C(6,16)–C(3,7,13,17) modes. There is a slight increase in the contribution of the $B_{1u}$ mode while the $g$ mode is slightly increased contribution to this mode. The $A_{2g}$ mode has now shifted to the N-stretching ($B_{1u}$) and $A_{1g}$ modes with almost equal contributions to both modes. The specific trend seen in the $\Delta_{\text{ip}}$ is $25 \leq 25-\text{DCM} > 19 \geq 22$.

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molecule has on 25 and 25-DCM. There is a 0.7° difference between the C(1,11)–C(10,20)–C(9,19) angle. However, there are only minor deviations between the other angles. This suggests that the inclusion of the solvent molecule does not greatly affect the overall structure. Moving to the structure of 19 compared to 25, the N–C(9,11,19)–C(10,20), C(4,14)–C(5,15)–C(16,16), and C(10,20)–C(11,11,19) angles increase by 2°, 2.5°, and 1.8°, respectively. Conversely, the C(1,11)–C(10,20)–C(9,19) angle is reduced by 3°. A small change of 0.9° is noted in the C(1,11)–C(6,14,16)–C(3,7,13,17) and N–C(6,14,16)–C(5,15) angles. A similar change is noted in the structure of 22; however, the C(4,14)–C(5,15)–C(6,16) angle shows a 1.3° reduction compared to 19. All other angles only deviate by at most 0.5° between 22 and 19, suggesting that endoperoxide formation only has minor effects on the porphyrin macrocycle, which is evident in both the NSD and skeletal deviation plots (Fig. S9 and S10) and is consistent with the UV/Vis data presented in Table 1.

Looking at the pyrrole tilt angles a specific trend becomes apparent. For the N21, N22, and N23 pyrrole rings the tilt angle trend is 25 ≤ 25-DCM < 19 ≤ 22 with an average 0.4–1.6° increase from 25 to 25-DCM, a ca. 9° increase from 25-DCM to 19, and a 2.4–3.2° increase from 19 to 22. The only deviation from this trend is seen in N24 where the trend becomes 25-DCM ≤ 25 < 19 ≤ 22. Moving to the atom deviations the 25 ≤ 25-DCM < 19 ≤ 22 is followed for the Δ24, ΔN, ΔCm, ΔCip, and ΔCopp deviations from the 24-atom least-squares-plane. These changes are quite evident in the NSD where there is a significant increase in the oop distortion modes, as demonstrated by the increase in the Δoop following the addition of the 5,15-strap.

The final structural parameter to look at is how the size of the core (N–C–N) changes between the porphyrins. The most obvious change is moving from the “rectangular” shape where the 5,15-axis is longer than the 10,20-axis, to a “squarer” shape where both the 5,15- and 10,20-axes are approximately the same distance. The former core elongation is often encountered in 5,15-disubstituted porphyrins, while the latter is typical for symmetric A4-type porphyrins. This is also affected by the length of the strap (as calculated from the distance between the Cortho–Cortho of the 5,15-phenyl substituents). Without a strap, the distance between these two atoms is in the range of 11.506–11.580 Å. Upon the addition of the strap, this distance is significantly shortened to 8.967(2) Å (19) with a smaller decrease in distance to 8.928(9) Å following endoperoxide formation (22). This is reflected in the ip distortion modes with a significant decrease in the Δip following the addition of the 5,15-strap, which prevents core elongation. From the above observations, it is clear that while there are only minor changes to the bond lengths and angles in the macrocycle ring the pyrrole tilts, atom deviations, and core elongation are changed as a result of the introduction of a strap between the 5,15-meso-substituents.

Finally, there are several structural changes in the packing patterns (Fig. S11–S14). In the structure of 25, there is evidence of stacking interactions between the porphyrin rings (Fig. S15). However, there is no indication of π-stacking between the porphyrin layers. When a solvent DCM molecule is included in the stacking, the pattern is skewed to form a tilted edge-on interaction between the porphyrin layers (Fig. S16). With the introduction of the strap across the 5,15-meso-substituents, several changes occur; the first is to note that the spacing between the porphyrin macrocycles is now expanded due to the strap creating a buffer zone between molecules as seen in 19 (Figure 5). No specific interactions are noted in the structure of 19. However, in the structure of 22, there is a clear head-to-head interaction between the endoperoxide moiety and the meso-sub-

Figure 5. Stacking interactions seen between moieties of 19.

Figure 6. Stacking interactions seen in 22 showing the head-to-head interaction [C–H153···O3 (2.479(2) Å, 168.7(2)°)] (left) and the edge-on interaction [C–H18···O3 (2.620(2) Å, 152.7(2)°)] (right).
stinent [C--H153--O3 (2.479(2) Å, 168.7(2)°)], which is directive in the crystal packing (Figure 6, left). This is accompanied by an edge-on interaction between the porphyrin macrocycle and the endoperoxide moiety [C--H18--O3 (2.620(2) Å, 152.7(2)°)] (Figure 6, right). As seen in the crystal packing, this results in head-to-head interactions that give rise to the loose packing system of porphyrin 25.

Conclusions

In summary, we presented the synthesis of three short-chained anthracene strapped porphyrins, their corresponding endoperoxides and Zn(II)complexes. The porphyrins were accessed using [2+2] condensation reactions, and endoperoxide formation was achieved with white light in [D]chloroform selectively on the outside of the anthracene strap. Upon heating to 85 °C, endoperoxide decay was observed and monitored by 1H NMR. As seen in the X-ray structures of 19 and 22, endoperoxide formation caused bending of the anthracene moiety to flank the core. This interesting structural effect has the potential for reversible on-off porphyrin core shielding and chemical modification of the strap may lead to a fully inaccessible core on one side. In the future, this approach may be utilized for switchable selective sensing applications. The X-ray crystal structures of a parent porphyrin and its corresponding endoperoxide were presented and macrocyclic distortion was confirmed with an oop distortion of 1.261 Å for the parent and 1.496 Å for the endoperoxide, which can be compared to 0.429–0.462 Å for 5,15-diphenylporphyrin, 25. For the same porphyrins, a 10–12 nm red-shift was observed in the UV/Vis spectra compared to 5,15-diphenylporphyrin, 25, further confirming the macrocyclic distortion in solution.

Experimental Section

X-ray Crystallography: The crystals were grown following the protocol developed by Hope by dissolving the porphyrins in either DCM or chloroform and layering with a second solvent (methanol or hexane) for liquid diffusion or allowing for slow evaporate over time.27

Single crystal X-ray diffraction data for all porphyrins were collected on a Bruker APEX 2 DUO CCD diffractometer by using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The crystals were mounted on an Oxford Cryosystems Cobra low-temperature device. The data were collected by using omega and phi scans and were corrected for Lorentz and polarization effects by using the APEX software.28–30 Using Olex2, the structure was solved with the XT structure solution program, using the intrinsic phasing solution method and refined against |F|2| with XL using least-squares minimization.31,32 Hydrogen atoms were generally placed in their calculated positions and refined as riding model: N–H = 0.88 Å, C–H = 0.95–0.98 Å, with 1.2 Ueq (C, N) for all hydrogen atoms. In the structure of 19, the distances between H36B···H31 and H34···H21A were fixed to remove the short contact present in the structure. The inner core nitrogen atoms were modelled over two positions at an occupancy of 50:50 %. In the structure of 22, the inner core nitrogen atoms were modelled over two positions at an occupancy of 50:50 %.

Normal-coordinate Structural Decomposition (NSD) Analysis: The theoretical background and development of this method were described by Shelnutt and co-workers23–25 NSD is a conceptually simple method that employs the decomposition of the conformation of the macrocycle by a basis set composed of its various normal modes of vibration,33 affording clear separation of the contributing distortions to the macrocycle conformation in a quantitative fashion. For calculations, we used the NSD engine program as provided by Shelnutt.34

Synthetic and Analytical Methods. All chemicals were commercially sourced and used without further purification. Dry DCM was obtained by passing through alumina under N2 in a solvent purification system and then further dried with activated molecular sieves.

Analytical thin-layer chromatography was performed using silica gel 60 (fluorescence indicator F254, pre-coated sheets, 0.2 mm thick, 20 cm x 20 cm; Merck) plates and visualized by UV irradiation (λ = 254 nm). Column chromatography was carried out using Fluka Silica Gel 60 (230–400 mesh; Merck). UV/Vis spectra were recorded in solutions using a Spectord 250 spectrophotometer from Analytic Jena (1 cm path length quartz cell). Photo-irradiations were performed in an NMR tube using a white light source (Philips, 15V–150 W lamp), equipped with a 400 nm cut-off filter (Schott GG 400). The NMR spectra were recorded on a Bruker AV 600, Bruker Advance III 400 MH or a Bruker DPX400 400 MHz or an Agilent 400 spectrometer. Accurate mass measurements (HRMS) were carried out using a Bruker microTOF-Q™ ESI-TOF mass spectrometer. Mass spectrometry was performed with a Q-Tof Premier Waters MALDI quadrupole time-of-flight (Q-TOF) mass spectrometer equipped with Z-spray electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) sources in positive mode with trans-2-[3-(4-tert-butyphenyl)-2-methyl-2-propenylidene]malononitrile as the matrix. Melting points were measured using an automated melting point meter, SMP50 (Stuart). IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. Compounds 7 and 8 and DPM 9, 10, and 11 were synthesized and characterized in accordance with literature.15,16

General Procedure A – Porphyrin Condensation Dipyrromethane (2 equiv.) and aldehyde (2 equiv.) were dissolved in dry DCM (120 mL). The reaction was shielded from light and TFA (cat.) was added. The reaction was stirred at r.t. for 3.5 h. TEA (3 mL) and H2O (cat.) was added and the mixture was heated to 70 °C for 1 h. The product was purified on a silica plug (1:1, DCM/hexane) followed by column chromatography (hexane with 2% ethyl acetate). The porphyrin was then precipitated from DCM and methanol or recrystallized from DCM and hexane.

General Procedure B – Endoperoxide Formation: Parent anthracene strapped porphyrin (1 equiv.) was dissolved in [D]chloroform (3 mL) and irradiated with white light for 15 min. Endoperoxide formation was monitored using 1H NMR.

General Procedure C – Zinc(II) Insertion: To a solution of parent porphyrin (1 equiv.) in DCM (10 mL) was added Zn(II)acetate (10 equiv.) in methanol and the reaction was stirred at 80 °C for 12 h. The product was purified on a silica plug (DCM) followed by column chromatography (3:1, DCM/hexane) and was recrystallized from DCM/methanol.

Strapped Porphyrin 19: 5,10,15,20-tetakis(9′,10′-bis(phenoxymethyl)anthracene)-porphyrin. Porphyrin 19 was synthesized in accordance with general procedure A using dipyrromethane (393 mg, 2.69 mmol),
2,2′-(anthracene-9,10-diylbis(methylene))bis(oxy))dibenzoaldehyde (600 mg, 1.35 mmol), DCM (120 mL), and p-chloranil (1.98 g, 8.08 mmol) to yield a purple solid (178 mg, 2.57 × 10^{-4} mol, 19%).

M.p. > 200 °C; Rf = 0.87 (DCM); 1H NMR (600 MHz, CDCl3): δ = 9.64 (s, 2H, CHβmeso), 9.04 (d, J = 4.3 Hz, 4H, CHαmeso), 9.01 (d, J = 7.1 Hz, 2H, CHβAr), 8.84 (d, J = 4.3 Hz, 4H, CHβAr), 7.74–7.70 (m, 2H, CHAr), 7.67–7.64 (m, 2H, CHβAr), 7.00 (d, J = 7.8 Hz, 2H, CHAr), 6.32 (d, J = 6.9, 2.7 Hz, 4H, CHαAr), 6.25 (dd, J = 6.6, 3.1 Hz, 4H, CHβAr), 4.59 (s, 4H, CH2), –3.50 ppm (s, 2H, NH); 13C NMR (600 MHz, CDCl3): δ = 158.6, 131.4, 130.1, 132.7, 126.1, 122.9, 121.0, 111.9, 118.8, 103.8, 61.6, 53.4 ppm; UV/Vis (DCM): λ_{max} (log ε) = 359 (4.41), 378 (4.42), 418 (5.34), 511 (4.06), 543 (3.19), 584 (3.53), 632 mm (2.64); IR (ATR): ν = 3296, 2545, 2162, 1690, 1596, 1557, 1530, 1474, 1444, 1405, 1283, 1217, 1139, 1105, 1058, 1045, 997, 974, 955, 857, 847, 821, 788, 749, 722, 692, 658, 639, 600, 568 cm^{-1}; HRMS (MALDI-TOF) m/z calcd. for C_{48}H_{32}N_{4}O_{4} [M]^+ : 696.2525, 696.2524 found.

Strapped Porphyrin 20: 5,10-(9′,10′-dihydro-9′,10′-epidioxyanthracene)-5,15-diphenyloxy)porphyrin. Porphyrin 20 was synthesized in accordance with general procedure B using porphyrin 19 (19 mg, 2.75 × 10^{-5} mol) to yield a purple solid (20 mg, 2.75 × 10^{-5} mol, quant.). M.p. > 200 °C; Rf = 0.74 (3:1, DCM/hexane); 1H NMR (400 MHz, CDCl3) δ = 8.98 (d, J = 7.0 Hz, 2H, CHβAr), 8.83 (d, J = 4.8 Hz, 4H, CHβAr), 8.70 (d, J = 4.7 Hz, 4H, CHβAr), 7.92 (t, J = 7.7 Hz, 2H, CHAr), 6.81 (d, J = 7.8 Hz, 2H, CHAr), 6.04 (d, J = 3.3 Hz, 4H, CHβAr), 5.09 (s, 4H, CH2), 3.72 (s, 4H, CH2), –2.57 ppm (s, 12H, NH); 13C NMR (600 MHz, CDCl3) δ = 155.9, 140.1, 133.6, 131.3, 130.4, 130.0, 129.1, 129.3, 127.2, 122.3, 122.2, 120.6, 118.6, 117.2, 112.4, 110.3, 78.6, 62.0 ppm; UV/Vis (DCM): λ_{max} (log ε) = 433 (5.03), 528 (3.77), 576 (3.67), 601 (3.65), 657 nm (3.48); IR (ATR): ν = 3273, 2066, 2932, 2833, 1787, 1688, 1598, 1560, 1466, 1447, 1241, 1110, 983, 967, 905, 792, 750, 730 cm^{-1}; HRMS (ESI) m/z calcd. for C_{60}H_{40}N_{4}O_{2} [M + H]^+ : 881.3050, 881.3125 found.
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Supporting Information (see footnote on the first page of this article): Spectroscopic data of all compounds and X-ray crystallographic data (NSD, crystal structures, packing, bond lengths and angles).

CCDC 1981333 (for 19), and 1981332 (for 22) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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