Synthesis and Structure of meso-Substituted Dibenzihomoporphyrins


Dedicated to Professor Tavarekere K. Chandrashekar on the occasion of his 65th birthday

Abstract: Bench-stable meso-substituted di(p/m-benzi)homo-porphyrins were synthesized through acid-catalyzed condensation of dipyrrole derivatives with aryl aldehydes. The insertion of a 1,1,2,2-tetraphenylethene (TPE) or but-2-ene-2,3-diyldibenzene unit in the porphyrin framework results in the formation of dibenzihomoporphyrins, merging the features of hydrocarbons and porphyrins. Single crystal X-ray analyses established the non-planar structure of these molecules, with the phenylene rings out of the mean plane, as defined by the dipyrromethene moiety and the two meso-carbon atoms. Spectroscopic and structural investigations show that the macrocycles exhibit characteristics of both TPE or but-2-ene-2,3-diyldibenzene and dipyrromethene units indicating the non-aromatic characteristics of the compounds synthesized. Additionally, the dibenzihomoporphyrins were found to generate singlet oxygen, potentially allowing their use as photosensitizers.

Introduction

The synthetic chemistry of expanded porphyrinoids has attracted considerable attention for the last twenty-five years.[1] Studies on macrocycles related to porphyrins have been prompted by their fascinating structure, flexible conformation, aromaticity, and unique coordination chemistry.[2] Expanded porphyrinoids have more than 18π-electrons in their conjugation pathway, which uniquely alters the reactivity of the macrocyclic core. Due to their special electronic and structural properties, expanded porphyrinoids are used in various applications such as non-linear optics (NLO),[3a] photodynamic therapy (PDT),[3b] and ion recognition.[3c]

The simplest expanded, conjugated analog of [18]-porphyrin(1.1.1.1) 1 is [20]-porphyrin(2.1.1.1) or [20π]-homoporphyrin 2 that exhibits five meso carbons and four pyrrole rings (Figure 1). In contrast to normal porphyrins, [20π]-homoporphyrins are non-aromatic. In 1971, Grigg reported the first azahomoporphyrin 3; however, this compound was found to be unstable and rearranged to the respective aziridine-fused porphyrin with only one sp3-carbon in the macrocycle.[4] Subsequent synthetic efforts by Callot and co-workers and structural studies from Weiss’s group established the first [20π]-homoporphyrin 4.[5] The latter compound was also unstable and decomposed even in the solid-state.

Eventually, the synthesis of bench-stable core-modified [20π]-homoporphyrins (such as 5) was reported by Ravikanth and co-workers.[6] 40 years after their initial discovery, the synthesis and coordination properties of fully conjugated [20π]-homoporphyrin derivatives 6 with Möbius topology was reported by Srinivasan and co-workers.[7]

Another class of porphyrin analogs, in which one or more pyrrole rings is replaced by a benzene ring, is known as benziporphyrin.[8] Diverse benziporphyrin structures ranging from non-aromatic to highly diautropic species have been reported and they are used as surrogate ligands in place of porphyrins, especially for heavy transition metals. Additionally, benziporp-
Porphyrins are hypothesized to stabilize metals in unusual oxidation states. Benzoporphyrins are classified into two sub-types: (a) $p$-benzoporphyrin 7 where the benzene ring is attached via a 1,4-phenylene linkage and (b) $m$-benzoporphyrin 8 with attachment via a 1,3-phenylene linkage. The aromaticity of benzoporphyrins is highly dependent upon the way this phenylene is linked into the macrocycle.\[9,10\] In general, $m$-benzoporphyrins are non-aromatic, whereas $p$-benzoporphyrins preserve the aromatic characters of porphyrin. The electronic properties of benzoporphyrins can be manipulated through core modification, meso-substitution, and metal coordination.

Considering these precedents of porphyrin-inspired macrocycles, we envisioned the synthesis of a new class of porphyrin that exhibits combined structural features of homoporphyrins and benzoporphyrins, i.e. di($p$-benz)homoporphyrins. Although structurally characterized dibenz corroles are known in the literature, they are strictly limited to incorporation of polycyclic aromatic hydrocarbons in the macrocycle, as shown for system 9 (Figure 1).\[11\] meso-Substituted benzohomoporphyrins of type 10 have not been reported in the literature. Additionally, porphyrins and related compounds are often singlet oxygen-generating photosensitizers of note. However, $\pi$-conjugated expanded porphyrins tend to aggregation which significantly decreases the singlet oxygen quantum yield.\[12\] While this can be counteracted by steric shielding, e.g., in nanostructures and out-of-plane coordinated porphyrins,\[12,13\] conformational distortion may also negatively impact this.\[14\]

Herein we report the synthesis of meso-substituted dibenz homoporphyrins, which contain phenyl or methyl substituents at the vinylene bridge and aryl substituents at the meso positions to control the conformational and electronic properties of the macrocycles. To compare the structural and electronic features, we targeted the synthesis of di($p$-benz)homoporphyrins and di($m$-benz)homoporphyrins which was achieved by introducing $p$- or $m$-phenylene unit in the porphyrin framework.

Results and Discussion

Synthesis

The synthesis of meso-substituted di($p$-benz)homoporphyrins is outlined in Scheme 1. In the first step, a McMurry coupling reaction was employed for the conversion of 4-bromobenzophenone (11) to 1,2-bis(4-bromophenyl)-1,2-diphenylethene 13.\[^{[15]}\] In the next step, 1,2-diphenylethene-1,2-diylbis(4,1-phenylene)bis(4-methoxyphenyl)methanol 15 was synthesized through reaction of 1,2-bis(4-bromophenyl)-1,2-diphenylethene 13 with nBuLi followed by addition of $p$-anisaldehyde. The synthesis of key dipyrrolic intermediate 17 was achieved by reaction of excess pyrrole with 15 in the presence of a catalytic amount of BF$_3$·Et$_2$O. In the final step, the acid-catalyzed condensation of 17 with pentafluorobenzaldehyde followed by oxidation with DDQ afforded the desired compound 19.

Scheme 1. Synthesis of meso-substituted di($p$-benz)homoporphyrins.

Different reaction conditions were trialed to obtain the maximum possible yield of compound 19. We observed the reaction of dipyrrole 17 with pentafluorobenzaldehyde in the presence of 1.0 equiv. of BF$_3$·Et$_2$O at room temperature for 15 h, providing the final compound 19 in 11% yield. Similarly, a reaction of compound 17 with pentafluorobenzaldehyde and 1.0 equiv.
of TFA yielded compound 19 in 12 % yield. However, the use of 2.5 equiv. acids (BF₃·Et₂O or TFA) significantly decreased the yield to 5–8 %. To further study the versatility of reaction conditions, we synthesized compounds 20 and 21. The synthesis of compound 20 started with the McMurry reaction of 1-(4-bromophenyl)ethanone (12) to yield 4,4′-(but-2-ene-2,3-diyldibis(bromobenzene) 14. Diol 16 and dipyrrole 18 were synthesized using the reaction conditions described earlier.[7b]

A condensation reaction of dipyrrole 18 with pentafluorobenzaldehyde yielded 20 in 13 % isolated yield. In a similar vein, compound 21 was afforded in 10 % yield using a reaction of dipyrrole 18 with 4-iodobenzaldehyde. The yields obtained in this project are in good agreement with reports documented in the literature.[6a,7b]

Building upon the progress made in synthetically accessing di(μ-benz)homoporphyrins, we extended our efforts towards the synthesis of the related di(μ-benzi)homoporphyrins. The synthesis of the target compounds 26, 27, and 28 is outlined in Scheme 2. In a similar manner to that outlined above, we started with the transformation of 1-(3-bromophenyl)ethanone 22 to 3,3′-(but-2-ene-2,3-diyldibis(bromobenzene) 23 using standard McMurry conditions.[16] Furthermore, a reaction of 23 with nBuLi and 4-anisaldehyde proceeded smoothly to access diol 24 in 83 % yield. A reaction of the diol 24 with 40 equiv. of pyrrole in the presence of BF₃·Et₂O gave the dipyrrole 25 in 46 % yield. A preliminary screen of the substrate scope was investigated by incorporating combinations of structural motifs such as pentafluorophenyl anthracenyl or 4-iodophenyl groups to access the macrocycles 26, 27, and 28.

The synthesized compounds were characterized using 1D/2D NMRs, MALDI-TOF-MS, UV/Vis spectroscopy, and single-crystal X-ray analysis. The NMR spectra in CDCl₃ and mass spectra of 19, 20, 21, 26, 27, and 28 are shown in Figures S1–S21 in the supporting information (SI). Figure 2 gives the 1H NMR spectrum of compound 19 and is consistent with the structure of 19 as being built of a TPE moiety linked with a meso-pentafluorophenyl dipyrromethene unit through two 4-methoxyphenylmethine bridges. The 1H NMR spectrum of 19 shows a significant downfield shift of the inner core NH at δ = 12.55 ppm. The β-pyrrolic protons appear with two sets of doublets (J = 5.2 Hz) at δ = 6.47 and 5.80 ppm. These preliminary details indicate that the effective π-conjugation is interrupted in the dibenzihomoporphyrin 19.

Figure 2. 1H NMR spectrum of compound 19 in CDCl₃.
These results are also supported by the 2D NMR spectra. The \(^1\text{H}-\text{H} \) COSY NMR spectrum of compound 19 in Figure 3 shows the correlation between the peaks; (i) 8.03 and 7.50 ppm, (ii) 7.01 and 6.80 ppm, (iii) 6.48 and 5.80. Overall, the spectral results for 19 are in close agreement with the reported non-aromatic porphyrin surrogates. Similar results were observed for the other synthesized porphyrin frameworks (20, 21, 26, 27, and 28).

Absorption spectra of 19, 20, 21, 26, 27, and 28 were recorded in CH\(_2\)Cl\(_2\) at 298 K. These compounds show two distinct absorptions; a strong sharp band (350–400 nm) and a weak broad band (550–800 nm), reflecting the non-aromatic nature of macrocyclic ring.\(^{[17a]}\) The latter band in compound 20 is ca. 10 nm red-shifted compared to compound 19, whereas the same band in 21 is ca. 7 nm red-shifted compared to 19. The long-wavelength absorbing band in the absorption spectra of di(m-benz)homo-porphyrins is blue-shifted compared to the corresponding di(p-benz)homo-porphyrins. These shifts and trends in absorption spectra reflect the combined effects of meso-substitution, 1,4-phenylene, and, 1,3-phenylene linkages. Figure 4 gives an example of the absorption spectrum of compound 19 and the respective protonated species. The addition of TFA to a solution of homobenziporphyrins resulted in a red-shift in their absorption spectra; for example, the long-wavelength absorbing band for 19 + TFA is ca. 150 nm red-shifted compared to 19. Similar trends were observed for compounds 20, 21, 26, 27, and 28; corresponding spectra are given in Figures S22–S23 in the SI.

The redshift upon protonation depends on the extent of the out-of-plane deformation of the macrocyclic core. Out-of-plane deformation leads to destabilization of the HOMOs followed by a reduction in the HOMO-LUMO gap, therefore, a redshift in absorption spectra observed.\(^{[17b]}\) Additionally, it was observed that porphyrins with electron-donating groups at meso-positions also exhibit large bathochromic shifts.\(^{[17c]}\) Therefore, the large red-shift upon protonation observed for dibenzihomoporphyrin derivatives is a combined result of protonation induced steric deformation of the macrocycle and electronic effect of the 4-methoxyphenyl groups.

Crystallography
The structures of 19, 20, and 27 were confirmed by single-crystal X-ray analysis. Compound 19 crystallized in the monoclinic lattice system with a \(P1\) space group (Figure 5). The dipyrromethene unit of the di(p-benz)homo-porphyrin 19 is planar and exhibits bond lengths between 1.30 Å to 1.45 Å which indicate the delocalization of the \(\pi\)-electrons. In contrast to the dipyrromethene unit, the \(p\)-phenylene units are out of the plane defined by the dipyrromethene moiety and the two meso-carbons, effectively interrupting \(\pi\)-conjugation in the macrocycle. The bond lengths in the 1,2-bisphenyl-1,2-bis-p-phenyleneethene unit are in the range of 1.47–1.48 Å, indicating more double bond than aromatic bond character. The angle...
between \( p \)-phenylene ring A and the dipyrromethene unit is 51.2(1)\(^\circ\) whereas the angle between \( p \)-phenylene ring B and the dipyrromethene unit is 54.7(1)\(^\circ\) (Figure 5).

![Figure 5. Top and side view of the molecular structure of compound 19 in the crystal.](image)

Compound 20 crystallized in the monoclinic space group \( P2_1/n \) (Figure 6). The crystal structure of compound 20 exhibits a similar non-planar conformation as described for compound 19. This shows that substitution at the ethylene unit (with either Ph or Me) did not affect the conformation of the macrocyclic core. The dipyrromethene unit in 20 is twisted as compared to the one in 19. The mean plane deviation of the atoms in the dipyrromethene unit in compound 20 is 0.036 Å while the angle between \( p \)-phenylene ring A and the dipyrromethene unit is 54.58(6)\(^\circ\) [50.30(7)\(^\circ\) for ring B].

![Figure 6. Top and side view of the molecular structure of compound 20 in the crystal.](image)

Di(\( m \)-benzil)homoporphyrin 27 crystallized in the monoclinic space group \( P2_1/c \) (Figure 7). The crystal structure analysis shows that the core is highly distorted when compared to di(\( p \)-benzil)homoporphyrins 19 and 20. Additionally, the anthracene unit is almost perpendicular to the dipyrromethene unit [76.44(4)\(^\circ\)]. The bond lengths of \( m \)-phenylene linkages indicate more double bond character as per the non-aromatic nature of the core. The angles between the \( m \)-phenylene rings and the dipyrromethene units are significantly larger than 19 and 20 [71.10(8)\(^\circ\) for ring A and 52.62(6)\(^\circ\) for ring B].

![Figure 7. Top and side view of the molecular structure of compound 27 in the crystal.](image)

Singlet Oxygen Quantum Yields

Singlet oxygen (\( ^1O_2 \)) is a key cytotoxic species generated during photodynamic therapy (PDT) for many photosensitizers. Hence, maximizing the production of \( ^1O_2 \) within malignant tissue can enhance the therapeutic value of a PDT drug or make the photosensitizers useful in photochemical reactions.\(^{12,18}\) Core-modified expanded porphyrins have been actively investigated for application to the photosensitizers. Expanded porphyrins exhibit absorption in NIR region, which is required for their use at the deepest possible tissue depths. The core modified expanded porphyrins are likely to have nonplanar skeleton and as a result triplet state quantum yield via intersystem crossing is enhanced.\(^{19}\) As shown above, these homobenziporphyrins exhibited a strong absorption band between 600–700 nm. In the following, we show that they act as efficient photosensitizers for the formation of singlet oxygen.

1,3-Diphenylisobenzofuran (DPBF), acts as a singlet oxygen trap by reacting with \( ^1O_2 \) to generate \( cis \)-dibenzoylbenzene.\(^{20}\) Thus, we employed the use of DPBF to measure the efficiency of the synthesized compounds (19, 20, 21, 26, 27, and 28). The decrease in absorbance of DPBF in the presence of di(\( p \)-benzil)homoporphyrins 19–21 and di(\( m \)-benzil)homoporphyrins 26–28 was recorded in DCM/MeOH (1:1) at a concentration of 0.13 mol L\(^{-1}\). The same concentration of 5,10,15,20-tetraphenylporphyrin (H\(_2\)TPP) was employed to calculate the relative quantum yields (\( \Phi_{\text{TPP}} = 0.62 \) in DCM).\(^{21}\) The relative singlet oxygen quantum yield (\( \Phi_{\text{BHP}} \)) for each of these homoporphyrins was calculated using the following equation (1):\(^{22}\)

\[
\Phi_{\text{BHP}} = \Phi_{\text{TPP}} \times S_{\text{BHP}}/S_{\text{TPP}}
\]

where \( \Phi \) represents quantum yield, \( S \) represents the slope, and BHP and TPP represent dibenzihomoporphyrin and 5,10,15,20-tetraphenylporphyrin, respectively.
Figure S27 and S28 represent the UV/Vis spectra of DPBF degradation in the presence of dipyridodiphenylporphyrinins. Figure 8 shows the decrease in DPBF absorption over time for 19, 20, 21, 26, 27, and 28. Determination of the singlet oxygen quantum yields in reference to H$_2$TPP revealed that compound 21 exhibited the lowest singlet oxygen quantum yield, whereas, compound 20 gave the highest value of quantum yield. Compound 20 exhibited the highest value of singlet oxygen quantum yield ($\Phi_20 = 0.23$) followed by compound 27 ($\Phi_27 = 0.14$), 19 ($\Phi_19 = 0.12$), 26 ($\Phi_26 = 0.12$) and 28 ($\Phi_28 = 0.07$). Compound 21 exhibited the lowest value of the quantum yield ($\Phi_{21} = 0.06$) as compared to the other synthesized compounds. The potency of compounds 19 and 20 is possibly due to fluorine atom insertion to their structures which has been known to confer a high level of singlet oxygen production making them potential entitites for photodynamic therapy.$^{[23]}$ Compound 27 has a significant singlet oxygen production due to the substitution of anthracene unit which has also been known to enhance the singlet oxygen production making them potential entities for PDT and phototherapy.$^{[23]}$ Compound 26 gave the highest value of quantum yield ($\Phi_26 = 0.14$), whereas compound 27 ($\Phi_27 = 0.12$), and 28 ($\Phi_28 = 0.14$) gave the highest value of quantum yield. Determination of the singlet oxygen production due to the substitution of anthracene unit which has also been known to enhance the singlet oxygen production making them potential entities for photodynamic therapy.$^{[23]}$ Compound 27 has a significant singlet oxygen production due to the substitution of anthracene unit which has also been known to enhance the singlet oxygen production making them potential entities for PDT and phototherapy.$^{[23]}$

**Experimental Section**

**General Information:** Condensation reactions were carried out under an argon atmosphere. Reactions involving moisture and/or air-sensitive reagents were carried out in pre-dried glassware and with standard Schlenk line techniques. All commercial reagents and anhydrous solvents were used as received from vendors (Fischer Scientific, and Sigma Aldrich). Dichloromethane (CH$_2$Cl$_2$) was dried with P$_2$O$_5$. Yields refer to chromatographically and spectrscopically (1H NMR) homogeneous material unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) and absorption spectroscopy. TLC carried out on silica gel plates. Gel silica 60 *Merck*, 230–400 mesh, or aluminum oxide (Brockmann Grade I) were used for flash column chromatography. Room temperature refers to 20–25 °C.

**Instruments:** Melting points are uncorrected and were measured with a Digital Stuart SPM 10 melting point apparatus. NMR spectra were recorded using Bruker DPX400 (400 MHz for 1H NMR, 101 MHz for $^{13}$C NMR, 377 MHz for $^{19}$F NMR), Bruker AV 600 (600 MHz for 1H NMR, 151 MHz for $^{13}$C NMR, 564 MHz for $^{19}$F NMR), and Bruker AV 400 (400 MHz for 1H NMR, 101 MHz for $^{13}$C NMR, 377 MHz for $^{19}$F NMR) instruments. Chemical shifts are given in ppm and referenced to the residual peak of the deuterated NMR solvent. The assignment of the signals was confirmed by 2D spectra (COSY, HMBC, HSQC). ESI mass spectra were acquired in positive or negative modes as required, using a Micromass time-of-flight mass spectrometer (TOF), or a Bruker microTOF-Q II spectrometer interfaced to a Dionex UltiMate 3000 LC. APCI experiments were carried out on a Bruker microTOF-Q III spectrometer interfaced to a Dionex Ultimate 3000 C or direct insertion probe in positive or negative modes. UV/Vis spectra were recorded in solutions using a Specord 250 spectrophotometer from Analytik Jena (1 cm path length quartz cell).

**Single Crystal X-ray Crystallography:** The crystals of compounds 19, 20, and 27 were grown following the protocol developed by Hope by dissolving the dibenzihomoporphyirins in DCM and layering with either MeOH or hexane for liquid diffusion over time.$^{[23]}$ Single crystal X-ray diffraction data for were collected on a Bruker APEX 2 DUO CCD diffractometer by using graphite-monochromated MoK$_\alpha$ ($\lambda = 0.71073$ Å) radiation (19 and 20) and Incoatec IIS CuK$_\alpha$ ($\lambda = 1.54178$ Å) (27) radiation. Crystals were mounted on a MiTeGen MicroMount and collected at 100(2) K by using an Oxford Cryosystems Cobra low-temperature device. Data were collected by using omega and phi scans and were corrected for Lorentz and polarization effects by using the APEX software suite.$^{[26]}$ 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.$^{[27]}$ Hydrogen atoms were generally placed in geometrically calculated positions and refined using a riding model. Details of data refinements are mentioned in Table S1. Mercury3.7$^{[28]}$ and Olex2 were used for preparation of the images.$^{[26]}$ Refinement details of 19: Pyrrole hydrogen were located on the difference map and refined as semi-free with restraints (DFIX). Refinement details of 27: Pyrrole hydrogen atoms were located on the difference map and refined using constraints (DFIX). A partially occupied DCM (40 %) was located in the void and was refined using a rigid group and restraints (SIMU).

**Conclusion**

In summary, the present study provides insight into the design of a new class of porphyrin-inspired macrocycles, i.e. dipyridodiphenylporphyrinins. These macrocycles were accessed using [3+1] condensation reactions between dipyrroles and aryl aldehydes. To compare the electronic properties, phenylene rings of compounds 19 and 20 were incorporated in the macrocycle using a riding model. Details of data refinements are mentioned in Table S1. Mercury3.7$^{[28]}$ and Olex2 were used for preparation of the images.$^{[26]}$ Refinement details of 19: Pyrrole hydrogen were located on the difference map and refined as semi-free with restraints (DFIX). Refinement details of 27: Pyrrole hydrogen atoms were located on the difference map and refined using constraints (DFIX). A partially occupied DCM (40 %) was located in the void and was refined using a rigid group and restraints (SIMU).
Singlet oxygen studies: The photo-irradiation of the samples was performed in quartz cuvettes (2×1×1 cm) under irradiation via a polychromatic light source (Philips, 15V–150 W lamp), equipped with a 400 nm cut-off filter (Schott GC 400) and a 532 nm diode-pumped solid state green laser system (CW532-0.4, average intensity of 10 mW cm⁻²). The temperature of the sample was maintained at 18 °C using a Peltier element (Cary Peltier 1×1 cell holder). Relative singlet oxygen (¹⁰O₂) yields (Φₛₛ) were calculated from the degradation slopes of the 1,3-diphenylisobenzofuran (DPBF) conversion in the presence of different photosensitizers. The absorbance of DPBF was observed after each irradiation. Singlet oxygen experiments were repeated twice and Φₛₛ values were observed in a standard deviation range of ± 0.05.

Compounds 13–18, and 23–25 were synthesized according to procedures reported in the literature.[27][28]

General Procedure 1: Dipyrrole (1.0 equiv.) was added to a solution of ary aldehyde (1.0 equiv.) in DCM followed by addition of 1.0 equiv. of BF₃·OEt₂ or TFA. The reaction mixture was stirred at room temperature for 15 h under inert atmosphere. DDQ (200 mg, 0.345 mmol) and DDQ (240 mg, 1.06 mmol) in 200 mL of CH₂Cl₂. The crude material was purified by alumina column chromatography (Brockmann grade I). Yield = 27 mg, 11%. M.p. 192 °C; δ = 159.8, 159.5, 148.5, 148.3, 144.5, 140.1, 135.5, 134.8, 134.0, 133.8, 131.8, 130.1, 126.8, 126.3, 126.0, 55.2, 18.5 ppm; UV/Vis (CH₂Cl₂): ε_max (log ε) = 376(4.65), 661(4.15); HRMS (MALDI-TOF) m/z calcd. for C₃₈H₃₈N₂O₂ [M + H⁺]⁺ 789.1978, found 789.1953.

Compound 26: Synthesized via General Procedure 1 from dipyrrole 25 (200 mg, 0.345 mmol), C₇H₅IO (72 mg, 0.345 mmol), TFA (24 µL, 0.345 mmol), and DDQ (240 mg, 1.06 mmol) in 200 mL of CH₂Cl₂. The crude material was purified by alumina column chromatography (Brockmann Grade I). Yield = 41 mg, 16%. M.p. 212 °C; δ = 0.45 (SiO₂, CH₂Cl₂/CH₃OH, 3:2, v/v); 1H NMR (400 MHz, CDCl₃): δ = 7.01 (d, J = 7.3 Hz, 4H), 6.92 (d, J = 8.6 Hz, 2H), 4.44 (d, J = 5.1 Hz, 4H), 5.96 (d, J = 4.7 Hz, 1H), 3.83 (s, 6H), 2.07 (s, 6H) ppm; 13C NMR (101 MHz, CDCl₃): δ = 143.6, 137.3, 133.2, 132.9, 130.3, 128.7, 113.2, 55.2, 18.5 ppm; UV/Vis (CH₃Cl): λ_max (log ε) = 378(4.65), 661(4.15); HRMS (MALDI-TOF) m/z calcd. for C₆₇H₃₈Cl₅O₂ (M + H⁺)⁺ 1130.2713, found 1130.2705.

Compound 27: Synthesized via General Procedure 1 from dipyrrole 25 (200 mg, 0.345 mmol), C₇H₅IO (72 mg, 0.345 mmol), TFA (26 µL, 0.345 mmol) and DDQ (240 mg, 1.06 mmol) in 200 mL of CH₂Cl₂. The crude material was purified by alumina column chromatography (Brockmann Grade I). Yield = 34 mg, 13%. M.p. 192 °C; δ = 0.60 (SiO₂, CH₃Cl); 1H NMR (400 MHz, CDCl₃): δ = 8.53 (s, 1H), 8.26 (d, J = 8.6 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.8 Hz, 1H), 7.51–7.39 (m, 4H), 7.38–7.30 (m, 1H), 7.11 (d, J = 25.5 Hz, 5H), 6.98 (s, 2H), 6.80 (d, J = 8.3 Hz, 3H), 6.74 (s, 1H), 6.63 (d, J = 4.3 Hz, 2H), 5.82 (d, J = 3.7 Hz, 2H), 3.79 (s, 6H), 2.10 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ = 159.4, 144.5, 133.9, 133.6, 131.8, 130.1, 128.9, 126.0, 125.8, 125.6, 113.0, 55.2, 21.1 ppm; UV/Vis (CH₃Cl): λ_max (log ε) = 346(4.39), 641(4.24); HRMS (MALDI-TOF) m/z calcd. for C₅₆H₄₃Cl₂O₂F₂ (M + H⁺)⁺ 753.2540, found 753.2517.

Compound 28: Synthesized via General Procedure 1 from dipyrrole 25 (200 mg, 0.345 mmol), C₅H₅N (80 mg, 0.345 mmol), TFA (26 µL, 0.345 mmol) and DDQ (240 mg, 1.06 mmol) in 200 mL of CH₂Cl₂. The crude material was purified by alumina column chromatography (Brockmann Grade I). Yield = 34 mg, 13%. M.p. 192 °C; δ = 0.60 (SiO₂, CH₃Cl); 1H NMR (400 MHz, CDCl₃): δ = 8.53 (s, 1H), 8.26 (d, J = 8.6 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.8 Hz, 1H), 7.51–7.39 (m, 4H), 7.38–7.30 (m, 1H), 7.11 (d, J = 25.5 Hz, 5H), 6.98 (s, 2H), 6.80 (d, J = 8.3 Hz, 3H), 6.74 (s, 1H), 6.63 (d, J = 4.3 Hz, 2H), 5.82 (d, J = 3.7 Hz, 2H), 3.79 (s, 6H), 2.10 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ = 159.4, 144.5, 133.9, 133.6, 131.8, 130.1, 128.9, 126.0, 125.8, 125.6, 113.0, 55.2, 21.1 ppm; UV/Vis (CH₃Cl): λ_max (log ε) = 346(4.39), 641(4.24); HRMS (MALDI-TOF) m/z calcd. for C₆₇H₃₈Cl₅O₂ (M + H⁺)⁺ 1130.2713, found 1130.2705.

Supporting Information (see footnote on the first page of this article): Spectroscopic data of all compounds, singlet oxygen production measurements, and X-ray crystallographic data.

Deposition Numbers 2025181 (for 19), 2025182 (for 20) and 2025183 (for 27) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.
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