3-Cyclobutenyl-1,2-dione-substituted Porphyrins. 2. A Simple and General Entry to Quinone−Porphyrin−Porphyrin−Quinone Tetrads and Related Molecules

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The synthesis of *meso*-linked quinone−porphyrin−porphyrin−quinone tetrads has been accomplished by the simple treatment of a CH_2Cl_2 solution of zincated 5-substituted-10,20-diphenylporphyrins (where the substituent = 3-cyclobutenyl-1,2-dione, various quinonyl derivatives, and *p*-anisyl) with 2,3-dichloro-5,6-dicyanoquinone (DDQ). The zincated porphyrinic quinones were synthesized from 5-(3-cyclobutenyl-1,2-dione)-10,20-diphenylporphyrin(Zn). The *meso*-linked dimer of 5-(3-cyclobutenyl-1,2-dione)-10,20-diphenylporphyrin(Zn) was also shown to be a useful precursor to *meso*-linked quinone−porphyrin−porphyrin−quinone tetrads. This DDQ-based oxidative dimerization appears to be general and effective for various zincated 5-substituted-10,20-diphenylporphyrins bearing both electron-withdrawing and -donating substituents. The oxidative dimerization was very sensitive to the reaction solvent (dimerization occurred in CH_2Cl_2, not in THF) and required the zincated porphyrins (the corresponding free base porphyrins did not undergo dimerization). When this solvent effect was applied to the reaction of I_2/AgO_2CCF_3 with zincated porphyrins, either the dimeric porphyrins or iodoporphyrins could be selectively prepared simply by selecting methylene chloride or THF as the reaction solvent, respectively.

Introduction

Multichlorophyll arrays are elegantly used by photosynthetic organisms in collecting, transferring, and converting light energy into electrochemical potential energy for ATP synthesis.[1−6] In these organisms the chlorophyll molecules are arranged within the framework of polypeptide backbones in specific geometries in order to perform their biological functions. The geometric arrangements impart to the arrays new properties different from those of their monomers. The beauty and the biological functions of these multichlorophyll structures stimulated tremendous interest in the study of multiporphyrin arrays,[3,7−14] which may have great potential as molecular electronic devices[15,16] and nonlinear optical materials.[11]

As simple multiporphyrin arrays, dimeric porphyrins with double bond,[17,18] aryl,[14,19−21] and triple bond[10,22,23] linkages have been studied extensively, and many of these compounds possess intriguing properties.[10,11,22−24] The simplest of dimeric porphyrins, those directly linked at a meso position, were unknown until the first rational synthesis by Susumu et al. in 1996.[25] Since then several additional papers describing the synthesis of dimeric porphyrins have appeared in the literature.[26−30] The synthetic methods include Smith's condensation of a dipyrromethane derivative with tetrakis(5-formyl-2-pyrrolyl)ethene,[26] and the oxidative dimerization of monomeric porphyrins chemically with silver salts[27,28] and

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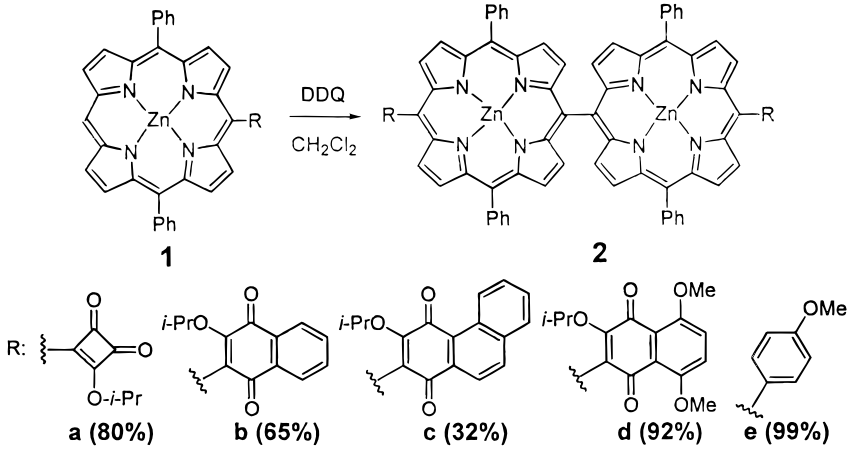
Scheme 1



electrochemically.[29,31] Most recently, directly linked bisporphyrins have been prepared by the 2,3-dichloro-5,6-dicyano-1,4-benzoquinone-induced oxidative dimerization of the anionic adducts formed upon addition of an organolithium reagent to a 5,15-disubstituted free base porphyrin.[30]

The use of cyclobutenedione substituted porphyrins for the synthesis of structurally diverse quinone-porphyrin dyads and quinone−porphyrin−quinone triads has been recently demonstrated.[32] This method allows the systematic synthesis and modification of porphyrinic quinones. While investigating this new chemistry, a new and simple procedure for the oxidative dimerization of zincated substituted porphyrins was discovered and is reported herein.

Results and Discussion

Treatment of 15-unsubstituted 5-(3-cyclobutenyl-1,2-dione)-10,20-diphenylporphyrin(Zn) **1a** with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in methylene chloride at room temperature afforded the *meso*-linked dimeric porphyrin **2a** in 80% isolated yield (Scheme 1). Similarly, the reactions of the 15-unsubstituted quinone diphenylporphyrin(Zn) derivatives **1b**−**d** and the *p*-anisyl analogue **1e** with DDQ in methylene chloride afforded the corresponding *meso*-linked dimeric porphyrins **2b**−**e** (Scheme 1).

The structures of these dimeric zincated porphyrins were determined by ^{1}H and ^{13}C NMR, FABMS, UV, and IR spectroscopy. For example, upon oxidation of **1b** to the dimer **2b**, the meso proton signal of **1b** disappeared, and one of the four β-proton signals of **1b** was shifted upfield by 0.6 ppm, the latter observation suggesting that these protons are located in the shielding region of the adjacent porphyrin ring.[27] This is typical for structures of type **2** due to the orthogonal relationship of the two porphyrin rings. Furthermore, close examination of the β-proton signals of **2b**−**d** revealed eight different doublets with very close chemical shifts, indicating the presence of eight different β-protons. This suggests that each of these compounds is a mixture of a pair of diastereomers, due to restricted rotation about both the porphyrin−porphyrin and the porphyrin−quinone single bonds at room temperature. The simplicity of the spectra of **2a** and **2e** support this explanation, since the 3-cyclobutenyl-1,2-dione substituent of **2a** rotates freely at room temperature (the quinone moieties of **2b**−**d** do not),[32] and the *p*-anisyl substituent of **2e** is symmetrical. The FAB mass spectrum of **2b** gave $M^+ = 1478.5$, which corresponds to the formula weight of the dimer **2b**; in addition, a cluster of peaks which had the same pattern as one calculated based upon the isotopic distribution of the formula was observed.

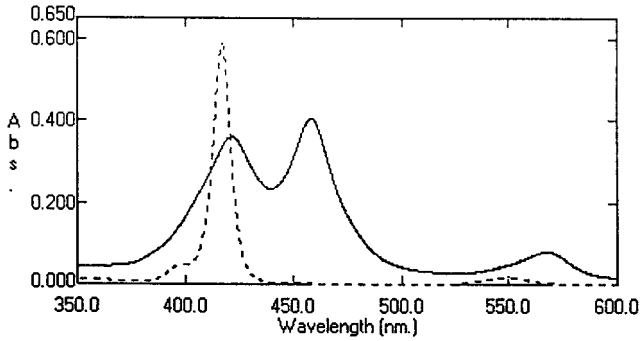


Figure 1. UV−visible spectrum of **1b** and dimer **2b**. Data was acquired at room temperature. **1b**: dotted line. **2b**: solid line.

Additional evidence for the structure of the dimer **2b** was obtained from its UV−visible spectrum,[25−27,29,31] which showed split Soret absorption bands at 420 and 456 nm of nearly equal intensity (Figure 1). This pattern of the B-band absorption is very typical for porphyrin dimers in which the two orthogonal porphyrin chromophores are strongly coupled.[21,25,33−36] On the basis of spectroscopic data, the structures of compounds **2a** and **2c**−**e** were determined in the same fashion as **2b** above. The UV−visible absorption data for these dimeric compounds are shown in Table 1.

Porphyrin **1e** bearing an electron-donating *p*-anisyl substituent also reacted smoothly with DDQ in methylene chloride and afforded **2e** in quantitative yield. In fact,

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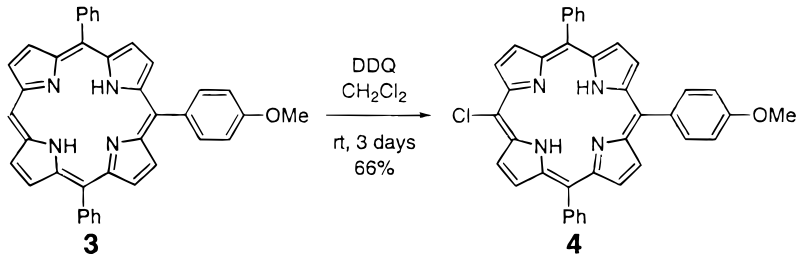
Scheme 2



Scheme 3

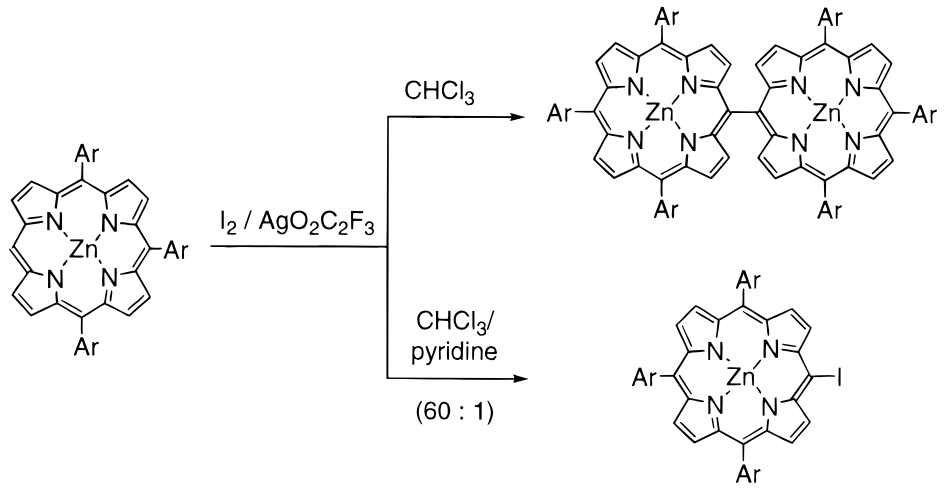


Table 1. UV−Visibile Absorptions of Compounds 2a−e[a]

compound	B-bands λ_{max} (nm)	log ϵ	Q-bands λ_{max} (nm)	log ϵ
2a	457.0	5.36	607.5	3.89
	420.0	5.32	563.5	4.64
2b	457.0	5.43	607.5	3.97
	420.0	5.39	563.5	4.72
2c	456.0	4.87	563.0	4.15
	420.5	4.88		
2d	456	4.87	615.0	3.51
	418.0	4.79	565.0	4.20
2e[b]	457.0	5.18	607.0	3.56
	420.0	5.04	565.0	4.39

[a] Data acquired at room temperature in Et_2O solution, $c = 1.0-3.4 \times 10^{-6}$ M. [b] Acquired in 10% methylene chloride/Et_2O.

this compound was more reactive than compounds **1a**−**d**. Attempts to form dimers from the free-base porphyrins by this method were not successful, suggesting that the zincated porphyrins are critical for this oxidative coupling reaction. For example, the reaction of 4-methoxyphenyl-10,20-diphenylporphyrin **3** with 4.6 equiv of DDQ in methylene chloride at room temperature only afforded 5-chloro-15-(4-methoxyphenyl)-10,20-diphenylporphyrin **4** in 66% yield along with recovered starting material (34%) after 3 days (Scheme 2). There was no evidence of dimer formation in this reaction. The chlorinated product might be formed from a Cl radical generated under the reaction conditions. This result demonstrates the importance of the metalated porphyrin in controlling the mode of reaction.[37] The effects of metal ions on the reactivities of porphyrins are well documented for other types of reactions.[17,38−41]

In 1997 it was disclosed that treatment of zincated 5,-15-diarylporphyrins in chloroform with $AgPF_6$ and a catalytic amount of I_2 led to the formation of a mixture of *meso*-joined porphyrin dimers, trimers, and tetramers.[27] It was subsequently reported that the presence of a very small amount of pyridine in the reaction mixture completely changed the reaction course, leading to iodination rather than oxidative dimerization (Scheme 3).[42] The authors suggested that generation of an *N*-iodopyridinium species might be responsible for the formation of the iodoporphyrin.

It seems more likely that coordination of pyridine to zinc[35,43,44] might be responsible for altering the course of the reaction. In fact, when the DDQ oxidation of **1a** was carried out in THF, a coordinating solvent,[45] no dimerization reaction was observed after 21 h. Pursuing this observation, a dramatic effect of solvent on the silver-promoted oxidative dimerization of zincated porphyrins was also observed in the reaction of **1a** (Table 2). In the noncoordinating solvents CH_2Cl_2 and toluene, the reaction of **1a** with I_2/AgO_2CCF_3 gave the porphyrin dimer **2a** as the major product. In contrast, in either THF or 1,4-dioxane the iodoporphyrin **5** was either the major or the exclusive product, depending on the order of addition of reactants and solvent. These results are consistent with the conjecture that coordination of pyridine to zinc

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Scheme 4

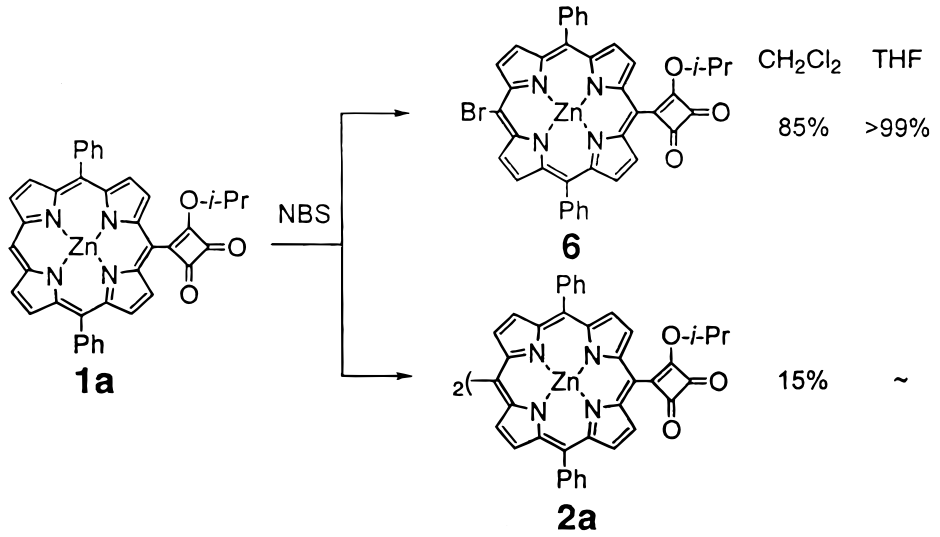
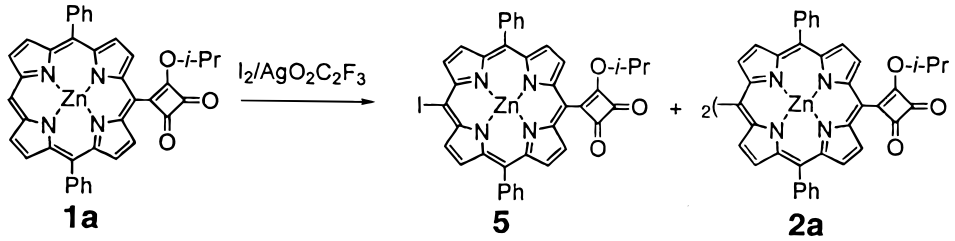


Table 2. Effect of Solvent on Product Distribution of the Reaction of 1a with I_2/AgO_2CCF_3



solvent	iodoporphyrin **5**, %	dimer **2a**, %
CH_2Cl_2	6	92
toluene	19	76
THF	>99	0
dioxane	83	13

is responsible for the previously reported suppression of the oxidative coupling reaction of zincated porphyrins by pyridine.[42]

It is difficult to rationalize the observed solvent effect without knowing the exact mechanism of this oxidative dimerization reaction. However, if the dimerization follows a one-electron oxidation mechanism, coordination of solvent to the zinc might preclude an inner-sphere, one-electron oxidation of the zincated porphyrin by suppressing coordination of the oxidant to the zinc.

Simply through the choice of an appropriate reaction solvent, the indicated solvent effect enables the synthesis of either iodoporphyrin **5** or porphyrin dimer **2a** with nearly complete selectivity using the reagent system I_2/AgO_2CCF_3 (Table 2). Iodoporphyrins resulting from this process could be very useful substrates in various cross-coupling strategies with less reactive coupling reagents. This solvent effect has also been applied to other reactions of porphyrins that are complicated by the formation of dimers. For example, the reaction of **1a** with *N*-bromosuccinimide (NBS) in CH_2Cl_2 afforded 85% of the desired bromoporphyrin **6** along with 15% of the dimer **2a**. When the same reaction was carried out in THF, the bromoporphyrin was obtained in quantitative yield (Scheme 4). Although NBS is mainly used as a brominating reagent, it also participates in one-electron oxidation reactions,[46] which might explain the formation of **2a** from the reaction of **1a** with NBS in CH_2Cl_2 (Scheme 4).

Qualitative comparison of the rates of the dimerization reactions revealed that porphyrins bearing electron-withdrawing groups were less reactive than the ones with electron-donating substituents. For example, dimerization of **1e** was faster than **1b**−**d**. The latter were all more reactive than **1a**. Interestingly, all porphyrins in this study, with the exception of 5-bromo-10,20-diphenylporphyrin(Zn), underwent oxidative dimerization. The oxidative dimerization of 5-bromo-10,20-diphenylporphyrin-(Zn) with DDQ in CH_2Cl_2 was compromised by rapid precipitation of a solid from the reaction mixture. This solid was not soluble in chloroform or methylene chloride, but slowly dissolved in dioxane or a mixture of Et_2O and CH_2Cl_2. The ^1H NMR spectrum in DMSO-d_6 was identical to pure 5-bromo-10,20-diphenylporphyrin(Zn) suggesting that the solid might be a molecular complex of the porphyrin and DDQ. 5-Bromo-10,20-diphenylporphyrin-(Zn) also was not oxidatively dimerized with silver salts.[28]

Attempts to synthesize unsymmetrical dimers from the oxidative coupling of two different porphyrins failed. Various reactions afforded only symmetrical dimers. For example, when an equimolar mixture of compounds **1a** and **1e** in CH_2Cl_2 was treated with DDQ, **1e** was consumed within 10 min and, at that point, **2e** was produced as the exclusive dimer. As the reaction progressed further, dimer **2a** then formed. An attempt to

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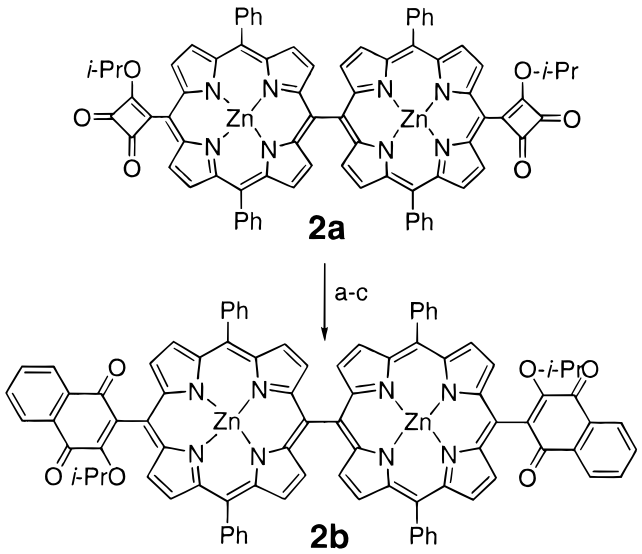
Scheme 5[a]



[a] (a) PhLi in THF; NH_4Cl workup; (b) reflux in xylene; (c) oxidize 68% overall.

induce oxidative-coupling between a free-base porphyrin and a zincated porphyrin only led to dimers of the zincated porphyrin and recovery of the free-base porphyrin. These observations suggest that the dimerization proceeds through the coupling of two zincated porphyrin radical cations, and not by the reaction of a zincated porphyrin radical cation with a neutral zinc porphyrin.

Like the simpler porphyrinic cyclobutenedione monomers,[32] compound **2a** is a potentially useful precursor to dimeric porphyrin−quinones. This is demonstrated by the formation of **2b** in 68% overall yield from the reaction of **2a** with phenyllithium followed by aqueous workup, thermolysis, and oxidation (Scheme 5).

Conclusions

In summary, a simple and general methodology is described that allows the controlled preparation of symmetrical, dimeric *meso*-linked porphyrinic systems bearing cyclobutenyl-1,2-diones, quinones, and aryl groups as substituents. Those bearing cyclobutenedione and quinone substituents represent a class of new acceptor−donor−donor−acceptor molecules.

Solvents play a very important role in the dimerization reaction. While the reactions of zincated porphyrins with DDQ in CH_2Cl_2 gave the corresponding dimeric porphyrins, this dimerization reaction did not occur in THF. When this solvent effect was applied to the reaction of I_2/AgO_2CCF_3 with zincated porphyrins, complete selectivity for the synthesis of either dimeric porphyrins or iodoporphyrins was achieved simply by selecting the correct solvent: methylene chloride gave the oxidative dimers and THF led to production of the iodoporphyrins.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded in deuterated solvents using solvent residuals as internal references ($CDCl_3$: 7.26 ppm ^1H, 77.0 ppm ^{13}C; acetone-d_6: 2.05 ppm ^1H, 206.7 ppm ^{13}C; DMSO-d_6: 2.50 ppm ^1H, 39.5 ppm ^{13}C). Melting points (uncorrected) were determined using a Thomas-Hoover capillary oil-immersion melting point apparatus. Silica gel 60, 230−400 Mesh (for Flash and Baeckstrom[47]] chromatography) was purchased from EM Science. Silica gel analytical plates with F-254 indicator were obtained from Merck and were visualized with UV light, phosphomolybdic acid, or iodine stain. Tetrahydrofuran (THF) was sparged with nitrogen and then dried over 4 Å molecular sieves to a water content of ≤50 ppm, as measured by Karl Fischer titration. Toluene was dried over molecular sieves overnight before use. All reactions were conducted under nitrogen unless noted otherwise.

Starting Materials. *N*-Bromosuccinimide, AgO_2CCF_3, I_2, $Zn(OAc)_2$, and 2,3-dichloro-5,6-dicyanoquinone (DDQ) were purchased from commercial sources and used without purification. The monomeric porphyrinic cyclobutenedione **1a**, porphyrinic quinones **1b**−**d**, 5-(*p*-anisyl)-10,20-diphenylporphyrin **3**, and 5-bromo-10,20-diphenylporphyrin(Zn) were synthesized by the procedure reported in a related paper.[32]

Preparation of Porphyrin Dimers by Oxidation with DDQ. Compound 2a. A mixture of porphyrin cyclobutenedione **1a** (110 mg, 0.166 mmol, 1.00 equiv) in methylene chloride (50 mL) and DDQ (370 mg, 1.630 mmol, 9.82 equiv) was stirred at room-temperature overnight under nitrogen. After removal of the solvent, the crude product was isolated by chromatography (Flash column, silica gel, 2 × 8 cm, hexanes−acetone 10:1 to 3:1) to afford **2a**, a green solid (88 mg, 0.066 mmol) in 80% yield. TLC (silica gel, hexanes acetone (3:1), R_f = 0.2); mp > 250 °C (THF−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1784 (s), 1754 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.31 (d, J = 4.8 Hz, 4 H), 9.08 (d, J = 4.8 Hz, 4 H), 8.62 (d, J = 4.8 Hz, 4 H), 8.20 (br d, J = 8.0 Hz, 8 H), 8.09 (d, J = 4.8 Hz, 4 H), 7.68 (m, 12 H), 5.93 (sept, J = 6.4 Hz, 2 H), 1.64 (d, J = 6.0 Hz, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.1, 194.9, 194.6, 188.0, 182.7, 154.5, 150.6, 147.6, 142.1, 134.5, 134.2, 133.4, 132.1, 130.1, 127.7, 126.6, 123.6, 103.1, 80.5, 23.0. UV−Vis λ_{max} (log ϵ, Et_2O) 420.0 (5.32), 457.0 (5.36), 563.5 (4.64), 607.5 (3.89) nm; LowRes FAB MS: 1325.7; HRMS (FAB) Calcd for $C_{78}H_{50}O_6N_8Zn_2$: 1322.2435. Found: 1322.2471.

Formation of 2a from 1a with I_2/AgO_2CCF_3 in Methylene Chloride. To a solution of **1a** (13 mg, 0.020 mmol, 1.0 equiv) in methylene chloride (2 mL) was added a mixture of I_2 (7 mg, 0. 026 mmol, 1.3 equiv) and AgO_2CCF_3 (6 mg, 0.026 mmol, 1.3 equiv) in methylene chloride (3 mL) at room temperature. After 5 min more, AgO_2CCF_3 (4 mg, 0.013 mmol, 0.65 equiv) was added to the reaction, which then proceeded to completion within 2 min. Methylene chloride (20 mL) was added to the mixture, which was washed once with aqueous $NaHCO_3$ and twice with water and then dried over sodium sulfate and separated by a vacuum column (SiO_2, 2 × 2.5 cm, 5:1 hexanes−acetone to elute 12 mg of **5**, 5:3 hexanes−acetone to elute 1 mg of **2a**).

Compound 2b. To the porphyrin quinone **1b** (22 mg, 0.03 mmol, 1.00 equiv) in methylene chloride (5 mL) was added DDQ (8 mg, 0.036 mmol, 1.2 equiv), and the mixture was stirred at room temperature for 30 min. After evaporation of the solvent, the reaction mixture was separated by chromatography (preparative TLC, silica gel, 20 × 20 cm, hexanes−acetone, 1:1). The product **2b** was obtained as a purple solid (14 mg, 0.01 mmol, 65%). TLC (silica gel, hexanes−acetone (3:1), R_f = 0.07); mp > 250 °C (THF-hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1672 (s), 1653 (m), 1599 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.21 (br d, J = 4.8 Hz, 4 H), 8.99 (d, J = 4.8 Hz, 2 H), 8.98 (d, J = 4.8 Hz, 2H), 8.64 (d, J = 4.4 Hz, 2H), 8.62 (d, J = 4.8 Hz, 2 H), 8.42 (dd, J = 7.6, 1.6 Hz, 2 H), 8.29 (dd, J = 7.6, 1.6 Hz, 2 H), 8.25−8.24 (*m*, 4 H), 8.15-8.13 (m, 4 H), 8.09 (d, J = 4.4 *Hz*, 2H), 8.08 (d, J = 4·4 Hz, 2H), 7.95−7.87 (m, 4 H), 7.66 (m, 12 H), 4.68 (sept, J = 6.0 Hz, 2 H), 0.69 (d, J = 5.6 Hz, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.0, 182.9, 158.9, 154.7, 154.6, 150.6, 150.0, 149.9, 149.2, 142.5, 134.5, 134.2, 132.9, 132.4, 131.8, 130.4, 127.2, 126.4, 122.0, 121.9, 120.4, 109.5, 22.8. 22.8. UV−Vis λ_{max} (log ϵ, Et_2O) 420.0 (5.39), 457.0 (5.43), 563.5 (4.72), 607.5 (3.97) nm; LowRes FAB MS: 1478.5. HRMS (FAB) Calcd for $C_{90}H_{58}O_6N_8Zn_2$: 1474.3062. Found: 1474.3027.

(47) Purchased from Baeckström SEPARO AB, Larsbergsvägen 24, S-181 39 Lindingö, Sweden.

From Compound 2a. To a 25 mL round-bottomed flask were placed **1a** (26 mg, 0.02 mmol) and THF (3 mL), and PhLi (0.501 M in THF, 0.26 mL) was added to the solution at −78 °C under nitrogen. As judged by TLC (hexanes−acetone 3:2), the starting material disappeared in a few minutes, and the reaction was quenched with saturated NH_4Cl-H_2O at −78 °C. The reaction was allowed to warm to room temperature and was extracted with ether. The ether extract was dried over sodium sulfate, evaporated, taken up in xylene, and heated at 150 °C under nitrogen for 1 h. The solution was then cooled to room temperature and stirred overnight under air. The product (20 mg, 68%) was isolated by preparative TLC (silica gel, 2:3 acetone−hexanes).

Compound 2c. Following the same procedure for **2b**, the porphyrin quinone **1c** (54 mg, 0.068 mmol, 1.00 equiv) in methylene chloride (20 mL) was treated with DDQ (70 mg, 0.308 mmol, 4.53 equiv). The product (17 mg, 0.011 mmol, 32%) was obtained as a purple solid after chromatography (flash column, silica gel, 2 × 7 cm, hexanes−acetone gradient, 10:1 to 2:1). TLC (silica gel, hexanes−acetone (3:1), $R_f = 0.3$); mp > 250 °C (THF−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1731 (w), 1650 (m), 1601 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.77 (d, $J = 8.4$ Hz, 2 H), 9.28 (d, $J = 4.8$ Hz, 4 H), 9.03 (d, $J = 4.8$ Hz, 2 H), 9.02 (d, $J = 4.8$ Hz, 2 H), 8.68 (d, $J = 4.8$ Hz, 2 H), 8.65 (d, $J = 4.8$ Hz, 2 H), 8.42 (d, $J = 8.4$ Hz, 2 H), 8.34 (d, $J = 8.4$ Hz, 2 H), 8.28 (d, $J = 5.6$ Hz, 2 H), 8.27 (d, $J = 6.0$ Hz, 2 H), 8.18 (br d, $J = 6.0$ Hz, 4 H), 8.14 (d, $J = 4.8$ Hz, 2 H), 8.12 (d, $J = 4.4$ Hz, 2 H), 8.06 (d, $J = 8.4$ Hz, 2 H), 7.79 (t, $J = 7.6$ Hz, 2 H), 7.76 (t, $J = 7.6$ Hz, 2 H), 7.67 (m, 12 H), 4.61 (sept, $J = 5.6$ Hz, 2 H), 0.76 (d, $J = 6.0$ Hz, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.8, 185.3, 159.8, 154.7, 154.6, 150.6, 150.0, 149.9, 149.4, 142.6, 142.5, 136.6, 135.6, 134.5, 134.2, 134.1, 134.0, 132.9, 132.0, 131.8, 130.7, 130.5, 130.3, 130.1, 129.0, 128.7, 127.9, 127.5, 126.5, 126.4, 122.8, 122.1, 122.0, 120.4, 109.1, 76.5, 22.8.UV−Vis λ_{max} (log ϵ, Et_2O) 420.5 (4.88), 456.0 (4.87), 563.0 (4.15) nm; FAB MS: 1573.7. HRMS (FAB) Calcd for $C_{98}H_{62}O_6N_8Zn_2$: 1574.3375. Found: 1574.3423.

Compound 2d. The reaction of porphyrin quinone **1d** (10 mg, 0.013 mmol, 1.00 equiv) in methylene chloride (2 mL) with DDQ (7 mg, 0.030 mmol, 2.31 equiv) at room temperature for 1 h afforded the product **2d** as a purple solid (10 mg, 0.006 mmol) in 92% yield. TLC (silica gel, hexanes−acetone, $R_f = 0.07$); Chromatographic purification (preparative TLC, silica gel, 20 × 20 cm, hexanes−acetone 1:1); mp > 250 °C (hexanes−THF, diffusion). IR (KBr pellet, cm^{-1}): 1730 (m), 1664 (m), 1603 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.21 (d, $J = 4.8$ Hz, 2 H), 9.20 (d, $J = 4.8$ Hz, 2 H), 8.98 (d, $J = 4.8$ Hz, 2 H), 8.96 (d, $J = 4.8$ Hz, 2 H), 8.65 (d, $J = 4.8$ Hz, 2 H), 8.60 (d, $J = 4.8$ Hz, 2 H), 8.26 (m, 4 H), 8.17 (m, 4 H), 8.15 (d, $J = 4.8$ Hz, 2H), 8.04 (d, $J = 4.8$ Hz, 2 H), 7.65 (m, 12 H), 7.48 (d, $J = 2.0$ Hz, 4 H), 4.73 (sept, $J = 6.4$ Hz, 2 H), 4.17 (s, 6 H), 3.89 (s, 6 H), 0.72 (d, $J = 6.0$ Hz, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 186.6, 182.3, 158.7, 154.5, 154.0, 153.9, 150.5 (2 carbons), 149.8, 149.7, 149.5, 142.8 (2 carbons), 135.7, 134.5, 134.3, 134.0, 133.8, 133.5, 132.6, 131.7, 131.6, 130.6, 128.2, 127.3, 126.4, 126.3, 125.5, 121.9, 121.7, 121.6, 121.3, 120.3, 119.6, 109.8, 75.8, 67.0, 57.1, 57.0, 22.9. UV−Vis λ_{max} (log ϵ, Et_2O) 418.0 (4.79), 456.0 (4.87), 565.0 (4.20), 615.0 (3.51) nm; FAB MS: 1597.6. HRMS (FAB) Calcd for $C_{94}H_{66}O_{10}N_8Zn_2$: 1594.3485. Found: 1594.3528.

Compound 2e. The reaction of porphyrin compound **1e** (60 mg, 0.096 mmol, 1.00 equiv) with DDQ (23 mg, 0.1 mmol, 1.1 equiv) in methylene chloride (10 mL) at room temperature for 3.5 h gave the product **2e** as a purple solid (60 mg, 0.048 mmol) in 99.9% yield. TLC (silica gel, hexanes−acetone (3:1), $R_f = 0.09$); Chromatographic purification (flash column, silica gel, 2 × 2.5 cm, hexanes−acetone 3:2 followed by flash column, silica gel, 8 × 2 cm, hexanes−acetone 5:2). mp > 250 °C (THF−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1734 (m), 1637 (m), 1602 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.06 (d, $J = 4.8$ Hz, 4 H), 8.99 (d, $J = 4.8$ Hz, 4 H), 8.65 (d, $J = 4.8$ Hz, 4 H), 8.22 (m, 12 H), 8.12 (d, $J = 4.8$ Hz, 4 H), 7.67 (m, 12 H), 7.34 (d, $J = 8.4$ Hz, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.2, 154.9, 150.5, 150. 4, 149.7, 142.9, 135.5, 134.4, 133.8, 132.0, 131.7, 131.6, 127.3, 126.4, 121.7, 121.5, 112.0, 55.6. UV−Vis λ_{max} (log ϵ, Et_2O−methylene chloride 9:1) 420.0 (5.04), 457.0 (5.18), 563.0 (4.39), 607.0 (3.56) nm; LowRes FAB MS:1261, HRMS (FAB) Calcd for $C_{78}H_{50}N_8O_2Zn_2$: 1258.2638. Found: 1258.2618.

5-(4-Methoxyphenyl)-10,20-diphenylporphyrin(Zn), 1e. 5,15-diphenyl-10-(4-methoxy phenyl) porphyrin, **3**[32] (20 mg, 0.035 mmol, 1.00 equiv) was dissolved in methylene chloride (10 mL) and treated with $Zn(OAc)_2$ (10 mg, 0.055 mmol, 1.57 equiv) in methanol (5 mL) at room temperature with stirring. After 3.5 h, TLC monitoring indicated disappearance of starting material. The reaction mixture was poured into water, and the organic layer was separated and washed twice with water. After removal of the solvent on a rotary evaporator, the residue was taken up by methylene chloride and filtered through a pad of SiO_2 under vacuum. The solvent was evaporated to dryness to afford the product as a red solid (22 mg, 0.035 mmol, 100%). mp > 250 °C (methylene chloride−hexanes, diffusion). ^1H NMR ($CDCl_3$, 400 MHz): 10.13 (s, 1 H), 9.31 (d, $J = 4.8$ Hz, 2 H), 9.04 (d, $J = 4.8$ Hz, 2 H), 9.01 (d, $J = 4.8$ Hz, 2 H), 8.98 (d, $J = 4.4$ Hz, 2 H), 8.23 (d, $J = 7.6$ Hz, 4 H), 8.12 (d, $J = 8.4$ Hz, 2 H), 7.81−7.77 (m, 6 H), 7.24 (d, $J = 8.8$ Hz, 2 H), 4.06 (s, 3 H). ^{13}C NMR (DMSO-d_6, 100 MHz): 159.1, 150.0, 149.9, 149.7, 142.7, 135.4, 135.3, 134.5, 132.4, 132.0, 131.7, 131.5, 127.4, 126.6, 120.4, 111.9, 105.5, 55.5. UV−Vis: λ_{max} (log ϵ, THF) 417 (5.49), 549 (4.04) nm. LowRes FAB MS: 630; HRMS (FAB) Calcd for $C_{39}H_{26}N_4OZn$: 630.1397. Found: 630.1398. Analytical data for the free base was previously reported.[32]

5-Chloro-15-(4-methoxyphenyl)-10,20-diphenylporphyrin, 4. A mixture of 5-(4-methoxyphenyl)-10,20-diphenylporphyrin, **3**[32] (22 mg, 0.038 mmol, 1.0 equiv) and DDQ (40 mg, 0.176 mmol, 4.6 equiv) in methylene chloride (6 mL) was stirred at room temperature for 3 days. The mixture was washed with water, dried over sodium sulfate, and separated by a vacuum column (SiO_2, 2 × 2.5 cm) eluting with 3:1 hexanes−CH_2Cl_2 to remove compound **4** and with 1:1 hexanes−CH_2Cl_2 to remove the starting material, **3** (8.0 mg, 32%). The product **4** was obtained as a purple solid (15.4 mg, 66%). TLC (silica gel, hexanes−CH_2Cl_2, 1:1, $R_f = 0.4$); mp >245 °C (CH_2Cl_2−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 3320 (w). ^1H NMR (DMSO-d_6, 400 MHz): δ 9.64 (d, $J = 4.8$ Hz, 2 H), 8.90 (d, $J = 4.8$ Hz, 2 H), 8.82 (d, $J = 4.8$ Hz, 2 H), 8.79 (d, $J = 4.8$ Hz, 2 H), 8.19 (dd, $J = 8.0$ Hz, 2.0 Hz, 4 H), 8.08 (d, $J = 8.8$ Hz, 2 H), 7.80−7.75 (m, 6 H), 7.28 (d, $J = 8.4$ Hz, 2 H), 4. 09 (s, 3 H), −2.72 (s, 2 H). UV−Vis λ_{max} (log ϵ, CH_2Cl_2): 419 (5.20), 517 (3.86), 553 (3.66), 652 (3.43) nm. MS (FAB): 602. HRMS (FAB) Calcd for $C_{39}H_{27}N_4OCl$: 602.1873. Found: 602.1848.

5-Iodo-15-(2-isopropoxy-cyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn), 5. To a 25 mL round-bottomed flask were added 5-(2-isopropoxy-cyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn), **1a** (13 mg, 0.02 mmol, 1 equiv), and THF (2 mL). Then a mixture of I_2 (10 mg, 0.039 mmol, 2.0 equiv) and AgO_2CCF_3 (10 mg, 0.045 mmol, 2.2 equiv) in THF (3 mL) was added at room temperature. After 5 min, additional AgO_2CCF_3 (5 mg, 0.022 mmol) was added, and the mixture was stirred for 10 min. After addition of CH_2Cl_2 (20 mL), the mixture was washed once with $NaHCO_3$ and twice with water and then dried over sodium sulfate. Vacuum column chromatography (flash column, silica gel, 2 × 2.5 cm, 5:1 hexanes−acetone) gave **5** as a green solid (16 mg, 100%). TLC (silica gel, hexanes−acetone, 3:2, $R_f = 0.5$); mp > 250 °C (CH_2Cl_2−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1782 (s), 1753 (s), 1572 (s). ^1H NMR (DMSO-d_6, 400 MHz): δ 9.67 (d, $J = 4.4$ Hz 2 H), 9.40 (d, $J = 4.8$ Hz, 2 H), 8.77 (d, $J = 5.2$ Hz, 2 H), 8. 75 (d, $J = 5.2$ Hz, 2 H), 8.17 (m, 4 H), 7.86−7.80 (m, 6 H), 5.77 (sept, 6.2 Hz, 1 H), 1. 49 (d, 6.0 Hz, 6 H). ^{13}C NMR (DMSO-d_6, 400 MHz): δ 197.9, 195.0, 194.5, 178.3, 151.3, 150.9, 149.7, 147.6, 141.9, 137.9, 134.2, 133.1, 132.6, 131.5, 127.8, 126.8, 122.3, 103.2, 84.8, 79.9, 22.5. UV−Vis λ_{max} (log ϵ, THF): 439 (5.20), 565 (3.92), 625 (3.99) nm. MS (FAB): 788. HRMS (FAB) Calcd for $C_{39}H_{25}N_4O_3IZn$: 788.0263. Found: 788.0276.

5-(2-Isopropoxy-cyclobutene-3,4-dionyl-15-bromo-10,20-diphenylporphyrin(Zn), 6. To a 250 mL round-bottomed flask were added 5-(2-isopropoxy-cyclobutene-3,4-dionyl-10,20-diphenylporphyrin(Zn) (**1a**) (199 mg, 0.30 mmol,

1.00 equiv), NBS (53 mg, 0.300 mmol, 1.00 equiv), and methylene chloride (200 mL). The mixture was stirred at room temperature for 2 h, solvent was evaporated, and the product **6** was isolated by column chromatography (flash column, silica gel, 2 × 12 cm, hexanes−THF 8:1) as a dark green solid (190 mg, 0.256 mmol, 85%). TLC (silica gel, hexanes−THF 3:1, R_f = 0.5); mp > 250 °C (THF−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1784 (s), 1751 (s), 1575 (s). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.65 (d, J = 4.8 Hz, 2 H), 9.40 (d, J = 4.8 Hz, 2 H), 8.79 (d, J = 4.8 Hz, 2 H), 8.78 (d, J = 4.4 Hz, 2 H), 8.18 (dd, J = 8.0, 1.6 Hz, 4 H), 7.87−7.81 (m, 6 H), 5.76 (sept, J = 6.0 Hz, 1 H), 3.59 (m, 4 H), 1.76 (m, 4 H), 1.49 (d, J = 6.4 Hz, 6 H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 197.9, 194.9, 194.5, 178.2, 150.4, 149.8, 148.5, 147.7, 141.9, 134.2, 132.9, 132.8, 132.7, 131.5, 127.8, 126.8, 122.2, 105.9, 103.2, 80.0, 67.0, 25.1, 22.5. UV−Vis λ_{max} (log ϵ, THF): 437 (5.36), 567 (3.00), 623 (3.20) nm. MS (FAB): 742. HRMS (FAB) Calcd for $C_{39}H_{25}N_4O_3$-BrZn: 740.0400. Found: 740.0422. Anal. Calcd for: $C_{39}H_{25}N_4O_3$-BrZn.THF: C, 63.37; H, 4.08; N, 6.88; O, 7.85; Found: C, 63.05; H, 4.37; N, 6.64.

Bromoporphyrin **6** (15 mg) was also obtained in quantitative yield by reaction of **1a** (13 mg, 0.020 mmol, 1.0 equiv) in THF (10 mL) with *N*-bromosuccinimide (4.0 mg, 0.22 mmol, 1.1 equiv) at room temperature for 50 min after removal of solvent and preparative plate chromatography.

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Supporting Information Available: Photocopies of ^{1}H and ^{13}C NMR and UV−vis spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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